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Surface Organometallic Chemistry of Tin: Reactivity of Two Chiral Organostannics, ((−)-menthyl)Me_3Sn and ((−)-menthyl)Me_2SnH, toward Silica

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Two chiral organostannics, the tetraalkyl ((−)-menthyl)Me_3Sn (**1**) and the hydride ((−)-menthyl)Me_2SnH (**2**), were synthesized. Their reactions with the surface of partially dehydroxylated silica were followed by analysis of evolved gases, IR, and ^{13}C and ^{119}Sn MAS NMR spectroscopic characterizations of the grafted organometallics. With both organostannics, a well-defined chiral surface organometallic compound, ≡Si−O−Sn((−)-menthyl)Me_2 (**3**), is obtained from the reaction of 1 mol of organotin complex with 1 mol of silica surface hydroxyl groups, with formation of 1 mol of methane (from **1**) or dihydrogen (from **2**). Side reactions leading to nonchiral species, such as ≡Si−O−$SnMe_3$ (**4**) or involving two surface silanol groups for one organotin molecule, giving for instance (≡Si−O)$_2$Sn((−)-menthyl)Me (**5**), also occur limiting thus the selectivity of the grafting reaction toward **3**. The amount of grafted tin and the nature of the grafted tin species depend on the type of organostannic and on temperature. When using the tetraalkyl ((−)-menthyl)Me_3Sn as a precursor, temperatures higher than 100 °C are required in order to graft tin onto the silica surface. Although the amount of grafted tin increases with temperature, the selectivity of the reaction toward **3** remains constant at 85% for temperatures lower than 160 °C and decreases at higher temperatures. With ((−)-menthyl)Me_2SnH, tin grafting occurs already at room temperature, but a temperature of 80 °C allows one to graft high tin amounts (4−6 wt % Sn) within a reasonable time, with 95−100% of the grafted tin present as **3** on the silica surface. The reaction is less selective at 100 °C. The chiral surface organometallic species **3** is thermally stable up to 160−200 °C.

Introduction

Former studies in surface organometallic chemistry have shown that well-defined organometallic fragments of different metals, starting from compounds such as $MgNp_2$,[1] $ZrNp_4$,[2,3] GeR_4 (R = *n*-Bu, Et),[4] or tin derivatives R_4Sn (R = Me, Et, *i*-Pr, *n*-Bu, Cy and Ph), (*n*-Bu)$_3$SnH, and (*n*-Bu)$_2$SnH_2,[5−7] can be grafted on the silica surface. In the case of organostannic compounds, using adequate experimental procedures, the grafting with the silanol groups of silica (≡Si−OH) obeys the following reactions:

$$\equiv\text{Si}-\text{OH} + \text{R}_4\text{Sn} \xrightarrow{150\ °\text{C}} \equiv\text{Si}-\text{O}-\text{SnR}_3 + \text{RH} \quad (1)$$

$$\equiv\text{Si}-\text{OH} + \text{Bu}_3\text{SnH} \xrightarrow{20-80\ °\text{C}} \equiv\text{Si}-\text{O}-\text{SnBu}_3 + \text{H}_2 \quad (2)$$

Similar grafting reactions of organostannic compounds were applied to alumina,[8] silica−alumina,[9] and zeolite surfaces.[10−12] The grafting reactions of Bu_3SnOMe and $Bu_2Sn(OMe)_2$ on silica and alumina have also been reported.[13] In the case of mordenite type zeolite, the organometallic fragments are located exclusively on the external surface of the zeolite crystals, even for tetramethyltin which could enter on pure steric considerations within this zeolite pore system.[10] The solids thus obtained have been shown to present adsorption properties considerably affected by the presence of the grafted complexes, in a way which is dependent on the bulkiness of the tin alkyl ligands and on its surface concentration. For instance, a mordenite modi-

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fied by grafted Me_3Sn- fragments adsorbs *n*-hexane, 2-methylpentane at a lower rate, small amounts of 2,3-dimethylbutane, and no significant amounts of 2,2,4-trimethylpentane whereas the unmodified solid adsorbs at the same rate equal amounts of these four hydrocarbons. The results can be explained by the restriction of the size of the pore entrances by the grafted organometallic fragments allowing, in some cases, the separation of mono- and dibranched hydrocarbons. The present study has been carried out in order to see if chiral organometallic fragments can be grafted on surfaces. In several recent papers, the synthesis of chiral organostannic compounds has been described.[14-19] The chirality is provided by one or several (−)-menthyl group bonded to tin. Compounds of the $((-)\text{-menthyl})_xR_{4-(x+y)}SnH_y$ type ($y = 0$ or 1; $x = 1-3$) seemed interesting to graft on microporous materials in an attempt to achieve enantiomeric separations by adsorption. Indeed, the (−)-menthyl group is chiral and presents an important steric hindrance which allow it to interact strongly by van der Waals interactions with hydrocarbon molecules at the pore openings of the zeolite.

We report here our results concerning the reactivity of two chiral organostannic compounds, the tetraalkyl (−)-menthylMe_3Sn (**1**) and the hydride (−)-menthylMe_2SnH (**2**), toward the surface of a high-specific-area Aerosil silica. The main objective in this study is to obtain well-defined organostannic compounds grafted on silica in which the chiral (−)-menthyl group is kept bonded to tin.

Experimental Section

Synthesis of the Two Chiral Organostannics. The two chiral organostannics (−)-menthylMe_3Sn (**1**) and (−)-menthylMe_2SnH (**2**) were synthesized according to the procedure described by Schumann et al.[14] The two compounds were characterized by chemical analysis, polarimetry, ^{13}C, ^{1}H, and ^{119}Sn NMR, IR, and mass spectrometries. The results were in good agreement with those of Schumann et al. These organostannics thus synthesized were used for the grafting reactions on silica surfaces. Besides, a mixture of ((−)-menthyl)Me_3Sn (predominant) and ((+)-neomenthyl)Me_3Sn (minor) was also prepared from a different synthetic route:[20]

$$((-)\text{-menthyl})Cl + Me_3SnLi \rightarrow \underset{80\%}{((-)\text{-menthyl})Me_3Sn} + \underset{20\%}{((+)\text{-neomenthyl})Me_3Sn} \quad (3)$$

(+)-neomenthyl (1*S*,2*S*,5*R*) differs from (−)-menthyl (1*R*,2*S*,5*R*) only by the absolute configuration of the C_1 carbon, bonded to tin. This mixture was used in order to compare its ^{13}C NMR spectrum with the MAS NMR spectra of the organostannic species grafted onto silica.

Procedures for Grafting the Organostannics onto Silica. The silica used as a support in order to graft the organostannics is an Aerosil silica from Degussa, with a BET surface area of 200 $m^2 \cdot g^{-1}$.

a. Silica Preparation. The grafting reactions of the organostannics on silica and the grafted species were studied by IR spectroscopy, by volumetric and GC quantitative analysis of the gases evolved during the reaction, by GC quantitative analysis of the products released from the sample after *n*-heptane washings at the end of the reaction, and by ^{13}C and ^{119}Sn solid-state NMR spectroscopies. For infrared studies, silica was compressed to prepare 10−30 mg pellets which were introduced in a glass sample holder. For the other experiments, Aerosil silica was compacted by mixing it with a small amount of water and by drying this mixture in an oven at 80−100 °C for 1 night. The thick pellet thus obtained was then carefully ground in a mortar in order to obtain the silica powder finally used.

b. Silica Thermal Treatment. Silica was first dehydrated and partly dehydroxylated by a thermal treatment at 350 °C (silica(350)) or at 500 °C (silica(500)) during 15 h under dynamic vacuum ($<3 \times 10^{-5}$ mbar).

c. Introduction of the Organostannics. This procedure was used for IR studies on compressed disks of silica, as well as for analytical or solid-state NMR experiments. The silica sample was cooled to liquid-nitrogen temperature, and the reaction vessel (infrared cell or glass reactor) was pressurized to 1 atm with helium. The organostannics were introduced via a syringe through a septum on the sample. Helium was then pumped out during 30 min ($<3 \times 10^{-5}$ mbar), and the sample was left to reach room temperature. For the GC quantitative analysis of the molecules evolved during the grafting reaction, a given amount of **1** or **2** (310 ± 30 μmol) was injected onto a precise mass of silica(500) (500 mg).

d. Grafting Reaction. The grafting reaction of these organostannics on silica was too slow or did not occur at room temperature. A thermal activation was then needed. Two procedures were used in order to perform the grafting reaction.

Procedure I. In this case, the reaction vessel containing the sample was a glass reactor or an infrared cell connected to the vacuum line. The problem with this procedure was that a part of the reaction vessel was not maintained at the desired temperature and condensation of the organotin occurred on the cold parts of the glass vessel. This procedure was mainly adopted for (−)-menthylMe_2SnH (**2**) grafting on silica. In the case of the (−)-menthylMe_3Sn (**1**) grafting reaction, the contact between the organostannic and the silica was not sufficient and thus the grafting reaction did not occur or was much slower.

Procedure II. To avoid products condensation on cold walls of the reactor, some experiments were conducted in glass vessels equipped with break seals which were sealed after the introduction of the organostannic and the helium evacuation. This procedure was mainly adopted for (−)-menthylMe_3Sn (**1**). In this case the thermal treatment necessary to allow the grafting reaction was conducted with the break-seal tubing containing the sample completely immerged in the oven at the desired temperature. After this thermal treatment, in the case of analytical or solid-state NMR experiments, the break seal was connected to the vacuum line and then opened in order to analyze the gas evolved during the grafting reaction. In the case of infrared studies in sealed tubings, the silica sample was first treated as previously described at the desired temperature (350 or 500 °C) within the infrared cell and the spectrum of the partly dehydroxylated silica was recorded. The sample holder containing the silica pellet was then transferred in air into a glass tubing which was connected to the vacuum line. The thermal treatment under vacuum was then repeated at the same temperature. The glass vessel containing the sample holder was then sealed after the organostannic introduction, and the grafting reaction was conducted as above. The reactor was then opened in an argon-filled glovebag, and the

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sample of silica modified by the grafted organostannic fragments was transferred within the glovebag into the infrared cell.

