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Surface Organometallic Chemistry of Tin: Reaction of Hydridotris(butyl)tin with the Surfaces of Partially Dehydroxylated Aluminas

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Abstract: Reaction of Bu_3SnH with the surface of partially dehydroxylated aluminas was followed by analysis of the evolved gases and infrared, ^{13}C CP-MAS NMR, and ^{119}Sn MAS NMR spectroscopies. At room temperature, the infrared and ^{13}C CP-MAS NMR data suggest an initial interaction of Bu_3SnH with the hydroxyl groups of the η-alumina$_{(500)}$ surface via hydrogen-type bonding with the δ-CH_3 groups of the butyl ligand. The formation of the grafted entity $>AlOSnBu_3$ was accompanied by the release of 1 mol H_2 per mole of Sn. Data were obtained on α-, γ-, and η-aluminas dehydroxylated at either 200 or 500 °C. The various NMR data coupled with published data for molecular analogs indicate that the tin atoms can be tetra- or pentacoordinated on the alumina surface. ^{27}Al NMR is used to estimate the ratio of octahedral to tetrahedral aluminum atoms in various aluminas. Detailed study of the ^{119}Sn NMR of the series of Sn/Al_2O_3 species revealed three basic types of tin coordination environments. Tin signals around 80 ppm present in some of the complexes are attributed to $>AlOSnBu_3$ or tetracoordinated tin. Peaks in the regions around −230 and −170 ppm are ascribed to a pentacoordinated tris(alkyl)tin fragment. The fifth ligand coordinated to tin may be either a hydroxyl group or a surface O^{2-} ion: formation of $(>AlO)(>AlOH)Sn(n\text{-}C_4H_9)_3$ and of $(>AlO)(>AlO^{2-})Sn(n\text{-}C_4H_9)_3$. The complexity of these resonances and the dependence thereof on the type of alumina used and the degree of dehydroxylation are attributed to the influence of the geometry of neighboring aluminum atoms on the tin chemical shift. These results apply the extreme sensitivity of tin chemical shifts to molecular enviroment, producing a method whereby surface organometallic complexes of tin can be used as molecular probes for determining surface structures of oxides. The ^{119}Sn NMR is shown to be much more sensitive than other previously used spectroscopic techniques, such as IR, Raman, and ^{29}Al NMR.

Introduction

Surface organometallic chemistry (SOMC) of main group elements has been the subject of several publications.[1-9] Metal alkyls of main groups elements (e.g., Mg, Li, Al, Zn, Ga) are known to react with hydroxyl groups of silica with liberation of the corresponding alkane R–H. These studies were mainly devoted to the determination of the concentration of surface hydroxyl groups, and little is known about the number, nature, and structure of the organometallic entities grafted. Such structural determination is the primary aim of our recent approach of SOMC. Can one graft onto a surface organometallic compounds of unusual oxidation state and/or coordination number which could lead to unexpected physical and/or chemical properties? For example, in a previous publication we showed that it is possible to graft tris(alkyl)tin fragments on a silica surface by reacting tetra(alkyl)tin complexes or tris(n-butyl)tin hydride with a partially dehydroxylated silica.[10] The surface organometallic complex $>SiOSnR_3$ was fully characterized using IR, ^{13}C CP-MAS NMR, and ^{119}Sn MAS NMR spectroscopies. The ^{119}Sn MAS NMR data strongly indicated that tin remained tetracoordinated.

It was of interest to try to prepare related surface complexes on alumina, the surface of alumina having a more complex structure than that of silica. Silica is known to have covalent Si–O bonds in which silicon always assumes a tetracoordinated structure. Alumina is known to have a more ionic character; thus aluminum atoms can be tetra- or hexacoordinated. In addition, their acidic and basic properties are very different by both the Brönsted and the Lewis descriptions. One could expect that the reaction of tin alkyl hydride with the surface of alumina could lead to surface structures different from those observed on silica. The study of such complexes could help us to have a better understanding of the chemical behavior of various aluminas. There are only a few studies dealing with the reactivity of alkyltin complexes with the surface of aluminas,[11-13] and no description at the molecular or atomic level has been reported of the surface structures generated.

Experimental Part

Reagents. Four different types of aluminas were used: an α-alumina (Alfa, 200 $m^2 \cdot g^{-1}$, called α-(A) in the following), two γ-aluminas (Degussa nonporous, 100 $m^2 \cdot g^{-1}$, and Rhône-Poulenc, 240 $m^2 \cdot g^{-1}$, called respectively γ-(D) and γ-(RP)), and an η-alumina prepared in the laboratory (200 $m^2 \cdot g^{-1}$). All these aluminas were treated under vacuum (10^{-4} Torr, 14

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h) either at 500 °C (alumina$_{(500)}$) or at 200 °C (alumina$_{(200)}$) prior to reaction with the organotin complex.

Bu_3SnH (Strem) was used without further purification. Its ^{119}Sn NMR spectrum showed that it contained small quantities of both $SnBu_4$ and Sn_2Bu_6.

Techniques. All experiments were carried out in Pyrex glassware under vacuum or dry argon. Bu_3SnH was introduced to the alumina sample via a syringe through a septum. The evolved gases (H_2, C_4H_8, C_4H_{10}, etc.) were quantitatively and qualitatively analyzed by volumetry (using a Texas Instruments 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 probehead was a commercial, double-tuned, 7-mm, double-bearing system from Bruker that allowed spinning frequencies up to 4 kHz. The samples were introduced in the rotor (made of zirconia) under a dry nitrogen atmosphere in a glovebox, and the rotor was tightly closed. Boil-off nitrogen was used for both bearing and driving the rotors. NMR and infrared spectroscopies indicate that, under these conditions, there is no decomposition of the samples during the course of the experiments.

For ^{13}C NMR, a typical cross-polarization sequence was used: 90° rotation of the ^1H magnetization (impulsion length, 6.2 ms), and then contact between carbon and proton during $T_C = 5$ ms, and finally recording of the spectrum under high-power decoupling. The delay between each scan was fixed to 5 s to allow for the complete relaxation of the ^1H nuclei. Chemical shifts are given with respect to TMS by using adamantane as an external reference ($\delta = 37.7$ ppm for the highest chemical shift). In several cases, adamantane was added to the sample in the rotor as an internal reference. No variation of the chemical shifts was detected in a comparison between shifts referenced internally and externally.

The ^{27}Al MAS NMR spectra of the different fully hydrated aluminas were recorded by using a single impulsion sequence. The delay between each scan 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 aluminum atoms with different e^2qQ parameters. The chemical shifts are given relative to $Al(H_2O)_6(NO_3)_3$ (1 M) used as an external reference.

^{119}Sn NMR spectra were recorded by using a single impulsion and high-power decoupling. The delay between each scan was 2.5 s, a value resulting in an apparently complete relaxation of the ^{119}Sn nuclei. The chemical shifts are given relative to $SnMe_4$ used as an external reference and with the IUPAC convention for chemical shifts (a higher chemical shift value corresponding to a higher frequency). In most cases, Sn_2Bu_6, present as an impurity in tris(*n*-butyl)tin hydride, was detected in the spectra and used as an internal reference ($\delta = -83.9$ ppm).

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 and Discussion

1. Reaction of Bu_3SnH with the Surface of a Partially Dehydroxylated η-Alumina. The infrared spectrum of a disk of η-alumina dehydroxylated at 500 °C overnight (η-alumina$_{(500)}$) exhibits several bands in the ν(OH) region, the most intense at 3790 (sh), 3775, 3730, and 3682 cm^{-1} (Figure 1a). The attribution of these bands, which are present on several types of aluminas, has been the subject of many studies[14-26] (*vide infra*).