Thermal Stability of the Two Organostannics. To study the thermal stability of the two organostannics, a glass tubing containing 50 mg of one organostannic under vacuum was heated at increasing temperatures, from 100 to 300 °C with 50 °C increments, during 15 h at each temperature. At the end of each step, the pressure within the glass reactor was measured with a Leybold DI200 gauge head which was connected via a grease-free stopcock. Under these conditions, (−)-menthylMe$_2$SnH decomposition occurred at 200 °C while (−)-menthylMe$_3$Sn was stable up to 300 °C. Practically, with the grafting reaction conditions chosen (20−100 °C for (−)-menthylMe$_2$SnH and 100−180 °C for (−)-menthylMe$_3$Sn), the thermolysis of both organostannics did not interfere.

Infrared Spectroscopy. IR spectra were recorded in situ in a cell equipped with CaF$_2$ windows on a Fourier transform Nicolet 205 spectrometer.

Volumetric and GC Analysis of the Evolved Gases. The total pressure of the gas phase evolved during the grafting reaction was measured using a Leybold DI200 gauge head. The gases were analyzed qualitatively and quantitatively by GC. Gaseous hydrocarbons were analyzed by FID after separation on a capillary column (Chrompack KCl/Al$_2$O$_3$), 50 m × 0.32 mm. The detection and titration of evolved hydrogen was carried out with a catharometer detector after separation on 5 Å molecular sieves.

Elimination of the Unreacted Organometallics and GC Analysis of Menthane. To eliminate the organostannic which did not react with silica and to measure the amount of menthane evolved during the grafting reaction, the samples were carefully transferred onto a glass frit and washed six times at room temperature with distilled *n*-heptane under argon. It was checked that there was no gas evolution during the washing treatment. A known amount of *n*-C$_{13}$, used as an internal standard, was then introduced in the washing solutions. The menthane concentration was measured by FID after separation on a capillary column (JW DB-5), 15 m × 0.32 mm. The solid was then treated overnight under vacuum at room temperature and then for 3 h at 100−150 °C in order to remove the physisorbed *n*-heptane. The modified silica could then be analyzed by solid-state NMR or sent for chemical analysis. In the case of (−)-menthylMe$_3$Sn (**1**) grafting on silica, according to procedure II, it was checked that, within experimental errors, the amount of unreacted organostannic, measured by GC as for menthane, corresponds to the difference of the known amount of **1** initially injected with the amount of grafted tin determined by chemical analysis.

NMR Spectroscopy. The spectra of the liquid organostannics dissolved in C$_6$D$_6$ were obtained on a Bruker AC-300 spectrometer. The spectra of the solid materials were recorded on a Bruker spectrometer DSX-300, equipped with a double bearing probe, allowing spinning frequencies of 3−7 kHz and operating at 75.47 MHz for ^{13}C and 111.9 MHz for ^{119}Sn. For ^{13}C studies, the spectra were recorded using either high-power proton decoupling (HP) in order to observe mainly highly mobile physisorbed species or the cross-polarization (CP) technique (contact time = 5 ms, duration time for obtaining the 90° pulse for ^{1}H = 6.2 or 3.8 μs) in order to observe predominantly the signals of the much less mobile grafted species. Typically, for CP experiments, 5000−100 000 scans were accumulated, depending on the amount of carbon on the sample. The ^{119}Sn MAS NMR spectra were recorded using a single-pulse sequence; the delay between pulses was 1−2 s, and 5000−300 000 scans were accumulated. The chemical shifts are given relative to external TMS for ^{13}C and to external SnMe$_4$ for ^{119}Sn.

Chemical Analysis of the Samples. The chemical analysis of the organostannics and of the modified silica were carried out at the "Service Central d′Analyze du CNRS" at Solaize, France. In the case of the solid samples (modified silica), Sn, C, and Si quantitative determinations were performed. The molar amount of tin grafted on silica, Sn$_g$, was then calculated. ((−)-menthyl)Me$_2$SnH was sealed under argon and sent for analysis to the "Pascher laboratory" at Remagen, Germany.

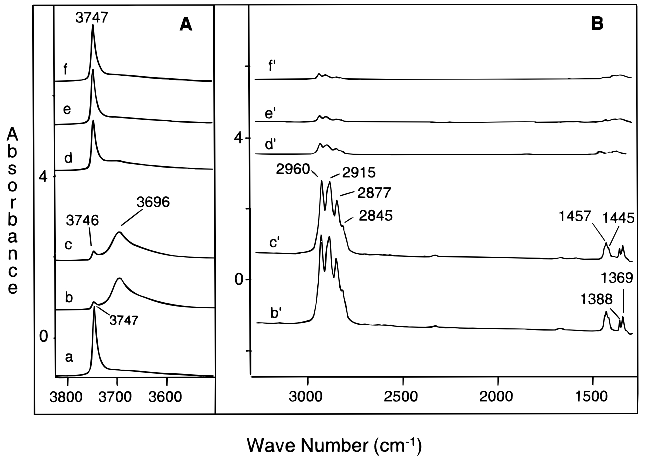

Figure 1. Adsorption of ((−)-menthyl)Me$_3$Sn on silica(350) followed by IR: (A) silanol vibrations of the solid; (B) spectra of the adsorbed phase (after subtraction of the silica contribution); (a) silica(350); (b, b′) sample a after introduction of ((−)-menthyl)Me$_3$Sn; (c, c′) sample b after a thermal treatment at 180 °C according to proceedure I (17 h); (d, d′) sample c after vacuum treatment at room temperature (2 h); (e, e′) sample d after vacuum treatment at 100 °C (2 h); (f, *f* ′) sample e after vacuum treatment at 200 °C (2 h). An amount of 0.4 wt % Sn was grafted at the end of the experiment.

Results

I. Reactivity of ((−)-menthyl)Me$_3$Sn (1) with Silica(350) and Silica(500). I.1. Infrared Study.

For this study, silica wafers are dehydroxylated at 350 °C (silica(350)). In Figure 1 are presented the infrared spectra of silica in the ν(OH) range, 3800−3500 cm^{-1} (Figure 1A, spectra a−f) and the spectra of the adsorbed phase obtained by difference with the spectrum of silica in the 3300−1300 cm^{-1} range (Figure 1B, spectra b′−f ′). The spectrum of the dehydroxylated silica presents one band characteristic of free silanol groups[21−24] at 3747 cm^{-1} (spectrum 1a). Upon ((−)-menthyl)Me$_3$Sn adsorption, the intensity of this band strongly decreases and a new band is observed at 3696 cm^{-1} (spectrum 1b). This broad band is assigned to the ν(OH) vibration of silica OH groups interacting with sorbed molecules. The bands of the adsorbed phase, typical of methyl and menthyl groups, appear at 2960 cm^{-1} (ν_{as}(CH$_3$)), 2915 cm^{-1} (ν_{as}(CH$_2$)), 2877 cm^{-1} (ν_s(CH$_3$)), 2845 cm^{-1} (ν_s(CH$_2$)), 1457 and 1445 cm^{-1} (δ(CH$_2$), δ(CH$_3$)), and 1388 and 1369 cm^{-1} (δ(CH$_3$)) (spectrum 1b′). The two last bands are characteristic of isopropyl groups.[25] After

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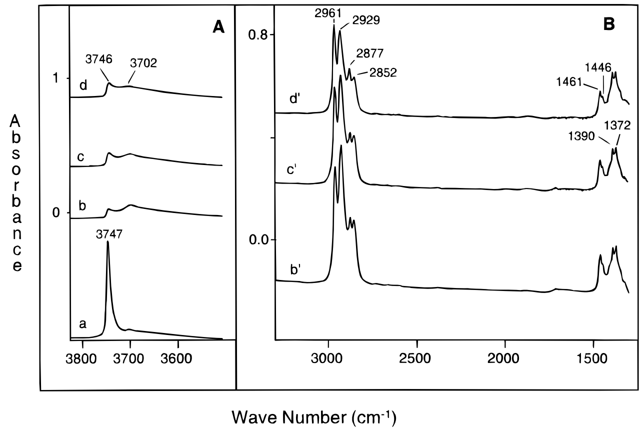

Figure 2. Grafting of ((−)-menthyl)Me_3Sn on silica(350) followed by IR spectroscopy: (A) silanol vibrations of the solid; (B) spectra of the grafted species (after subtraction of the silica contribution); (a) silica(350); (b, b′) sample a after reaction with ((−)-menthyl)Me_3Sn at 180 °C (17 h) according to proceedure II; (c, c′) sample b after a vacuum treatment at 100 °C (2 h); (d, d′) sample c after a vacuum treatment at 200 °C (1 h). An amount of 2.1 wt % Sn was grafted at the end of the experiment.

heating of the samples at 180 °C during 17 h, by using procedure I, with no evacuation under vacuum, the spectra remain unchanged (spectra 1c and 1c′). All new bands disappear almost completely after evacuation of the infrared cell (<3 × 10^{-5} mbar) at increasing temperatures, room temperature (spectra 1d and 1d′), 100 °C (spectra 1e and 1e′), and 200 °C (spectra 1f and 1f ′), while the intensity of the band corresponding to the free silanol groups is almost entirely restored. Chemical analysis of this sample indicates a poor tin content, 0.4 wt % Sn. This shows that in these conditions very few firmly grafted species are present on the silica surface.

Since with procedure I the organostannics can condense on a cold part of the infrared cell, it was decided to operate with the sample holder containing the silica pellet sealed in a glass tubing, as described in procedure II. After the introduction of the organostannic on the sample, the glass tubing was completely immerged in an oven at 180 °C during 17 h. The spectra obtained by using this method are presented in Figure 2. The spectrum of silica treated at 500 °C (recorded before sealing the sample in the glass tubing) presents one band at 3747 cm^{-1} as previously (spectrum 2a). After the introduction of the organostannic and the heating treatment, the intensity of this band decreases dramatically and a new band appears at 3702 cm^{-1} (spectrum 2b). The bands of the adsorbed phase appear at 2961 cm^{-1} ($\nu_{as}(CH_3)$), 2929 cm^{-1} ($\nu_{as}(CH_2)$), 2877 cm^{-1} ($\nu_s(CH_3)$), 2852 cm^{-1} ($\nu_s(CH_2)$), 1461 and 1446 cm^{-1} ($\delta(CH_2)$, $\delta(CH_3)$), and 1390 and 1372 cm^{-1} ($\delta(CH_3)$) (spectrum 2b′). In this case, the adsorbed species are still present on the sample after evacuation at 100 °C (spectra 2c and 2c′). The spectrum is not affected by this treatment and is only slightly affected by an evacuation of the cell at 200 °C (spectra 2d and 2d′). The tin content of this sample is 2.1 wt % Sn. The signals observed can then be assigned to strongly grafted species and not to weakly bonded physisorbed species as it was the case in Figure 1.

The integrals of the absorbance between 3800 and 3500 cm^{-1} (ν(OH) bands) were calculated from the infrared spectra in an attempt to evaluate the proportion of the silanol groups which disappeared during the grafting reaction of the organostannic on silica. The results are given in the 2nd column of Table 1.

Table 1. Integrals of the Absorbance of the Silanol ν(OH) Vibration Bands (3747 and 3700 cm^{-1}) of Silica Interacting with Physisorbed Species and Silica Modified by Organometallic Fragments Resulting from the Grafting Reaction with ((−)-menthyl)Me_3Sn and ((−)-menthyl)Me_2SnH

	integral of the absorbance[a,b]	
organostannic used	((−)-menthyl)Me_3Sn	((−)-menthyl)Me_2SnH
silica	1.35 (silica(350))	1.00 (silica(500))
silica + physisorbed species	1.75	1.45
silica + grafted fragments	0.85	0.75
silanol consumption (%)[c]	50	45
wt % Sn	2.1	2.3
calcd silanol consumption (%)[d]	31	45

[a] Between 3800 and 3500 cm^{-1}. [b] In arbitrary unit, per gram of silica, with a value standardized to 1.00 for silica(500). [c] Values obtained from the IR data. The relative extinction coefficients of the two bands at 3747 and 3700 cm^{-1} were determined from the spectra. [d] Values calculated by assuming that (i) the silanol density is 1.5 OH/nm^2 for silica(500) and (ii) there is formation of a mono(siloxy)organotin species.

For silica(350), the integral of the absorbance is more important than for silica(500) (1.35 compared to 1.00). This is consistent with a decrease of the silanol concentration with temperature. Upon physisorption of ((−)-menthyl)Me_3Sn on silica(350), two bands are observed at 3747 and ca. 3700 cm^{-1} (spectrum 1b) and the integral of the absorbance increases from 1.35 to 1.75 while no generation of silanol groups is expected in this case. This shows that the ν(OH) band of free silanols at 3747 cm^{-1} and the broad band at ca. 3700 cm^{-1} assigned to ν(OH) bands of silanols interacting with physisorbed molecules or with grafted organometallic fragments (when the grafting reaction has occurred)[5] do not present the same extinction coefficient. At the end of the grafting reaction, when no more physisorbed species are present on the solid surface, the band at ca. 3700 cm^{-1} is still observed (spectra 2b−d). This shows that the grafted organometallic fragments interact with the silanol groups of silica. Compared to the initial silica, the integral of the ν(OH) band decreases from 1.35 to 0.85. This decrease is assigned to the consumption of the silanol groups of silica(350) (ca. 50% from calculation) upon the organostannic grafting on silica (reaction 1).

I-2. Quantitative Analysis of the Molecules Evolved during the Grafting Reaction. Influence of Temperature. For this study, procedure II was used. The samples were heated within sealed glass break-seal tubings during 72 h in an oven at a given temperature. In Figure 3 are presented the influence of the reaction temperature on the amount of grafted tin (Figure 3A), on the amount of the different hydrocarbons evolved during the grafting reaction (Figure 3B), and on the C/Sn_g ratio of the grafted organometallic fragments (Figure 3C) obtained by independent measurements of microanalysis (see Experimental Section). If all the tin was grafted onto silica, this would correspond to a theoritical maximum amount of 6.5 wt % of grafted tin. For an Aerosil silica sample activated at 450 °C under vacuum, the number of silanol groups has been estimated to 1.2−1.5 OH/nm^2.[26] If each OH group could react with one organostannic molecule to give one grafted organotin species, a maximum of 4.0−5.1 wt % of grafted tin would be expected. In the range 100−180 °C, the amount of grafted tin increases almost linearly from 1.1 wt % to 4.6% as it can be seen in Figure 3A. For thermal treatment above 160 °C, the color of the samples turns from white to dark gray, indicating the presence of side reactions. From Figure 3B it can be seen that below this temperature the amount of both hydrocarbons evolved per grafted tin is constant, 0.85 methane and 0.15 menthane, i.e., 1.0 mol of hydrocarbon (methane and menthane) evolved/mol of grafted tin. This result is in agreement with the formation of mono(siloxy) species, **3** (85%) and **4** (15%), through the following reactions, similar to (1):

$$\equiv Si{-}O{-}H + \underset{\mathbf{1}}{(menthyl)Me_3Sn} \rightarrow \underset{\mathbf{3}}{\equiv Si{-}O{-}Sn(menthyl)Me_2} + CH_4 \quad (4)$$

$$\equiv Si{-}O{-}H + \underset{\mathbf{1}}{(menthyl)Me_3Sn} \rightarrow \underset{\mathbf{4}}{\equiv Si{-}O{-}SnMe_3(menthyl)Me_2} + menthane \quad (5)$$

For higher temperatures, the amount of each hydrocarbon dramatically increases, reaching 1.03 methane and 0.26 menthane (i.e. 1.29 mol of hydrocarbon evolved/mol of grafted tin at 180 °C). This might be explained by the formation of bis(siloxy) species as **5** and **6** obtained from **3** or **4** on the silica surface:

$$\equiv Si{-}O{-}H + \underset{\mathbf{3}}{\equiv Si{-}O{-}Sn(menthyl)Me_2} \rightarrow \underset{\mathbf{5}}{(\equiv Si{-}O)_2Sn(menthyl)Me} + CH_4 \quad (6)$$

$$\equiv Si{-}O{-}H + \underset{\mathbf{3}}{\equiv Si{-}O{-}Sn(menthyl)Me_2} \rightarrow \underset{\mathbf{6}}{(\equiv Si{-}O)_2SnMe_2} + menthane \quad (7)$$

$$\equiv Si{-}O{-}H + \underset{\mathbf{4}}{\equiv Si{-}O{-}SnMe_3} \rightarrow \underset{\mathbf{6}}{(\equiv Si{-}O)_2SnMe_2} + CH_4 \quad (8)$$

The C/Sn$_g$ ratio remains constant, close to 12 for temperatures lower than 160 °C (theoretical values: **3**, C/Sn$_g$ = 12; **4**, C/Sn$_g$ = 3; **5**, C/Sn$_g$ = 11; **6**, C/Sn$_g$ = 2) and then decreases to values lower than 9 for higher temperatures (Figure 3C). This evolution and the one of the total amount of evolved hydrocarbons (Figure 3B(c)) are logically opposite.

Influence of the Grafting Time. The results obtained on the influence of temperature have shown that the grafting reaction rate increased with temperature and that at temperatures lower than 160 °C, 1 mol of hydrocarbon is evolved/mol of grafted tin. We chose therefore to prepare the samples at 150 °C. In Figure 4 are presented the influence of reaction time for a grafting reaction conducted at 150 °C on the amount of grafted tin (Figure 4A) and of the different hydrocarbons evolved during the grafting reaction (Figure 4B) and on the C/Sn$_g$ ratio of the grafted organometallic fragments (Figure 4C). The reaction time varies from 3 to 72 h. At 150 °C the amount of grafted tin on silica increases with time and seems to reach a pseudoplateau, between 3.5 and 4.0 wt %, while the distribution among the hydrocarbons evolved remains constant with time, 0.85 methane (Figure 4B(b)) and 0.15 menthane (Figure 4B(a)), i.e., a total amount of 1 mol of hydrocarbon evolved/mol of grafted tin (Figure 4B(c)). The C/Sn$_g$ ratios do not vary much either with time, with an average value of ca. 12 (Figure 4C).

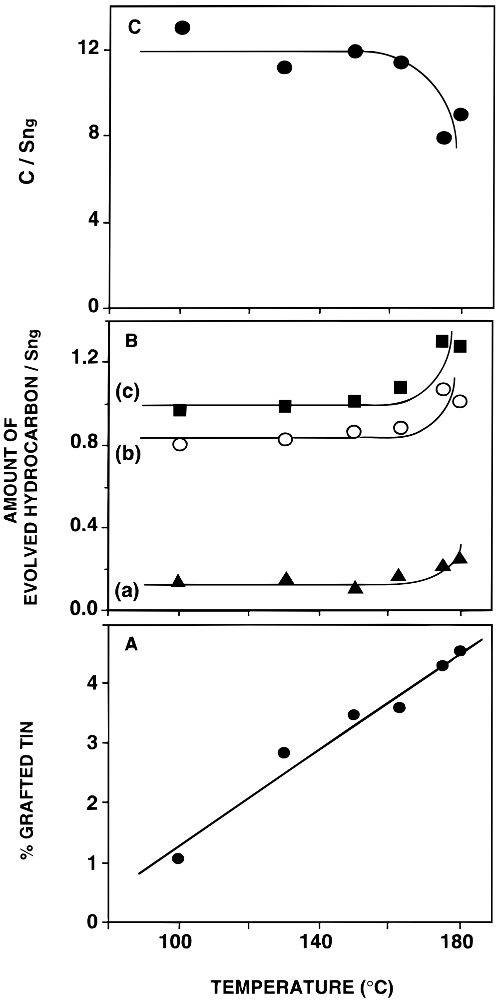

Figure 3. Influence of temperature on ((−)-menthyl)Me$_3$Sn grafting on silica(500). A: amount of grafted tin (wt % Sn); B: amount of hydrocarbons evolved per grafted tin atom: (a) menthane emission; (b) methane emission; (c) total hydrocarbon = menthane + methane; C: molar amount of carbon per mole of grafted tin (C/Sn$_g$ ratio of the solid after chemical analysis).