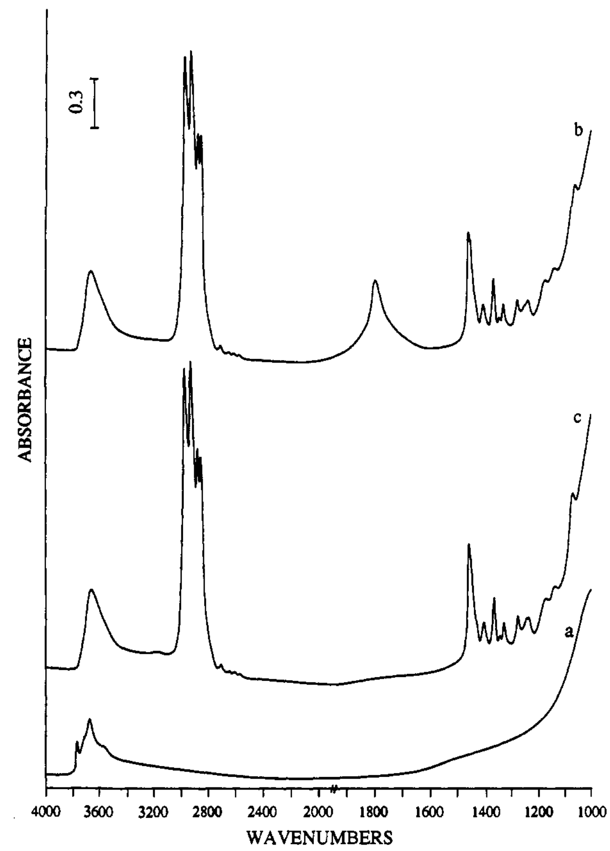

Figure 1. Infrared spectra of (a) η-alumina$_{(500)}$; (b) the sample from a just after introduction of Bu_3SnH at 25 °C; (c) the sample from b after 24 h at 25 °C.

Chart 1

When Bu_3SnH is introduced at 25 °C, as in the vapor phase, to this disk, the following modifications of the spectrum are evident within minutes (Figure 1b). (i) In the ν(OH) region, the four bands are replaced by a broad band centered at ca. 3654 cm^{-1}. This is consistent with the interaction of Bu_3SnH with all remaining surface OH groups via hydrogen bonding, a phenomenon observed in the reaction of Bu_3SnH with the silica surface.[10] (ii) New bands typical of butyl groups are observed at 2957, 2926, 2872, and 2855 cm^{-1} (ν(CH) bands) and in the 1500–1000-cm^{-1} region (δ(CH) and ρ(CH) bands). (iii) A band is present at 1809 cm^{-1}, assigned to the ν(SnH) vibration of the starting complex.

This spectrum changes with time: the intensities of the ν(CH), δ(CH) and ρ(CH) bands remain constant, while the intensity of the region around 1809 cm^{-1} decreases and becomes more complex (Figure 2). A new peak appears at 1785 cm^{-1}, and there are perhaps shoulders at 1742 and 1860 cm^{-1}. All these bands disappear within 12 h (Figures 1c, 2). By comparison with the data obtained for Bu_3SnH/silica,[10] those changes suggest an initial interaction of Bu_3SnH with the hydroxyl groups of the η-alumina$_{(500)}$ surface via van der Waals-type bonding either with the CH groups of the butyl ligands or with the SnH functionality (Chart 1).

After 12 h, all ν(SnH) bands have disappeared (Figure 1c). An analysis of the gas phase carried out after 12 h of interaction on a similar but larger sample reveals the exclusive evolution of molecular hydrogen (0.94 mol per mole of grafted tin) without any hydrocarbon.

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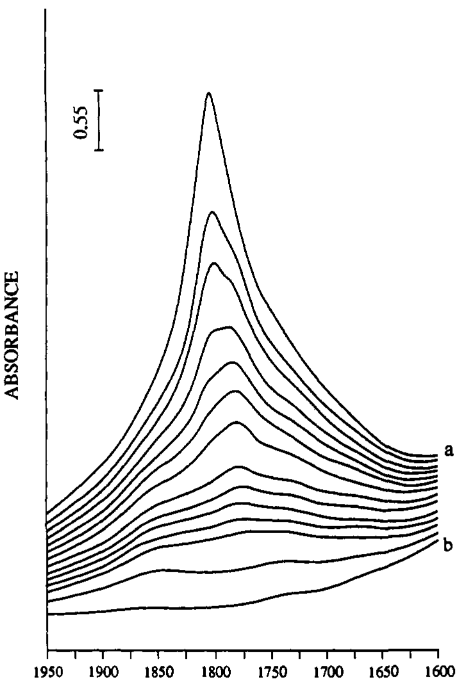


Figure 2. Evolution with time of the infrared spectrum in the 1900–1600-cm^{-1} region during the reaction at 25 °C of Bu_3SnH with the surface of an η-alumina$_{(500)}$, from (a) $t = 0$ to (b) $t = 12$ h.

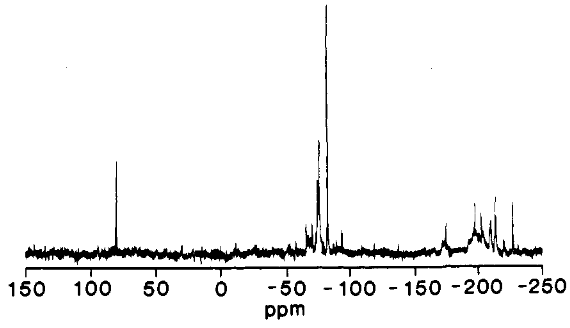


Figure 3. ^{119}Sn MAS NMR of Bu_3SnH on η-alumina$_{(500)}$ after reaction at 25 °C.

Similar observations were made when Bu_3SnH was introduced to an η-alumina$_{(200)}$: broadening of the ν(OH) bands of the alumina as well as appearance of a new band at 1785 cm^{-1}. After 12 h of reaction, 1.03 mol of H_2 per mole of grafted tin was evolved.

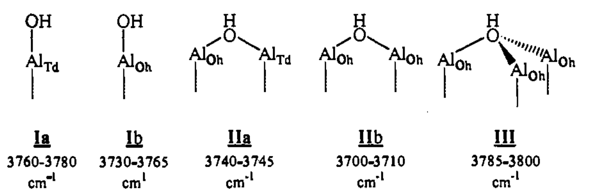
As a first approximation, these results may be rationalized as an initial physisorption of Bu_3SnH, followed by reaction 1:

$$>\mathrm{AlOH} + \mathrm{Bu_3SnH} \rightarrow \underset{\mathbf{1}}{>\mathrm{AlOSnBu_3}} + \mathrm{H_2} \qquad (1)$$

We have tried to characterize **1** more precisely by MAS NMR spectroscopy. The ^{13}C CP-MAS spectrum of a sample of η-alumina$_{(200)}$ treated with Bu_3SnH for 12 h presents two sharp signals at 13.0 and 26.7 ppm, a broad signal at 15–18 ppm, and a peak of low intensity at 11.3 ppm *(vide infra)*.