I.3. NMR Studies. ^{119}Sn NMR. In Figure 5, spectrum 5a shows the ^{119}Sn NMR spectrum of ((−)-menthyl)Me$_3$Sn (**1**) in solution in C$_6$D$_6$. When ((−)-menthyl)Me$_3$Sn is physisorbed on silica, the same spectrum is obtained, only a small broadening of the lines being detected. Spectrum 5b corresponds to the

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[26] Morrow, B. A. Spectroscopic Characterisation of Heterogeneous Catalysts. *Stud. Surf. Sci. Catal.* **1990**, *57A*, 161.

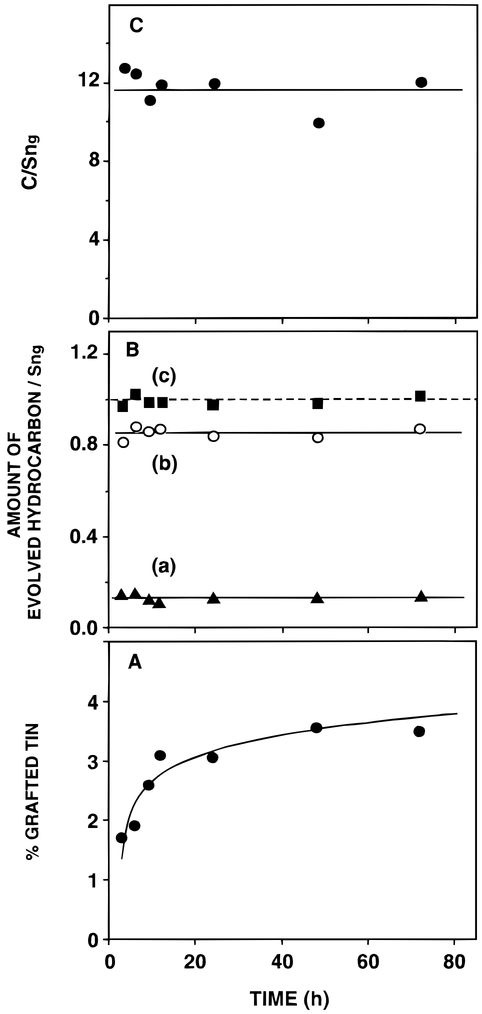


Figure 4. Influence of reaction time on ((−)-menthyl)Me_3Sn grafting on silica(500) at 150 °C. A: amount of grafted tin (wt % Sn); B: amount of hydrocarbons evolved per grafted tin atom: (a) menthane emission; (b) methane emission; (c) total hydrocarbon = menthane + methane; C: molar amount of carbon per mole of grafted tin (C/Sn_g ratio of the solid after chemical analysis).

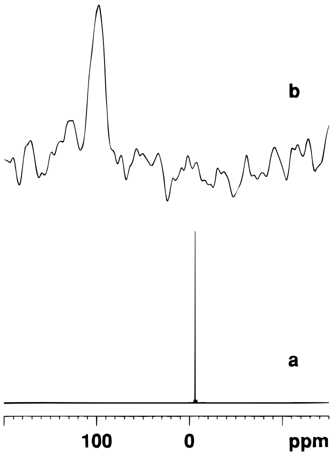


Figure 5. ^{119}Sn proton decoupled NMR spectra of (a) ((−)-menthyl)Me_3Sn in C_6D_6; (b) organostannic fragments (MAS) after ((−)-menthyl)Me_3Sn grafting on silica(500) at 150 °C (163h; 4.2 wt % Sn).

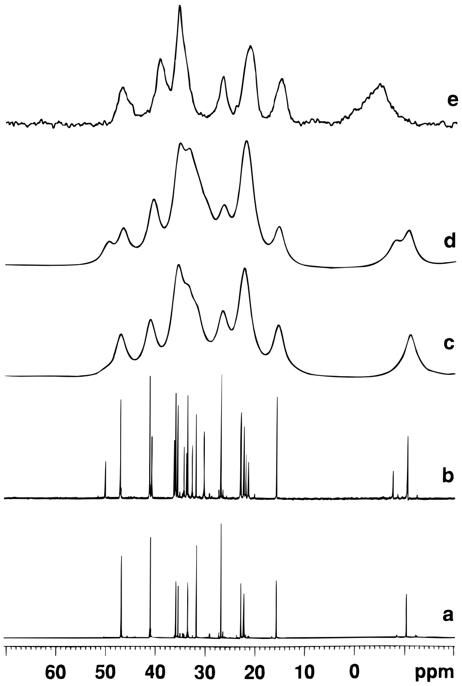


Figure 6. ^{13}C proton-decoupled NMR spectra of (a) ((−)-menthyl)Me_3Sn in C_6D_6, (b) mixture of ((−)-menthyl)Me_3Sn (80%) and ((+)-neomenthyl)Me_3Sn (20%) in C_6D_6 ((−)-menthyl, 1*R*,2*S*,5*R*; (+)-neomenthyl, 1*S*,2*S*,5*R*); (c) spectrum a in which each signal has been enlarged by a Gaussian function in order to simulate the immobilization of the compound on the silica surface; (d) spectrum b in which each signal has been enlarged by a Gaussian function; (e) organostannic fragments (CP/MAS) after ((−)-menthyl)Me_3Sn grafting on silica(500) at 150 °C (163 h; 4.2 wt % Sn).

solid (4.2 wt % Sn) resulting from the reaction of silica-(500) with this organostannic at 150 °C and after further washings of the material with *n*-heptane in order to eliminate the physisorbed species. While the pure organostannic presents one sharp signal at −6.3 ppm, one broad signal clearly appears on the rather noisy solid-state NMR spectrum at +98 ppm for the organometallic fragments grafted on silica(500) (spectrum 5b).

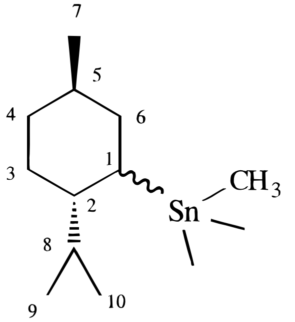
^{13}C NMR. The ^{13}C NMR spectra are shown in Figure 6. Spectrum 6a corresponds to pure liquid ((−)-menthyl)-Me_3Sn (**1**) (similar to that of the compound physisorbed on silica) with the signal of the three methyl groups bonded to tin at −10.2 ppm and the 10 signals of the 10 carbons of the menthyl group (C_1-C_{10}). Their respective chemical shifts are listed in Table 2. Spectrum 6b corresponds to a mixture of ((−)-menthyl)Me_3Sn (predominant) and ((+)-neomenthyl)Me_3Sn (minor).[20]

Spectra 6c,d correspond respectively to spectra 6a,b with a multiplication of the NMR signals by a Gaussian function in order to simulate the immobilization of the species on the silica surface and to compare these spectra with the observed spectrum of the grafted species, 6e (4.2 wt % Sn). For this sample, the position and the assignment of the different ^{13}C NMR chemical shifts are also reported in Table 2.

II. Reactivity of ((−)-Menthyl)dimethyltin Hydride (2) with Silica(500). Since tin hydrides are more reactive than tetraalkyl ones, the grafting reaction of ((−)-menthyl)dimethyltin hydride could be followed directly in the infrared cell or the glass reaction vessel, according to procedure I (see Experimental Section).

II.1. Infrared Study. Upon adsorption of ((−)-menthyl)dimethyltin hydride on silica(500), the absorbance of the ν(OH) band of silica at 3747 cm^{-1} decreases

Table 2. ^{119}Sn and ^{13}C NMR Chemical Shifts in ppm for ((+)-neomenthyl)Me_3Sn, ((−)-menthyl)Me_3Sn, ((−)-menthyl)Me_2SnH, and ((−)-menthyl)$_x$$Me_ySn$ Fragments Supported on Silica(500) Prepared (A) from ((−)-menthyl)Me_3Sn (1) at 150 °C and (B) from ((−)-menthyl)Me_2SnH (2) at 80 °C



	((+)-neomenthyl)Me_3Sn[a]	((−)-menthyl)Me_3Sn[a]	((−)-menthyl)Me_2SnH[a]	A[b]	B[b]
^{119}Sn[c]	−8.2	−6.3	−98.3	98	103
CH_3	−7.6	−10.4	−12.7 −12.9	−4.8	−5.6
C_1	32.5	31.8	31.5	35.9	36.0 ($C_1 + C_4 + C_5 + C_8$)
C_2	49.6	46.9	47.2	47.2	47.4
C_3	29.8	26.8	26.8	26.9	27.1
C_4	36.5	35.8	35.8	35.9	36.0 ($C_1 + C_4 + C_5 + C_8$)
C_5	34.2	35.4	35.4	35.9	36.0 ($C_1 + C_4 + C_5 + C_8$)
C_6	40.3	41.0	41.6	39.8	40.0
C_7	21.8	22.8	22.7	21.6	21.4 ($C_7 + C_9$)
C_8	33.6	33.5	33.5	35.9	36.0 ($C_1 + C_4 + C_5 + C_8$)
C_9	21.2	22.2	22.1	21.6	21.4 ($C_7 + C_9$)
C_{10}	15.7	15.7	15.6	15.1	15.4

[a] In C_6D_6. [b] The best precision for the chemical shifts is ±0.3 ppm in this case. [c] Reference is Me_4Sn.

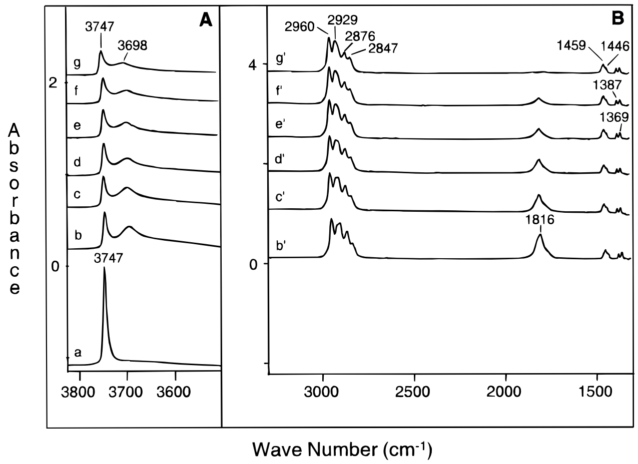


Figure 7. ((−)-menthyl)Me_2SnH interaction with silica-(500) followed by IR: (A) silanol vibrations of the solid; (B) spectra of the adsorbed phase (after subtraction of the silica contribution); (a) silica(500); (b, b′) sample a after introduction of ((−)-menthyl)Me_2SnH; (c, c′) sample b after 24 h at room temperature; sample c after thermal treatment at 60 °C; (d, d′) 4 h; (e, e′) 18 h; (f, f ′) 28 h; (g, g′) sample f after vacuum treatment at room temperature (2 h). An amount of 2.3 wt % Sn was grafted at the end of the experiment.

and a broad band appears at ca. 3700 cm^{-1} (comparison of spectra 7a,b in part A in Figure 7). This last band is assigned to ν(OH) of silica OH groups interacting via van der Waals forces with adsorbed molecules. The bands of the adsorbed species appear at 2960 cm^{-1} (ν_{as}(CH_3)), 2915 cm^{-1} (ν_{as}(CH_2)), 2876 cm^{-1} (ν_s(CH_3)), 2847 cm^{-1} (ν_s(CH_2)), 1816 cm^{-1} (ν(SnH)), 1459 and 1446 cm^{-1} (δ(CH_2), δ(CH_3)), and 1387 and 1369 cm^{-1} (δ(CH_3)) (spectrum 7b′ in part B in Figure 7). If the infrared cell is quickly opened to the vacuum line, these bands disappear and the intensity of the ν(OH) band of silica at 3747 cm^{-1} is fully restored. This shows that these bands can be assigned to simply physisorbed species. If the reaction is allowed to proceed for 24 h at room temperature, infrared bands assigned to free and interacting OH groups are still present (spectrum 7c) and the absorbance of the ν(SnH) band at 1816 cm^{-1} decreases in intensity without fully disappearing (spectrum 7c′). This indicates that some ((−)-menthyl)-dimethyltin hydride is still present on silica. It can be already seen from this infrared study that ((−)-menthyl)-Me_2SnH is less reactive toward silica than Bu_3SnH since this last hydride entirely reacted, under similar conditions, with silica in less than 24 h at room temperature.[5] If the temperature is raised to 60 °C at increasing reaction times, 4 h (spectra 7d,d′), 18 h (spectra 7e,e′) and 28 h (spectra 7f,f ′), the absorbance of the ν(SnH) band decreases with time, while the rest of the spectrum remains almost unchanged. After heating of the sample at 60 °C during 28 h and evacuation for 2 h at room temperature, the ν(SnH) band at 1816 cm^{-1} disappears completely (spectrum 7g′), showing that no more ((−)-menthyl)dimethyltin hydride is physisorbed. Chemical analysis of the pellet showed that an amount of 2.3 wt % Sn was grafted.

The integrals of the absorbance between 3800 and 3500 cm^{-1} (ν(OH) bands) were also calculated in this case, as previously for the interaction of **1** with silica-(350). The results are given in the 3rd column of Table 1. Upon physisorption of ((−)-menthyl)Me_2SnH on silica(500) (spectrum 7b), the ν(OH) band of free silanols at 3747 cm^{-1} and the broad band at ca. 3700 cm^{-1} assigned to ν(OH) bands of silanols interacting with physisorbed molecules do not present the same extinction coefficient since the integral of absorbance increases from 1.00 to 1.45 while no silanol generation is expected. During the grafting reaction, the integral of the ν(OH) bands decreased from 1.00 to 0.75 compared to the initial integrated absorbance of the ν(OH) band of silica. This decrease is assigned to the consumption of the silanol groups of silica(500) (ca. 45% from calculation) upon the organostannic grafting on silica (reaction 2).

II.2. Quantitative Analysis of Molecules Evolved during the Grafting Treatment. Influence of Time and Temperature. In Figure 8 is presented the evolution of the gases evolved with time during grafting reactions conducted at room temperature (Figure 8A), 80 °C (Figure 8B,B′), and 100 °C (Figure 8C,C′). At room temperature, only dihydrogen is detected in the gas phase. At 80 and 100 °C, dihydrogen (Figure 8B,C) and methane (Figure 8B′,C′) are detected. For each gas, the rate of evolution and the amount evolved increase with temperature. After ca. 40 h at 80 °C, the amount of grafted tin is 3.9 wt % with $H_2/Sn_g = 1.0$, $CH_4/Sn_g = 0.02$, and $C/Sn_g = 12$ while, at 100 °C, an amount of 4.5 wt % tin is grafted with $H_2/Sn_g = 1.0$, $CH_4/Sn_g = 0.12$, and $C/Sn_g = 12$. For these samples, no menthane is detected after several *n*-heptane washings. At this point, from the previously presented IR study and from these results concerning the amounts of gases evolved during the grafting reaction, it appears that ((−)-menthyl)Me_2SnH reacts too slowly with silica at room temperature and a thermal activation is necessary. However 100 °C seems a temperature a bit too high since a non-negligeable amount of methane is produced. According to the higher reactivity of the ≡Sn−H bond compared to that of the ≡Sn−CH_3 bond, ((−)-menthyl)Me_2SnH should react preferentially with silica according to reaction 9, producing dihydrogen and a mono(siloxy)trialkyltin surface species, ≡Si−O−Sn(menthyl)Me_2 (**3**), rather than the surface hydride **7** and methane, as presented by reaction 10. The evolution of methane may be explained by side reactions as (6) (degradation of species **3** into **5**) or (10), and it is better to minimize the amount of methane produced during the grafting reaction in order to avoid a mixture of tin species on the silica surface (see below in the discussion).

$$\equiv\text{Si–O–H} + (\text{menthyl})\text{Me}_2\text{SnH} \rightarrow \underset{\mathbf{3}}{\equiv\text{Si–O–Sn(menthyl)Me}_2} + \text{H}_2 \quad (9)$$

$$\equiv\text{Si–O–H} + (\text{menthyl})\text{Me}_2\text{SnH} \rightarrow \underset{\mathbf{7}}{\equiv\text{Si–O–SnH(menthyl)Me}} + \text{CH}_4 \quad (10)$$

$$\equiv\text{Si–O–H} + \underset{\mathbf{7}}{\equiv\text{Si–O–SnH(menthyl)Me}} \rightarrow \underset{\mathbf{3}}{(\equiv\text{Si–O})_2\text{Sn(menthyl)Me}} + \text{H}_2 \quad (11)$$

The extent of these side reactions compared to reaction 9 may be obtained from the molar ratio $(H_2 - CH_4)/H_2$. If reaction 9 occurs selectively, $(H_2 - CH_4)/H_2 = 1.0$. However, if side reactions occur in parallel, then this value decreases. The evolution of this ratio with time is presented in Figure 9 for samples prepared at 80 °C (curve A) and at 100 °C (curve B). Fom these curves, it appears clearly that (i) methane formation increases with time and (ii) methane formation is more important at 100 °C than at 80 °C. At room temperature (22 °C), no methane is detected but the reaction is very slow.

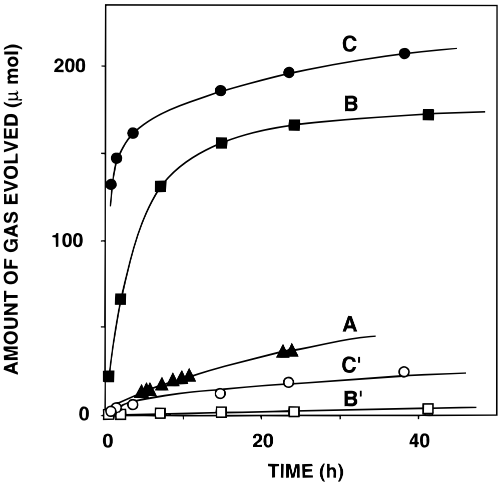


Figure 8. Amounts of gas evolved during the grafting reaction of ((−)-menthyl)Me_2SnH onto silica(500) (500 mg): at 25 °C, (A) H_2; at 80 °C, (B) H_2 and (B′) CH_4; at 100 °C, (C) H_2 and (C′) CH_4.

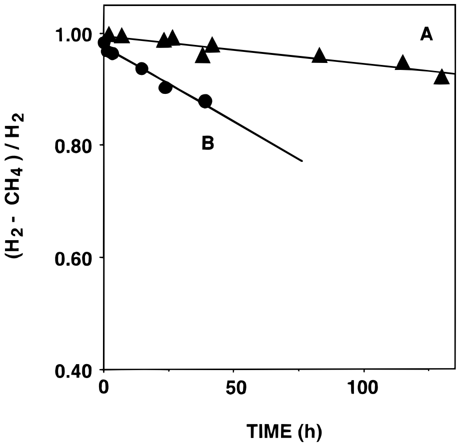


Figure 9. Evolution of the $(H_2 - CH_4)/H_2$ ratio with time during the grafting reaction of ((−)-menthyl)Me_2SnH on silica(500) (A) at 80 °C and (B) at 100 °C.