The ^{119}Sn MAS NMR spectrum of a sample of η-alumina$_{(500)}$ treated with Bu_3SnH is very complex: we will divide our analyses into three spectral regions (Figure 3). (i) A peak at +80.1 ppm is likely due to $>AlOSnBu_3$ by comparison with the spectrum obtained for $>SiOSnBu_3$, in which Sn is uniquely tetracoordinated (*vide infra*).[10] (ii) Several peaks appear in the region between −60 and −90 ppm. The most intense peak in this region corresponds to Sn_2Bu_6, an impurity present in Bu_3SnH which did not undergo reaction. (Chemical analysis (1 mol of H_2 evolved per mole of grafted tin) indicates that most of the tin is grafted as $>AlOSnBu_3$. It seems surprising, at first glance, to have a strong signal for physisorbed Sn_2Bu_6. A simple explanation would be that the T_1 relaxation time of such a compound is probably lower than that of "chemisorbed" (or grafted) tin organometallics. As a consequence, its signal is greatly enhanced. It must also be pointed out that such peaks should not be detected using cross-polarization, their mobility avoiding the efficiency of the polarization transfer. For this reason, the ^{13}C peaks of Sn_2Bu_6 are not observed in our experiments. They are detected only by using a contact time larger than 10 ms.) The other peaks in this region are likely due to Bu_3SnH interacting weakly with the η-alumina$_{(500)}$ surface. (iii) Several resonances are also observed in the spectral region about 250 ppm upfield from the peaks attributed to $>AlOSnBu_3$ (−170/−230 ppm); they may be assigned to pentacoordinated tin, as suggested by the spectra of molecular analogs.[27]

Chart 2



Even if chemical analysis suggests the formation of a well-defined compound which could be $>AlOSnBu_3$, the ^{13}C and ^{119}Sn NMR data are not similar to those obtained for $>SiOSnBu_3$.[10] Obviously, it is the complexity of the η-alumina structure which is at the origin of such phenomena. As already mentioned, the surface of η-alumina, which reflects to some extent its bulk structure because alumina has an ionic character, is more complicated than that of silica; the multiplicity of OH groups indicated by infrared spectroscopy is an obvious clue of such complexity.[26] The discussion in the literature concerning the various types of OH groups on several aluminas and their respective concentrations has not arrived at a consensus.[14–26] Nevertheless, one may reasonably accept the Knözinger analysis, according to which five different types of hydroxyl groups are present on various types of aluminas. There would be hydroxyl groups linked to one (**Ia** and **Ib**), two (**IIa** and **IIb**), or even three aluminum atoms (**III**), each aluminum atom being able to adopt tetra (Td, tetrahedral) or an hexa (Oh, octahedral) (Chart 2).

The ν(OH) bands in vibrational spectra were assigned on the basis of the net charges on the hydroxyl groups.[14]

The relative concentrations of these various kinds of surface hydroxyl groups depend significantly on the structure of the alumina (α, β, γ, δ, η).[16–25] Some aluminas such as α-alumina exhibit exclusively hexacoordinated aluminum atoms. Others also exhibit tetracoordinated aluminum atoms (e.g., η-alumina). As such, most aluminas exhibit two peaks in the ^{27}Al NMR (hexa- and tetracoordinated alumina), thus allowing the measure of the relative abundance of both species (*vide infra*).

2. Influence of the Structure of Alumina: Reaction between Bu_3SnH and α- and γ-Aluminas. In the preceding section, we have shown that a simple reaction occurs between Bu_3SnH and the OH groups of an η-alumina. The corresponding ^{119}Sn NMR data present a more complicated picture of this reaction. There are numerous signals attributable to species $SnBu_3$/alumina, indications of four- and five-coordinate tin centers linked to differing alumina environments. We begin to untangle the complexity by noting that there is a very large dependence of ^{119}Sn chemical shift on the nature and the number of contact atoms in the coordination environment, thus the large separation between tetracoordinate and pentacoordinate species (the "three regions" discussed above). The further complexity displayed in

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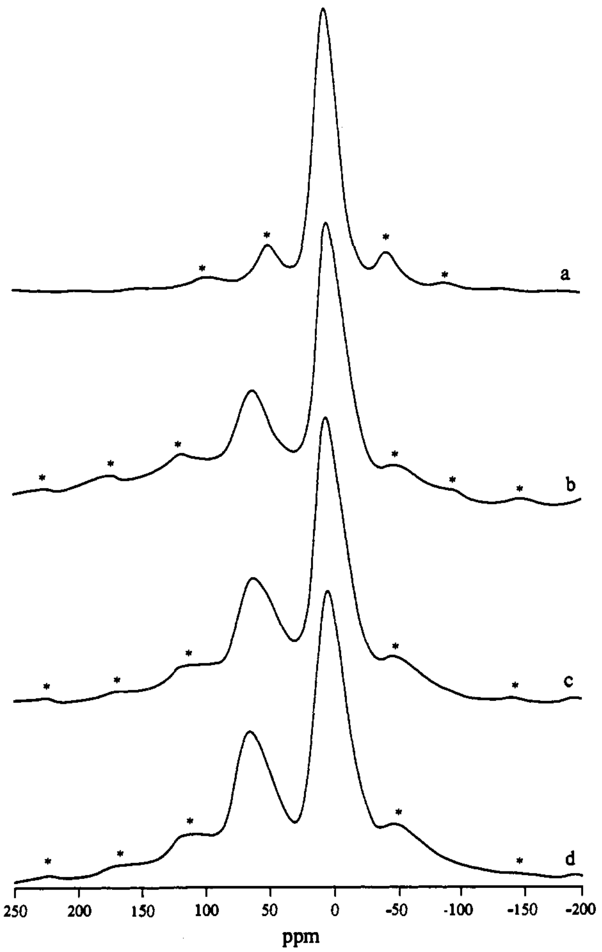

Figure 4. ^{27}Al MAS NMR spectra of the following aluminas$_{(25)}$: (a) α-(A); (b) γ-(D);, (c) γ-(RP); (d) η.

the ^{119}Sn spectra can be explained assuming that the coordination number of the aluminum atoms linked to the surface oxygens is a key parameter to explain the chemical shift of the ^{119}Sn NMR signals observed on η-alumina for the surface compound (>AlO-SnBu$_3$). Thus we would expect that varying the structure of the alumina on which the tin alkyl fragment is grafted, and thus the ratio of octahedral to tetrahedral aluminum atoms, we should be able to predict the complexity of the ^{119}Sn spectra of the reaction products. It was with this hypothesis that we extended our investigation to several other aluminas of different origin: an α-alumina from Alfa (α-A), a γ-alumina from Rhône-Poulenc (γ-RP), and another γ-alumina from Degussa (γ-D).

(a) Estimation of the Ratio Td/Oh Al Sites by ^{27}Al MAS NMR. ^{27}Al NMR spectroscopy is a good way to estimate the respective amount of Td and Oh sites in various aluminas.[25,28-32] The ^{27}Al NMR spectral data for the four different aluminas (fully hydroxylated) are given on Figure 4 and Table 1. ^{27}Al NMR spectra of the surface compound (>AlOSnBu$_3$) showed no significant change with respect to the fully hydroxylated alumina starting materials.

The α-alumina$_{(500)}$, which possesses only octahedral aluminum atoms,[21,28] presents, quite logically, only one resonance at 4.3 ppm. The other aluminas, which possess both octahedral and tetrahedral aluminum atoms, give two types of resonances at ca. 5 (Oh Al) and 60 ppm (Td Al). From the respective integrations of those peaks, it is possible to have a rough estimate of the ratio Td/Oh. (Some hypotheses and/or simplifications were made. (i) The intensity of the spinning side bands is not taken into account, while, rigorously, it should be added to the area of the center band. (ii) We assume that, for octahedral aluminum, the e^2qQ parameter is not equal to zero, that is, that the resonance at ca. 5 ppm corresponds only to the $-^1/_2 \rightarrow +^1/_2$ transition. (iii) Unfortunately, as can be seen in Figure 4, the peaks corresponding to tetrahedral aluminum overlap with the first side band of the peak at ca. 5 ppm. In order to calculate the true intensity of the peak at 5 ppm, it is assumed that the octahedral center band/side band intensity ratio is the same for all aluminas. As all spectra were recorded with the same spinning rate of the rotor, such hypothesis is reasonable.)

Table 1. ^{27}Al MAS NMR Chemical Shifts of the Various Aluminas and Estimation of Their Ratios of Octahedral/Tetrahedral Sites (Td/Oh)

	δ (ppm)		
alumina	Td Al	Oh Al	Td/Oh
α		4.3	0
γ-D	61.4	7.2	0.34
γ-RP	59.9	5.3	0.41
η	62.1	4.9	0.52

Table 2. Evolved Gases During the Reaction of Bu_3SnH with Aluminas

alumina	%Sn	hydrogen[a]	butane[a]
α(500)	6.8	1.04	0.10
γ-D(500)	7.2	0.97	0.12
γ-RP(500)	6.2	1.03	0.13
η(500)	8.3	0.94	0.08
α(200)	6.8	1.03	0.08
γ-D(200)	8.4	0.92	0.04
γ-RP(200)	9.0	0.98	0.03
η(200)	9.3	1.03	0.03

[a] In mol/mol(Sn)$_s$.

Table 1 gives the ratios Td/Oh estimated this way. If the absolute values should be viewed with some caution, the trend η-Al_2O_3 > γ-Al_2O_3 (RP) > γ-Al_2O_3(D) ≫ α-Al_2O_3 can be reasonably concluded from examination of Figure 4.

(b) Infrared Study of the Reactions between Bu_3SnH and the Surfaces of Various Aluminas. These studies were carried out on the three different aluminas$_{(500)}$ (α-(A), γ-(D), γ-(RP)). The starting IR spectra of each exhibit bands in the ν(OH) region at 3775, 3730, and 3682 cm^{-1} (Figure 5a) which have been assigned to OH groups linked to different Oh Al sites: (Al^{VI})OH, (Al^{VI})$_2$-OH, and (Al^{VI})$_3$OH. Hydroxyl groups coordinated to Td Al sites are not detected on the samples, a phenomenon broadly reported in the literature for alumina$_{(500)}$. The broad bands below 3680 cm^{-1} are reasonably assigned to OH interlinked by hydrogen bonds.

Reactions between Bu_3SnH and these aluminas$_{(500)}$ are similar to those observed on η-alumina$_{(500)}$. Immediately after the introduction of the tin complex, there is a broadening of the ν(OH) bands and an appearance of bands associated with Bu$_3$SnH. The band attributable to ν(SnH) is at first a single broad peak at 1803 cm^{-1} but becomes more complex within 1 h. The overall intensity of the ν(SnH) region steadily decreases over the course of 12 h (Figure 5b). The intensity of the ν(CH) bands remains constant with time. As observed for the reaction with η-alumina, 1 mol of H_2 is evolved per mole of grafted tin (Table 2). Evidently, reaction 1 proposed on η-alumina also occurs on α-(A), γ-(D), and γ-(RP) aluminas.

A similar study performed on these same aluminas dehydroxylated at 200 °C gave similar infrared data. Before reaction, all exhibit a sharp band at 3678 cm^{-1}, a shoulder at 3723 cm^{-1},

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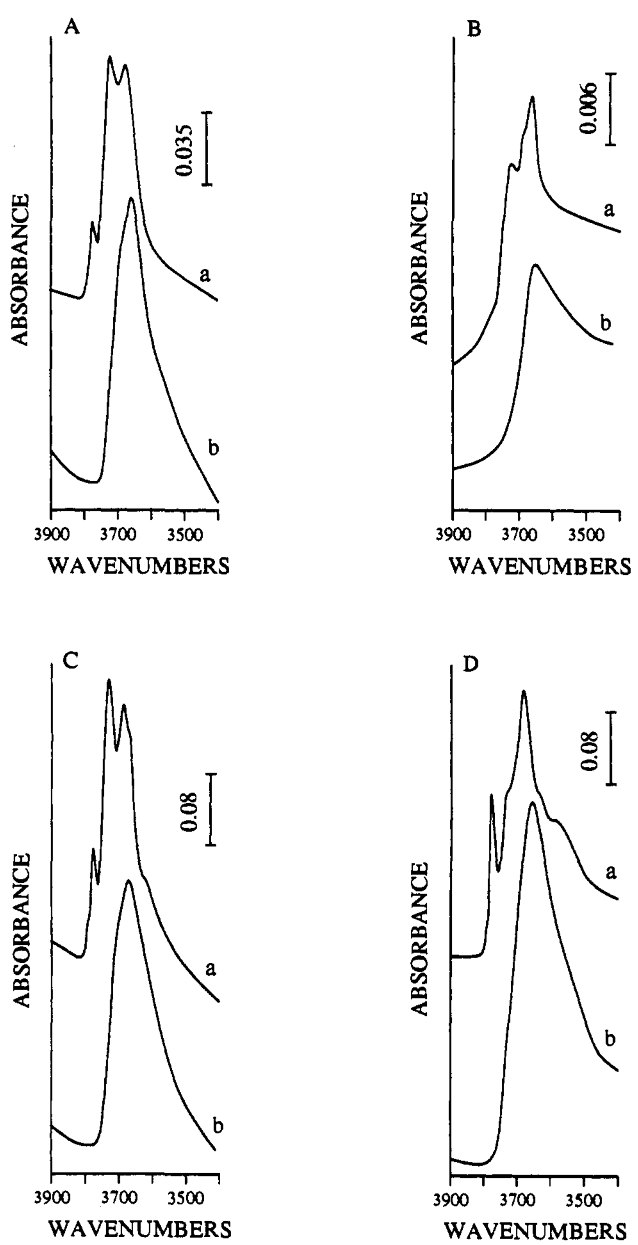


Figure 5. Infrared spectra in the spectral region 3900–3400 cm^{-1} of the following solids: (a) alumina$_{(500)}$; (b) >AlOSnBu$_3$. Aluminas: (A) α-(A); (B) γ-(D); (C) γ-(RP); (D) η.

and, in the case of γ-alumina, a shoulder at 3767 cm^{-1}. All of the solids show a broad band situated between 3400 and 3600 cm^{-1}. The high-frequency bands have already been ascribed in the literature to hydroxyl groups coordinated to Al(VI), species as already described for alumina$_{(500)}$, but here the frequencies are at slightly lower values.[17] The broad band at a frequency below 3600 cm^{-1} has been ascribed to hydroxyl groups exhibiting hydrogen bonding with their neighbors.

Reactions of Bu$_3$SnH with the aluminas$_{(200)}$ give rise to the familiar bands for the butyl groups (ν(CH) and δ(CH) vibrations). The ν(OH) bands of the starting aluminas are broadened and shifted to a slightly lower frequency. Simultaneously, two ν-(SnH) vibrations appear at 1809 and 1785 cm^{-1} which are ascribed respectively to the ν(SnH) vibrations of free SnH and of SnH complexed to hydroxyl groups (or O^{2-} ions) via hydrogen bonding. As for aluminas$_{(500)}$, the ν(SnH) band decreases while hydrogen is formed. After 24 h, the reaction is complete. The stoichiometric formation of 1 mol of hydrogen per mole of grafted tin (Table 2) leads us to suggest the formation of the same complex as on aluminas$_{(500)}$.