At 80 °C, the reaction seems to be fast enough and less than 5% methane is present in the gas phase. Therefore various samples containing 3.5−6.0 wt % tin on silica(500) were prepared at 80 °C with H_2/Sn_g ratios close to 1.0 or slightly exeeding this value (average: 1.04; A in Figure 10), CH_4/Sn_g ratios lower than 0.05 (average: 0.03; B in Figure 10), and C/Sn_g ratios close to 12 (average: 11.8; C in Figure 10).

II.3. NMR Studies. ^{119}Sn NMR. The ^{119}Sn NMR spectra are presented on Figure 11. Spectrum 11a corresponds to ((−)-menthyl)Me_2SnH (**2**) in solution in C_6D_6 (proton decoupled). When ((−)-menthyl)Me_2SnH is physisorbed on silica, the same spectrum is obtained, only a small broadening of the lines being detected. Spectrum 11b corresponds to the solid (3.9 wt % Sn) resulting from the reaction of silica(500) with this organostannic at 80 °C and after further *n*-heptane washings of the material in order to get rid of the physisorbed species. While **2** presents one sharp signal at −98.3 ppm, one broad signal appears at +103 ppm

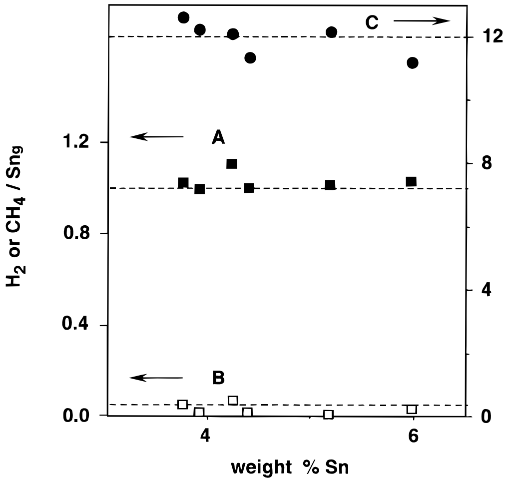


Figure 10. ((−)-menthyl)Me_2SnH grafting on silica(500) at 80 °C of (A) H_2/Sn_g, (B) CH_4/Sn_g, and (C) C/Sn_g (after analysis of the solid) ratios plotted against the grafted tin content of the samples (wt % Sn).

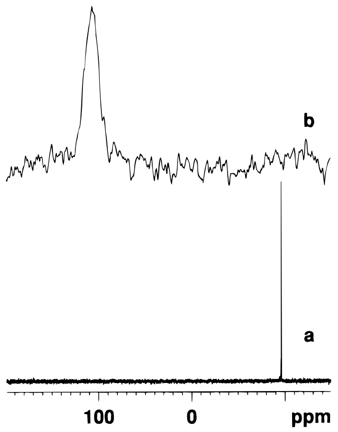


Figure 11. ^{119}Sn proton-decoupled NMR spectra of (a) ((−)-menthyl)Me_2SnH in C_6D_6 and (b) organostannic fragments (MAS) after ((−)-menthyl)Me_2SnH grafting on silica-(500) at 80 °C (40 h; 3.9 wt % Sn).

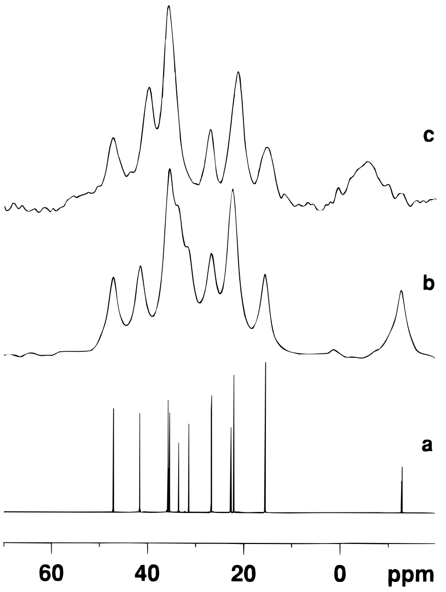


Figure 12. ^{13}C proton-decoupled NMR spectra of (a) ((−)-menthyl)Me_2SnH in C_6D_6, (b) spectrum a in which each signal has been enlarged by a Gaussian function in order to simulate the immobilization of the compound on the silica surface, and (c) organostannic fragments (CP/MAS) after ((−)-menthyl)Me_2SnH grafting on silica(500) at 80 °C (40 h; 3.9 wt % Sn).

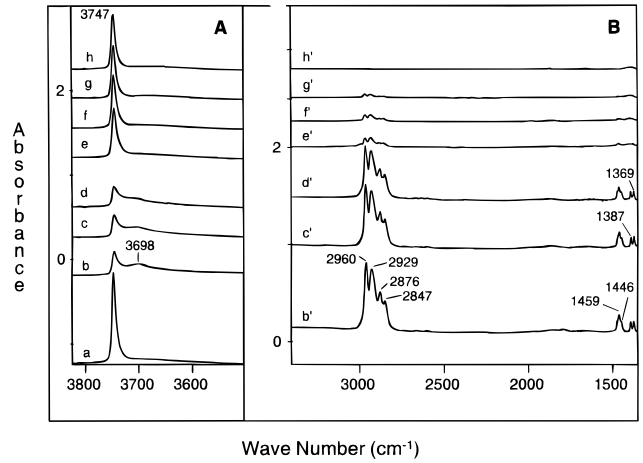


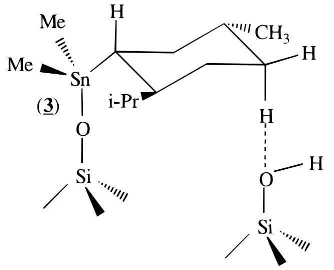
Figure 13. Thermal decomposition of **3**, formed on silica-(500) from **2** at 60 °C, followed by IR: (A) silanol vibrations of the solid; (B) spectra of the grafted species (after subtraction of the silica contribution); (a) silica(500); (b, b′) ≡Si−O−Sn((−)-menthyl)Me_2 (**3**), after treatment under vacuum at room temperature (4 h); (c, c′) b after treatment under vacuum at 100 °C (17 h); (d, d′) c after treatment under vacuum at 150 °C (17 h); (e, e′) d after treatment under vacuum at 200 °C (17 h); (f, f′) e after treatment under vacuum at 250 °C (17 h); (g, g′) f after treatment under vacuum at 300 °C (17 h); (h, h′) g after treatment under vacuum at 350 °C (17 h).

in the solid-state NMR spectrum for the organometallic fragments grafted on silica.

^{13}C NMR. The ^{13}C NMR spectrum of **2** in solution in C_6D_6 corresponds to Figure 12a; it is similar to that of the compound physisorbed on silica. The respective positions of the peaks are listed in Table 2. Spectrum 12b corresponds to spectrum 12a with a multiplication of the NMR signals by a Gaussian function in order to simulate the immobilization of the species on the silica surface. This last spectrum can be compared with the observed spectrum of the grafted species, Figure 12c. For this sample, the position and the assignment of the different ^{13}C NMR signals are also reported in Table 2.

III. Thermal Stability of the Grafted Organometallic Fragments. The thermal stability of the grafted organometallic species was studied by infrared spectroscopy (Figure 13): in part A is presented the spectrum of the solid in the range of the silica ν(OH) bands, and in part B is presented the spectrum of the adsorbed phase obtained by difference with the spectrum of silica. In part A, spectrum 13a shows, at 3747 cm^{-1}, the ν(OH) band of silica OH groups before the grafting reaction. Spectra 13b and 13b′ concern a sample formed by the reaction at 60 °C of ((−)-menthyl)Me_2SnH with silica(500) and elimination of the physisorbed phase under vacuum. The infrared cell was then closed, and the sample was heated during 15 h at 100 °C; the cell was then opened on the vacuum line during 2 h while the pellet was maintained at the same temperature. The resulting spectra (13c,c′) are shown on Figure 13. The experimental procedure described above was repeated at increasing temperatures, 150 °C (spectra 13d,d′), 200 °C (spectra 13e,e′), 250 °C (spectra

Scheme 1. Interaction of 3 with an Unreacted Silanol Group of Silica



13f,f′), 300 °C (spectra 13g,g′), and finally 350 °C (spectra 13h,h′). It appears clearly that the ν(CH) (2960, 2929, 2876, and 2847 cm^{-1}) and δ(CH) bands (1459, 1446, 1387, and 1369 cm^{-1}) of the alkyl groups bonded to tin disappear quite completely after a thermal treatment at 200 °C while they are still present after the treatment performed at 150 °C.

Discussion

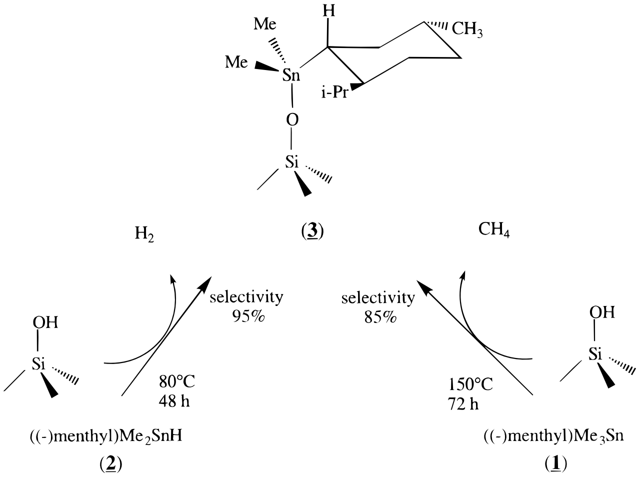
In the course of this study we have followed the interaction of two chiral organotin compounds, ((−)-menthyl)Me$_3$Sn (**1**) and ((−)-menthyl)Me$_2$SnH (**2**), with two types of silica (silica(350) and silica(500)). We wish to discuss here the nature of this interaction with the silanols of silica, the nature of the grafted organometallic entities, the structure at a molecular level of the major surface organotin compound, and finally its thermal stability.