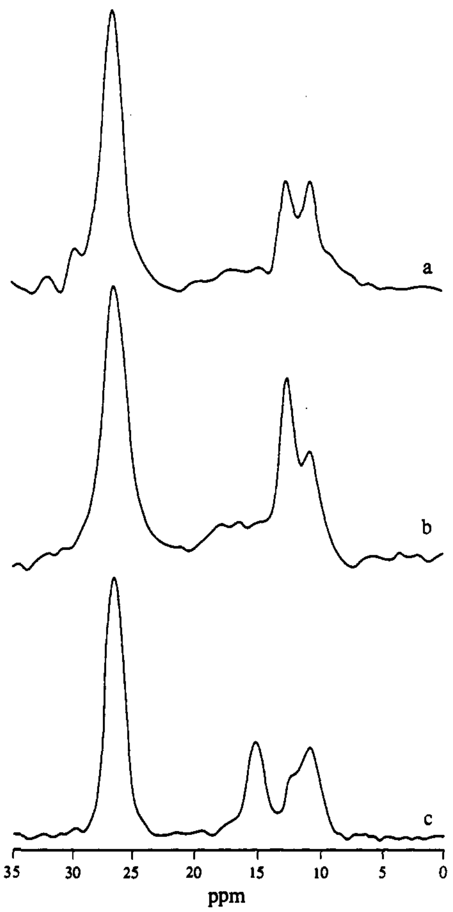
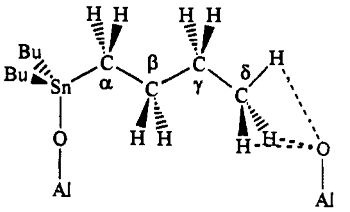


Figure 6. ^{13}C CP-MAS NMR spectra of the solids obtained after reaction of Bu$_3$SnH at 25 °C with (a) α-alumina$_{(500)}$; (b) γ-(D)-alumina$_{(500)}$; and (c) for comparison, silica$_{(500)}$.

Chart 3



(c) Characterization by ^{13}C CP-MAS and ^{119}Sn MAS NMR. In any case and whatever the degree of dehydroxylation of the various aluminas, the ^{13}C CP-MAS NMR spectra of the grafted SnBu$_3$ fragment exhibit similar features (Figures 6 and 7).

An intense peak at 26.9 ppm is ascribed to the β- and γ-carbons of the *n*-butyl chain.[10] Two peaks at 11.3 and 13.0 ppm were assigned to the terminal CH$_3$ carbons, either free (13.0 ppm) or interacting with the surface of alumina (11.3 ppm) via a hydrogen-type bonding[10] (Chart 3).

The relative intensity of the peaks at 13.0 and 11.3 ppm shows a complex dependence on many parameters, such as tin loading, dehydroxylation temperature, and alumina structural type. A more systematic study of the influence of Sn loading on the relative intensities of these two peaks indicates some correlation.[33]

Noteworthy is the fact that on alumina we did not observe a well-resolved peak near 15 ppm, the α-C peak, seen in the case of silica (Figure 6c). A broad feature is present between 15 and 19 ppm which could correspond to the α-C peak broadened by the variety of surface sites of the alumina (*vide infra*).

The ^{119}Sn NMR spectra are also very similar to those obtained on η-alumina. Due to the fact that chemical shifts of tin complexes

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(33) Grand, M.-O.; Lefebvre, F.; Basset, J.-M., unpublished results.

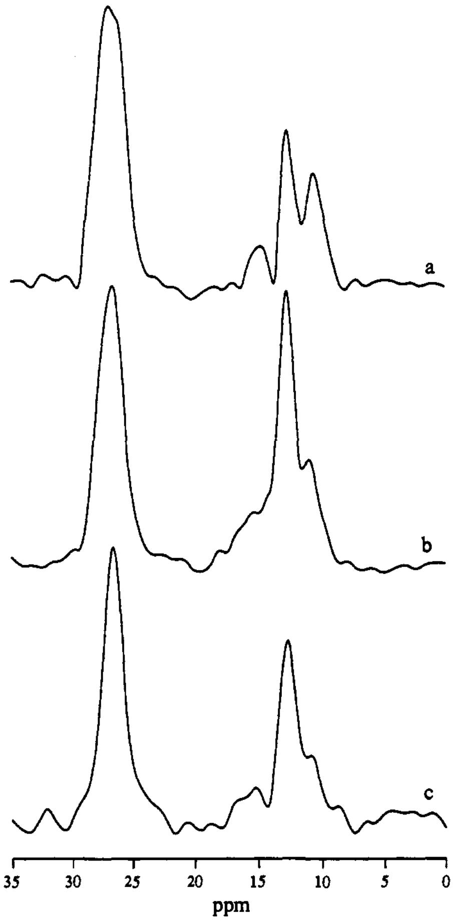

Figure 7. ^{13}C CP-MAS NMR spectra of the solids obtained after reaction of Bu_3SnH at 25 °C with various aluminas$_{(200)}$: (a) α-(A); (b) γ-(D); (c) η.

Table 3. ^{119}Sn NMR Chemical Shifts of Some Tin Organometallic Complexes

surface	%Sn	species	coord	δ (ppm)	ref
$SiO_{2(500)}$	4.8	$>SiOSnBu_3$	4	105	10
$SiO_{2(200)}$	4.1	$>SiOSnBu_3$	4	101	10
		Bu_3SnCl^a	4	153	35
		$Bu_3SnOSiPh_3{}^a$	4	94	10
		$Bu_2SnBr_2{}^a$	4	92	38
		Bu_3SnOMe^b	4	83	34
		$(CH_2{=}CH)_2SnCl_2{}^a$	4	–30	40
		$Bu_2Sn(O^iPr)_2{}^b$	4	–34	34
		Ph_3SnCl^a	4	–45	37
		$(CH_2{=}CH)_3SnCl^a$	4	–53	38
		Bu_3SnH^a	4	–83	10
		$Bu_3SnSnBu_3$	4	–83	43
		$MeSn(O^tBu)_3{}^c$	4	–177	35
		Bu_3SnCl^d	5	–35	36
		$Me_2Sn(OBu)_2{}^c$	5	–133	35
		$Bu_2Sn(OMe)_2{}^b$	5	–165	34
		$(CH_2{=}CH)_3SnCl^e$	5	–216	38
		Ph_3SnCl^e	5	–227	37
		$MeSn(O^sBu)_3{}^c$	5	–302	35
		$Bu_2SnBr_2{}^d$	6	–262	39
		$Bu_2Sn(OC(O)Me)_2{}^d$	6	–335	39
		$(CH_2{=}CH)_2SnCl_2{}^e$	6	–394	40
		$MeSn(O^iBu)_3{}^a$	6	–452	35

[a] In $CDCl_3$. [b] In C_6D_6. [c] Neat liquid. [d] In hmpa (hexamethylphosphortriamide). [e] In dmso.

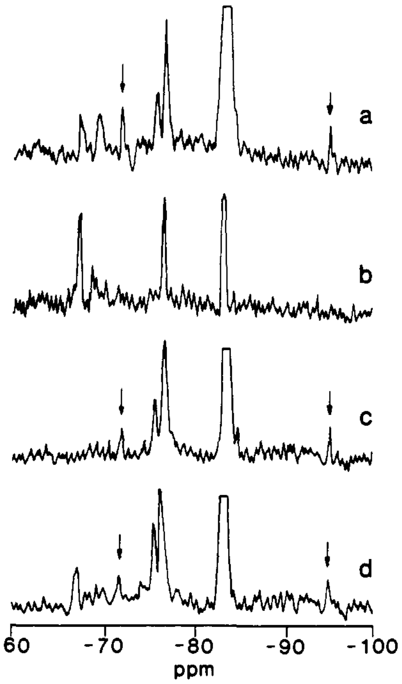

Figure 8. ^{119}Sn MAS NMR spectra of Bu_3SnH on various alumina$_{(500)}$ after reaction at 25 °C. Spectral region, –100/–60 ppm. (a) α-(A); (b) γ-(D); (c) γ-(RP); (d) η (the arrows indicate the coupling).

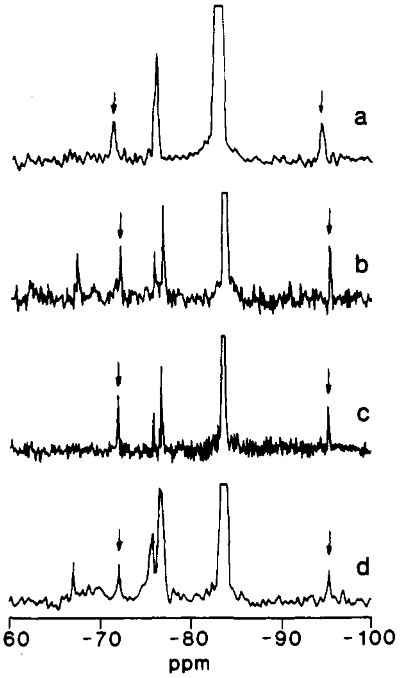

Figure 9. ^{119}Sn MAS NMR spectra of Bu_3SnH on various alumina$_{(200)}$ after reaction at 25 °C. Spectral region, –100/–60 ppm. (a) α-(A); (b) γ-(D); (c) γ-(RP); (d) η (the arrows indicate the coupling).

are extremely specific of the tin environment and coordination number (Table 3), we will examine the three spectral regions corresponding to the different "inner-sphere" coordination environments. (By different inner-sphere coordination environments, we mean the numbers and types of atoms bound covalently to tin.) We ascribe peaks in the region between –100 and –60 ppm to physisorbed species bound by SnH/surface hydroxyl interactions, the often observed peak around 80 ppm to tetracoordinated $>AlOSnBu_3$, and peaks in the region between –160 and –240 ppm to pentacoordinated tin species.

We address first the region centered around the chemical shift of Bu_3SnH, –83 ppm. (Figures 8 and 9 and Table 4). We attribute these peaks to physisorbed Bu_3SnH interacting weakly (likely through the Sn–H bond) with various types of surface OH groups. The largest peaks in the region at –83.9 ppm and its two satellites peaks (The two satellites at ca. –73 and –96 ppm correspond to a coupling of ca. 2600 Hz, due to a Sn–Sn coupling, and

Table 4. ^{119}Sn MAS NMR Chemical Shifts of Bu_3SnH/Aluminas after Reaction at 25 °C in the Spectral Region –100/–60 ppm (Chemical Shifts of $Bu_3SnSnBu_3$ Omitted)

alumina	%Sn	chemical shifts (ppm)[b]			
α(500)	6.8	–77.1	–76.2	–69.7	–67.7
γ-D(500)	7.2	–77.3			–68.0
γ-RP(500)	6.2	–77.3	–76.6		
η(500)	8.3	–77.1	–76.2		–67.9
α(200)	6.8	–77.0			
γ-D(200)	8.4	–77.0	–76.1		–67.5
γ-RP(200)	9.0	–77.0	–76.0		
η(200)	9.3	–77.0	–76.1		–68.0

[a] The chemical shifts listed in this table and in Tables 5 and 6 were obtained by using resolution enhancement. Only peaks with a sufficient S/N ratio are listed. [b] Precision of the chemical shifts is ±0.2 ppm.

comparison with literature data showed that this value is in agreement with the value reported for Sn_2Bu_6 (^1J(Sn–Sn) = 2625 Hz).[42]) are due to $Bu_3SnSnBu_3$, an impurity in the starting material, and thus have nothing to do with the reaction. Several other peaks are observed slightly downfield. For the several aluminas studied, we find the Sn signal at very reproducible positions (±0.2 ppm, Table 4). This is surprising for a solid-state NMR spectrum, as such reproducibility is usually reserved for solution NMR. We believe the tin chemical shifts correspond to well-defined surface species in which Bu_3SnH, keeping its molecular integrity, interacts with specific surface OH types. We exclude species in which tin is covalently bound to surface oxygen (either as a tetracoordinate $>AlOSnR_3$ or as pentacoordinated tin), because this would produce a large shift of the tin signal to higher field (Table 3). That leaves us with the possibility of interaction between either the alkyl chains or the hydride with the surface. We exclude the interaction of the alkyl chains with the surface as the explanation of the changes in chemical shift because we have already remarked in our study of Bu_4Sn and $Bu_3SnSnBu_3$ that physisorption mediated by such an interaction produces no change in chemical shift (*vide supra* and ref 10). It is therefore logical to ascribe these different peaks to the tetracoordinated Bu_3SnH adsorbed on the surface, in which it is the hydride which interacts with several types of surface OH groups. (Recall here that the ν(SnH) bands of Bu_3SnH adsorbed on η-alumina$_{(500)}$ are composed of several peaks and shoulders in the 1800-cm^{-1} region, in agreement with a multiplicity of OH groups interacting with the tin hydride complex (vide supra).)

A single peak around 80 ppm was often observed (Figures 10 and 11 and Table 5). By comparison with results obtained for $>SiOSnBu_3$ or with molecular analogues (Table 3),[34] it is readily ascribed to the surface complex $>AlOSnBu_3$, in which tin is tetracoordinated. The appearance of this signal was not systematic and was not correlated to any single parameter (type of alumina, temperature of dehydroxylation, tin loading). The reason why tetracoordinated tin alkyl is observed only in some cases is not at all clear and may have several origins, this question would require broader experimental studies, perhaps coupled with molecular modeling studies. (For example, on silica, which has OH groups of low nucleophilic character, tris(alkyl)tin always adopts a tetracoordination.[10] On alumina, highly nucleophilic OH groups and/or O^{2-} ions may lead to the formation of pentacoordinated species.)

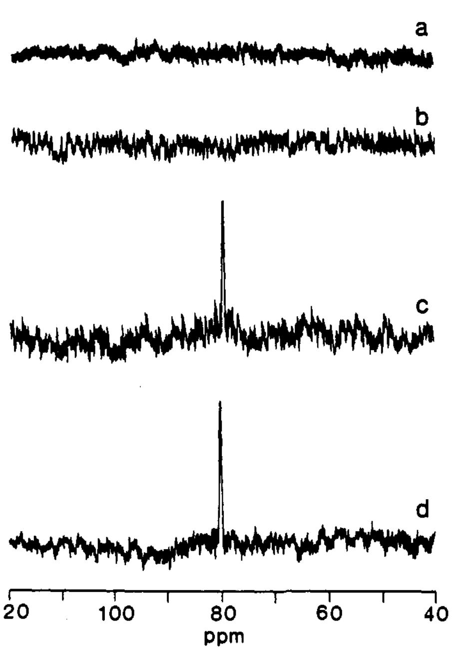

Figure 10. ^{119}Sn MAS NMR spectra of Bu_3SnH on various alumina$_{(500)}$ after reaction at 25 °C. Spectral region, +40/+120 ppm. (a) α-(A); (b) γ-(D); (c) γ-(RP); (d) η.