Interaction of the Organostannics with the Silanol Groups of Silica. Regarding the nature of the reacting groups on the silica surface, infrared spectroscopy gives us qualitative and quantitative informations. With **1** interacting with silica(350) at room temperature, adsorption is a reversible process. There is a quantitative regeneration of the free silanols after evacuation. These silanols were interacting via van der Waals interactions with the C−H bonds of **1**. Infrared spectroscopy clearly shows that while 2.1 wt % of tin was grafted on silica, ca. 50% of the silanols have reacted with the compound at 180 °C. There are some bridged OH remaining (band at ca. 3700 cm^{-1}), suggesting that some silanols have not reacted and are likely interacting with the grafted tin compound via hydrogen bonding. Such kind of interaction has been already observed several times in surface organometallic chemistry[5] (Scheme 1).

With **2** interacting with silica(500), there is also a reversible physical adsorption at room temperature as evidenced by infrared spectroscopy (quantitative regeneration of the ν(OH) signal at 3747 cm^{-1} after adsorption and evacuation). If **2** is allowed to react for a longer time or if temperature is raised at 60 °C, a fair but not total fraction (ca. 45%) of the silanols is consumed. Similarly, the grafted organotin compound interacts with the remaining silanols via hydrogen bonding (band at ca. 3700 cm^{-1}).

Nature of the Organostannic Entities. In the range of temperature studied, according to previous results obtained with several organotin compounds, different reactions can be reasonably considered between the organostannics **1** or **2** and the silica surface, depending on what bond of the starting organometallic will be broken (reactions 4, 5, 9, or 10) and on the formation or not of multigrafted species (reactions 6−8 and 11). Concerning the nature of the grafted organometallic entity, it is clear that starting from **1** or **2** with silica(500), a well-defined structure is obtained predominantly, ≡Si−O−Sn(menthyl)Me$_2$ (**3**), according to reactions 4 or 9. We have seen however that **3** is not obtained fully selectively. Starting from **1**, some menthane evolution indicates that ≡Si−O−SnMe$_3$ (**4**) is also formed in minor amount, and starting from **2**, some methane evolution shows that other side reactions occur besides reaction 9. It should be pointed out that **3** can be obtained by two different routes, the most selective being by reaction of the tin hydride derivative, **2**. We shall examine this structure before entering into other minor species such as ≡Si−O−SnMe$_3$ (**4**), (≡Si−O)$_2$Sn(menthyl)Me (**5**), or (≡Si−O)$_2$SnMe$_2$ (**6**) (Scheme 2).

Scheme 2



NMR Characterizations of the Organostannic Surface Species. The relatively well-defined chiral compound **3** has been characterized by IR, microanalysis for Sn$_g$ and C concentrations and GC quantitative analysis of the evolved products during the grafting reaction. The corresponding ^{119}Sn NMR broad signal is present at ca. 100 ppm, close to the position which was observed for ≡Si−O−Sn(n-Bu)$_3$ (103 ppm). According to several former studies, the grafting of an organostannic compound to give mono(siloxy) ≡Si−O−SnR$_3$ surface species produces a deshielding of the tin atom which results in a downfield shift of the ^{119}Sn signal of ca. 70−150 ppm, starting from a tetraalkyl, or ca. 200 ppm, starting from a monohydride trialkyl,[5,6] consistently with a four-coordinated tin atom as in a (RO)-R′$_3$Sn compound.[27,28] The broad ^{119}Sn NMR signal observed at 100 ppm can then be assigned to mono(siloxy)trialkyltin(IV) species. In the case of ((−)-menthyl)Me$_3$Sn (**1**) grafting on silica, some menthyl groups were lost during the reaction since some menthane was evolved and the mono(siloxy) ≡Si−O−SnMe$_3$ (**4**) may have been formed. These species, which were obtained selectively from Me$_4$Sn grafting on silica at 180 °C and studied in detail, should give a ^{119}Sn NMR signal at 136 ppm.[5] It seems possible that this signal is present in spectrum a in Figure 5 (first peak at the left

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of the main signal) but the signal/noise ratio is to low to conclude. In the case of ((−)-menthyl)Me_2SnH (**2**) grafting on silica, this signal does not appear (spectrum b in Figure 11). The only mono(siloxy)trialkyltin(IV) species which can give a ^{119}Sn NMR signal at 100 ppm is then ≡Si−O−Sn(menthyl)Me_2 (**3**), resulting from reactions 4 or 9 starting respectively from **1** or **2**. Bis(siloxy) type species have already been observed for a dibutyltin(IV)-containing polyhedral oligosilsesquioxanes, with a ^{119}Sn NMR signal at −37 ppm in a solvent and at −36.5 ppm by MAS NMR,[29] consistently with a four-coordinated tin atom as in a monomeric $(\text{RO})_2\text{R}'_2$Sn complex,[27,28] and after tetrabutyltin grafting on a mesoporous MCM-41 silica previously thermally treated at 200 °C, with a signal at ca. −40 ppm.[30] In this last case, the signal was difficult to observe since many spinning sidebands were observed due to the anisotropy of the chemical shifts around the tin atom. In our case, no other ^{119}Sn signal was detected by MAS NMR between −300 and 300 ppm either because no tin species other than mono(siloxy) are formed on the silica surface or since other species do not give signals sharp enough to be detected.

The ^{13}C CPMAS NMR spectra of the solids after the organostannic grafting reaction (spectra e in Figure 6 and c in Figure 12) show that methyl and menthyl groups bonded to tin are still present in the surface organometallic fragments. By comparison of the spectrum of the liquid organostannic (after a line broadening of the NMR signals by a Gaussian function) with the spectrum of the grafted organometallic fragments (comparison of spectra c and e in Figure 6 or b and c in Figure 12), it can be seen that the general shape of the spectra with seven broad ^{13}C resonance bands is rather similar. However two main differences can be observed: (i) The signal of the methyl groups bonded to tin is more deshielded for the organometallic fragments grafted on silica than for the liquid organometallics. It appears on the surface at ca. −5 ppm, whereas it resonates at −10.4 ppm for ((−)-menthyl)Me_3Sn and it appears as a doublet at −12.7 and −12.9 ppm for ((−)-menthyl)Me_2SnH. (ii) The shoulders, due to C_1 and C_8 carbon atoms, which appear on the high-field part of the stronger signal, at ca. 36 ppm, in the spectrum simulated from the one of the liquid (c in Figure 6 or b in Figure 12) do not appear on the spectrum of the surface organometallics (e in Figure 6 or c in Figure 12). These observations can be explained by a shift to lower fields of the carbon atoms directly bonded to tin in the surface complexes compared to liquid organostannics. This low-field shift (ca. 6 ± 2 ppm) has already been observed for several surface organostannic compounds and is related to the exchange of one carbon by one oxygen in the coordination sphere of tin.[5,6,31] In particular, the C_1 carbon atom, which appears at 31.5 or 31.8 ppm for **1** and **2** (liquid form), would be shifted to ca. 36.5 ppm for the grafted mono(siloxy) species. The observed strongest ^{13}C signal at ca. 36.0 ppm in the CP MAS NMR spectrum of the surface species can then be assigned to the sum of the contribution of C_1 (ca. 36.5 ppm), C_4 (ca. 36 ppm), C_5 (ca. 35.5 ppm), and C_8 (ca. 33.5 ppm) carbons of the grafted species. Other minor shifts can be noticed by comparing the position of the ^{13}C NMR signals given in the four last columns of Table 2. As for ≡Si−O−Sn(cyclohexyl)$_3$,[6] it can be noticed that the signals corresponding to carbon atoms in β position of the tin atom (C_2 and C_6) are not strongly shifted upon the organostannics grafting on silica. The ^{13}C NMR signal of ≡Si−O−SnMe_3 (**4**) species should appear at −7.8 ppm.[5] Unfortunately, the width of the methyl signal at ca. −5 ppm in spectrum e in Figure 6 is too large to conclude to the presence of such species.

By comparison of the ^{13}C NMR spectra 6d,e in Figure 6, it can also be shown that as expected the configuration of the C_1 carbon is kept. If an inversion had occurred, (−)-menthyl (1*R*,2*S*,5*R*) would be transformed into a (+)-neomenthyl group (1*S*,2*S*,5*R*). By comparison of the chemical shifts of the C_1-C_{10} carbons of liquid ((−)-menthyl)Me_3Sn and ((+)-neomenthyl)Me_3Sn in Table 2, it can be seen that the most important differences are for C_2 ($\Delta\delta = 2.7$ ppm) and C_3 ($\Delta\delta = 3.0$ ppm). Spectrum 6d corresponds to a mixture of ((−)-menthyl)Me_3Sn (ca. 80%) and ((+)-neomenthyl)Me_3Sn (ca. 20%) which has been modified with a line broadening of the NMR signals by a Gaussian function. $\text{C}_2{}^+$ and $\text{C}_3{}^+$ of (+)-neomenthyl appear respectively as shoulders at 49.6 and 29.8 ppm. The compararison of spectra d and e in Figure 6 clearly shows that no shoulder at ca. 50 or 30 ppm, which can be assigned to the C_2 or C_3 carbon of the (+)-neomenthyl group, is present on the low-field part of the signals corresponding to C_2 (47.2 ppm) or C_3 (26.9 ppm) of the surface organostannic (spectrum 6e).