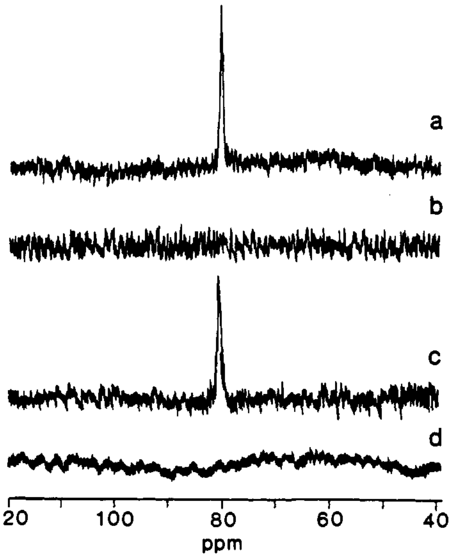

Figure 11. ^{119}Sn MAS NMR spectra of Bu_3SnH on various alumina$_{(200)}$ after reaction at 25 °C. Spectral region, +40/+120 ppm. (a) α-(A); (b) γ-(D); (c) γ-(RP); (d) η.

The third domain of chemical shift is situated between –240 and –160 ppm (Figures 12 and 13 and Table 6). The first hypothesis to explain such high-field resonances could be the formation of $(>AlO)_2SnBu_2$, substitution of an R group for an OR group, resulting in a high-field shift of about 100 ppm (Table 3). We rule this out because only a very small amount of butane was detected during the interaction of Bu_3SnH with those aluminas (Table 2). Only 1 mol of H_2 per mole of grafted tin is observed. The second hypothesis is the formation of a pentacoordinated tin surface complex. The "fifth" ligand could be either a neighboring hydroxyl or a surface O^{2-} ion (Chart 4). (We have adopted an ionic description of the bond between the coordinated oxygen and the aluminum surface atom in order to take into account the

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Table 5. ^{119}Sn MAS NMR Chemical Shifts of Bu$_3$SnH/Aluminas after Reaction at 25 °C in the Spectral Region 40/120 ppm

alumina	%Sn	chemical shifts (ppm)[a]
α(500)	6.8	
γ-D(500)	7.2	
γ-RP(500)	6.2	80.0
η(500)	8.3	80.0
α(200)	6.8	80.1
γ-D(200)	8.4	
γ-RP(200)	9.0	80.6
η(200)	9.3	

[a] Precision of the chemical shifts is ±0.2 ppm.

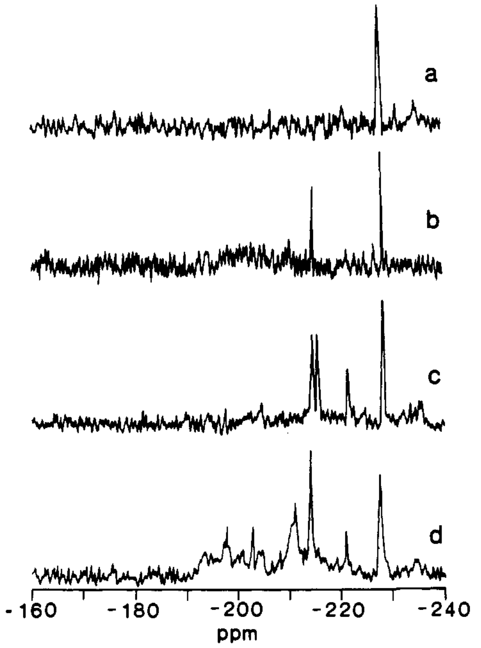


Figure 12. ^{119}Sn MAS NMR spectra of Bu$_3$SnH on various alumina$_{(200)}$ after reaction at 25 °C. Spectral region, −240/−160 ppm. (a) α-(A), (b) γ-(D), (c) γ-(RP), (d) η.

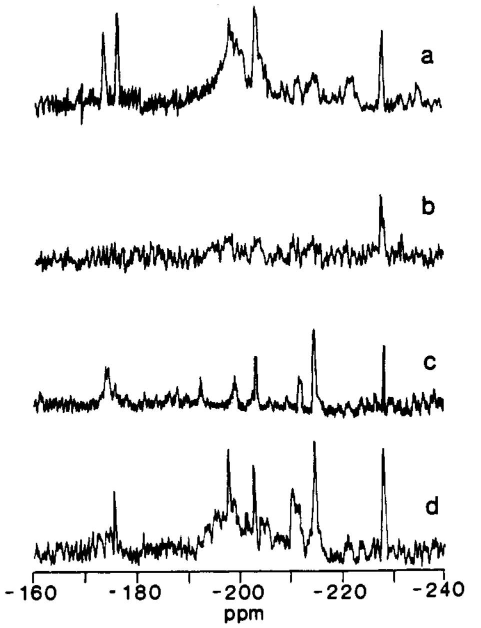


Figure 13. ^{119}Sn MAS NMR spectra of Bu$_3$SnH on various alumina$_{(500)}$ after reaction at 25 °C. Spectral region, −240/−160 ppm. (a) α-(A); (b) γ-(D); (c) γ-(RP); (d) η.

rather ionic character of alumina, especially when dehydroxylation occurs. It is obviously an oversimplification of the bonding between the O^{2-} ion and the tin atom.)

Table 6. ^{119}Sn MAS NMR Chemical Shifts of Bu$_3$SnH/Aluminas after Reaction at 25 °C in the Spectral Region −240/−160 ppm

Chemical shifts (ppm)[a] aluminas$_{(500)}$[b]				Chemical shifts (ppm)[a] aluminas$_{(200)}$[b]			
α	γ-D	γ-RP	η	α	γ-D	γ-RP	η
−227.5	−227.7	−227.7	−227.9	−227.9	−227.8	−227.8	−227.9
						−220.9	−221.2
		−214.3	−214.4		−214.3	−215.0	−214.4
						−214.3	
		−211.0	−210.0				−211.3
−202.9		−202.8	−202.8				−202.9
−200[c]			−199[c]				−199[c]
		−198.3	−197.6				−197.9
		−192.8					
−175.9		−173.8	−175.6				
−172.9							

[a] Precision of the chemical shifts is ±0.3 ppm. [b] Tin analysis; cf. Table 4. [c] Broad signal (precision of the chemical shift is ±1.5 ppm).

Chart 4

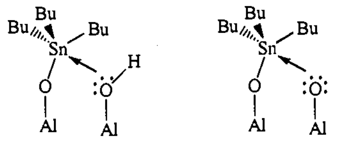
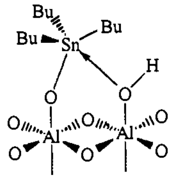


Chart 5



Once again, the chemical shift values are extremely precise and reproducible from sample to sample (Table 6). For example, an intense peak is observed at −227.7 ± 0.2 ppm in all samples. (Often two satellite peaks are observed at ca. −234 and −220 ppm. However, their respective intensities compared to that of the peak at −227.7 ppm are not constant from one sample to one another. It should correspond to a coupling constant of 1540 Hz, a value which is larger than the $^1J(^{119}\text{Sn}-^{13}\text{C})$ coupling constants for tetravalent and tetracoordinated tetrakis(alkyl)tin complexes (320 Hz).[43] However, it has been observed that an increase of the coordination number of tin leads to a strong increase of the coupling constant.[39,44]) Other, less obvious series of signals are indicated by their positions in the rows of Table 5.

The absolute chemical shifts of the peaks in the region between −240 and −160 ppm indicate a coordination number around tin of 5. We now advance the hypothesis that the peaks present in different samples indicate species common to those different solids. We will now attempt to relate the complexity in these NMR spectra to the complexity of the alumina surface.

We shall consider first the most simple case of the α-alumina$_{(200)}$, which is known to have only octahedral aluminum atoms and a monolayer of hydroxyl groups.[21] This alumina gives only a single and sharp resonance at high field (−227.7 ppm), as already described (Figure 12a). The most simple explanation can be advanced in which the tris(alkyl)tin adopts the configuration depicted in Chart 5.

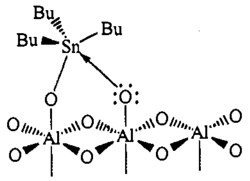
The other aluminas$_{(200)}$ (γ-(D), γ-(RP), and η), which contain both tetrahedral and octahedral aluminum atoms, are expected to give much more complicated spectra. The number of possibilities is quite large because the number of OH groups which exist on those aluminas (five according to the model of Knözinger[26]) may possess in adjacent positions any one of the five types of hydroxyl groups able to coordinate to the grafted tin complex and probably more than five types of O^{2-} arising from the partial dehydroxylation. In principle, there is a

Table 7. ^{13}C NMR Chemical Shifts of Bu_3SnH/Alumina after Reaction at 25 °C: Comparison with Molecular Complexes

		δ (ppm)						
surface	species[a]	C_α	C_β	C_γ	C_δ	C_δ'	coord	ref
Al_2O_3 $\alpha_{(500)}$	$>AlOSnBu_3$	15–19	26.9	26.9	13.1	11.3	*b*	*c*
Al_2O_3 $\gamma\text{-}D_{(500)}$	$>AlOSnBu_3$	15–19	26.8	26.8	13.0	11.3	*b*	*c*
Al_2O_3 $\alpha_{(200)}$	$>AlOSnBu_3$	15–18	26.9	26.9	13.0	11.3	*b*	*c*
Al_2O_3 $\gamma\text{-}D_{(200)}$	$>AlOSnBu_3$	15–18	26.9	26.9	13.1	11.2	*b*	*c*
Al_2O_3 $\eta_{(200)}$	$>AlOSnBu_3$	15–18	26.7	26.7	13.0	11.3	*b*	*c*
$SiO_{2(500)}$	$>SiOSnBu_3$	15.2	26.7	26.7	13.0	11.3	4	10
$SiO_{2(200)}$	$>SiOSnBu_3$	15.2	26.7	26.7	12.9	11.3	4	10
	Bu_3SnH[d]	8.3	30.2	27.2	13.7		4	41
	Bu_3SnOMe[d]	14.1	28.4	27.4	13.7		4	42
	$Bu_3SnOSiPh_3$[d]	16.5	27.8	27.1	13.7		4	10
	$Bu_2Sn(O^iPr)_2$[d]	19.2	27.5	27.0	13.6		4	41
	Bu_3SnCl[d]	17.3	27.6	26.5	13.3		4	36
	Bu_3SnCl[e]	21.3	27.7	26.5	13.2		5	36
	$Bu_3SnOC(O)Me$[d]	16.3	27.7	26.9	13.5		4	36
	$Bu_3SnOC(O)Me$[e]	18.6	27.7	26.6	13.2		5	36

[a] %Sn, cf. Table 4. [b] Cf. text. [c] This work. [d] In $CDCl_3$. [e] In hmpa.

Chart 6



considerable number of different possible species which could be written as $Bu_3Sn(OAl<)(O(H)Al<)$ and $Bu_3Sn(OAl<)(O^{2-}\text{-}Al<)$. The other aluminas$_{(200)}$ give spectra with more resonances than the α-alumina. It is notable that they all possess the signal at −227.7 ppm attributed to species **I** (two adjacent octahedral aluminum atoms). Further speculation into the assignment of these peaks would be inutile.

The aluminas$_{(500)}$ present an interesting new feature. The further dehydroxylation has produced isolated O^{2-} ions.[14] In most samples, the products of the reactions of these aluminas with Bu_3SnH exhibit low-field resonances which are not observed in the case of alumina$_{(200)}$ at −175.9 and −172.9 ppm. Those resonances could be ascribed to a pentacoordinated tin in which surface-exposed O^{2-} ion would be the fifth ligand (Chart 6).

If one assumes that there are various kinds of pentacoordinated tin tributyl fragments on the alumina surface, then one can explain easily why the number of ^{13}C resonances of the α-C on the butyl chain is large (*vide supra*). From the literature data on molecular analogues, it is known that when the tin geometry is modified from tetra- to pentacoordination (e.g., for a tris(butyl)tin species), this leads to a downfield shift of the α-C of 2–4 ppm (last four lines of Table 7).

Conclusion

The introduction of Bu_3SnH to partially dehydroxylated alumina at room temperature is shown to proceed by initial physisorption of the tin hydride, the principal interaction being between surface hydrogen bonds and either the δ-CH groups of the butyl ligand or the SnH functionality. Over time, 1 mol of H_2 per mol of grafted tin is released during the formation of the grafted entity $>AlOSnBu_3$. These results are reproduced with four different aluminas dehydroxylated at 200 and 500 °C. Although only one chemical species is produced in these experiments, the ^{119}Sn NMR spectra present a multiplicity of signals in several regions of chemical shifts. The data show unambiguously that the tin atoms can be tetra- or pentacoordinated on the surface. The relative complexity of the ^{119}Sn spectra in the regions assigned to pentacoordinate tin depend on the degree of dehydroxylation of the alumina and the type of alumina. Despite the complexity of some of these spectra, there is a precise repetition of resonances over a wide variety of alumina. Several possible structures are proposed to explain these resonances and their reproducibility from sample to sample. The fifth ligand coordinated to tin may be either a hydroxyl group (or OH^- ion) or a surface oxygen (or O^{2-} ion): formation of $(>AlOH)(>AlO)Sn(n\text{-}C_4H_9)_3$ and of $(>AlO)(>AlO^{2-})Sn(n\text{-}C_4H_9)_3$. However, it cannot be excluded that formation of polymeric tin entities grafted on the oxide occurs, leading to compounds bound to both the support and other tin complexes.

Both physisorption and chemisorption of the tin organometallic give information on the active sites of the surface. The observation of Bu_3SnH interacting with the hydroxyl groups of the surface can be considered as the first step of the grafting reaction and so could increase our knowledge of the mechanism of the reaction of organometallics with the surface of oxides.

The results suggest therefore that surface organometallic complexes of tin could be used as molecular probes for determining surface structures of oxides. This is made possible by the use of ^{119}Sn NMR, which is shown to be much more sensitive to the molecular and atomic environment than any other previously used spectroscopic techniques, such as IR, Raman, and ^{29}Al NMR. It is clear that, at the moment, a precise attribution of all the NMR peaks cannot be made. However, by a systematic study of the reactivity of Bu_3SnH with several hydroxylated solids, it should be possible to improve considerably our knowledge of their surface structures.