In conclusion, for the grafting of both organostannics on silica, ((−)-menthyl)Me_3Sn (**1**) and ((−)-menthyl)Me_2SnH (**2**), ^{119}Sn and ^{13}C NMR studies are in agreement with the presence of a well-defined mono(siloxy) species: ≡Si−O−Sn((−)-menthyl)Me_2 (**3**). Possibly small amounts of ≡Si−O−SnMe_3 (**4**) also exist starting from **1**, but this is not obvious from the NMR studies. Besides, there is no evidence for the existence of bis(siloxy) or other surface organotin species.

((−)-menthyl)Me₃Sn (1) Grafting on Silica. At temperatures lower than 160 °C, the results obtained are consistent with the formation of a mixture of mono(siloxy) species, ≡Si−O−Sn((−)-menthyl)Me_2 (**3**) and ≡Si−O−SnMe_3 (**4**), in the proportion 0.85/0.15. In the conditions of our study, this proportion does not depend either on temperature or on reaction time:

$$\equiv\text{SiOH} + \underset{\mathbf{1}}{(\text{menthyl})\text{Me}_3\text{Sn}} \rightarrow 0.85\underset{\mathbf{3}}{\equiv\text{Si}-\text{O}-\text{Sn}((-)\text{menthyl})\text{Me}_2} + 0.85\text{CH}_4 + 0.15\underset{\mathbf{4}}{\equiv\text{Si}-\text{O}-\text{SnMe}_3} + 0.15\text{menthane} \quad (12)$$

The mechanism of this reaction can be described as an electrophilic cleavage of a Sn−C bond by a silanol group.[32] Since there are three methyl for one menthyl group in **1**, the Sn−Me bond appears then $^1/_3$(0.85/0.15) = 1.9 times more reactive than the Sn−menthyl bond.

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This can be explained by steric and electronic effects since the carbon of a methyl group is more accessible and more negatively polarized than C_1 of menthyl. In the case of the electrophilic cleavage of Sn−alkyl bonds by dibromine or diiodine in polar solvents (S_E2), it has also generally been observed that the carbon leaving the tin atom is predominantly the less substituted.[14,33,34]

At temperatures higher than 160 °C, more than 1 mol of hydrocarbon was evolved/mol of grafted tin atom (1.29 hydrocarbon molecules per grafted tin at 180 °C) while the C/Sn_g ratio of the solid dramatically decreased to values lower than 8.0, in agreement with the observed menthyl loss. This might indicate the presence of some bis(siloxy) species. But we did not try to characterize by ^{119}Sn NMR the organometallic fragments obtained above 160 °C.

To obtain large amounts (more than 3 wt % Sn) of $\equiv Si-O-Sn((-)\text{-menthyl})Me_2$ (**3**) species from ((−)-menthyl)Me_3Sn (**1**) grafting on silica with a good selectivity, the thermal treatment must be conducted according to procedure II (see Experimental Section) at temperatures lower than 160 °C during more than 48 h. However, in these conditions, only 85% of the grafted tin is present as **3**, due to the fact that $\equiv Si-O-SnMe_3$ (**4**) species are likely to be formed too, with a loss of the chiral ((−)-menthyl) group.

((−)-menthyl)Me_2SnH (2) Grafting on Silica. For ((−)-menthyl)Me_2SnH (**2**) grafting on silica, only dihydrogen and low amounts of methane were evolved. At temperatures lower than 80 °C, since ratios very close to the theory are observed, $H_2/Sn_g = 1.0$ and $C/Sn_g = 12$, with less than 5% methane (Figure 10) and no menthane and according to NMR and IR characterizations, the grafting reaction can be well depicted by reaction 9. The question which then arises is how is methane formed? Its proportion in the gas evolved during the grafting reaction increases with time and can reach up to 12% of the gas-phase evolved at 100 °C after 40 h (Figure 9). Two possibilities may be foreseen:

(i) Methane may be produced by reaction 10, and the surface hydride obtained, $\equiv Si-O-SnH(\text{menthyl})Me$ (**7**), would react fastly with another silanol group to give a bis(siloxy) species, $(\equiv Si-O)_2Sn(\text{menthyl})Me$ (**5**), according to reaction 11. In this case, the reaction scheme would be two parallel reactions [(9) and (10) + (11)].

(ii) Another possibility is that methane is produced from the reaction of $\equiv Si-O-Sn(\text{menthyl})Me_2$ (**3**), obtained by reaction 9, with another silanol group to give the same bis(siloxy) species (**5**), according to reaction 6. The reaction scheme would then be two successive reactions [(9) + (6)].

These two cases would agree with a ratio $H_2/Sn_g = 1.0$ and with a low methane production if (i) reaction 10 is slow compared to (9) and reaction 11 is fast compared to (10) or (ii) reaction 6 is slow compared to (9). In the first case (i), methane would be a primary product, and in the second case (ii), a secondary product of the grafting reaction. According to the plots presented in Figure 10, it can be seen that methane proportion in the gas mixture evolved increases with time and tends to zero at the begining of the reaction. This seems to indicate that methane comes from a secondary reaction and would be in favor of the second hypothesis (reaction 9 and then reaction 6). On the other hand, the results obtained starting from ((−)-menthyl)Me_3Sn (**1**) showed that bis(siloxy) species are not formed from **3** at temperatures lower than 160 °C. This does not seem in agreement with reaction 6 wich would occur even at 100 °C according to the second hypothesis. For ((−)-menthyl)Me_2SnH grafting on silica, bis(siloxy) species have not been detected by solid-state NMR either. These species are very difficult to detect intrinsically, as it was written above, and for the sample studied, less than 2% of the total amount of grafted tin would be under this form according to gas evolution measurements. The results obtained may be however explained by the second hypothesis, considering that ((−)-menthyl)Me_2SnH (**2**) may catalyze reaction 6 which produces methane and bis(siloxy) species. Trialkyltin hydride compounds, R_3SnH, are indeed known to produce $R_3Sn^\bullet$ radicals.[35] It would then be possible that these species activate the silica surface creating $^\bullet O-Si\equiv$ radicals which would react with $\equiv Si-O-Sn(\text{menthyl})Me_2$ (**3**) to form $(\equiv Si-O)_2Sn(\text{menthyl})Me$ (**5**) through a radical mechanism. This explanation is still under study and will not be discussed into more details here, but it seems in good agreement with the experimental results, especially for the sample which has been prepared from **2** at 100 °C.

Another possible side reaction is a tin condensation between $\equiv Si-O-Sn(\text{menthyl})Me_2$ (**3**) and unreacted ((−)-menthyl)Me_2SnH (**2**):

$$\equiv Si-O-Sn(\text{menthyl})Me_2 + (\text{menthyl})Me_2SnH \rightarrow \underset{\mathbf{8}}{(\text{menthyl})Me_2Sn-SnMe_2(\text{menthyl})} + \equiv SiOH \quad (13)$$

Reactions similar to (13) are known in molecular organometallic chemistry, between trialkyltin hydride R_3SnH and R_3SnX compounds, where X is an electronegative group, to give distannanes $R_3Sn-SnR_3$.[35,36] The intervention of this reaction, beside (9), would lead to an increase in the H_2/Sn_g ratio, since the distannane (**8**) should be removed after the *n*-heptane washings (Scheme 3).

The extent of these side reactions is very small for the samples prepared at 80 °C. From the results presented in Figure 10, it can be concluded that according to our model, 97% of the grafted tin is present as a mono(siloxy) species, $\equiv Si-O-Sn(\text{menthyl})Me_2$ (**3**). However these side reactions increase with temperature and with time. For a sample which was prepared according to procedure II (see Experimental Section), heated at 80 °C for 48 h and then left with no particular care at room temperature for 5 months, less than 65% of the grafted tin is present as **3** on the silica surface: 2.3 wt % Sn with $H_2/Sn_g = 1.22$; $CH_4/Sn_g = 0.21$, and menthane/$Sn_g = 0.06$.

To avoid side reactions such as (6), (7), or (13) starting from **2**, the thermal treatment must be conducted according to procedure I (see Experimental Section) at

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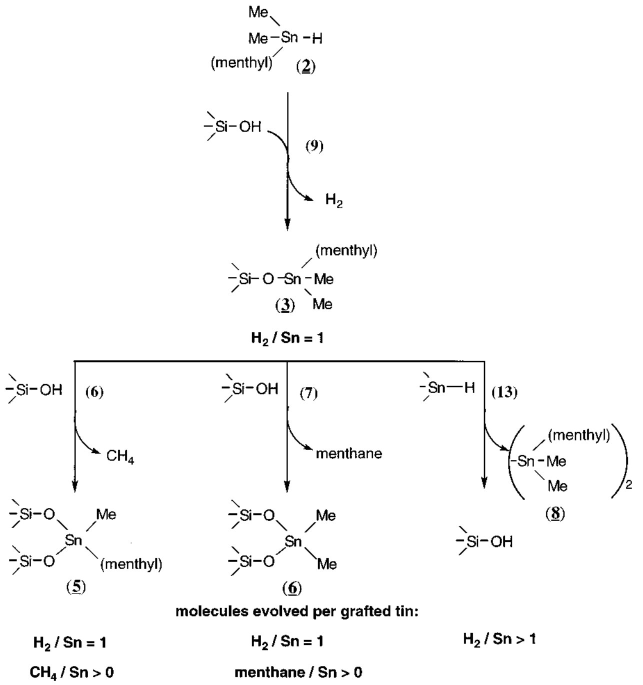
Scheme 3. Influence of the Side Reactions 6, 7, and 13 on the Molecules Evolved during the Grafting Reaction of ((−)-menthyl)Me$_2$SnH (2) on Silica, Where (9) Is the Expected Major Reaction



temperatures lower than 80 °C during less than 48 h and the excess of trialkyltin hydride should then be quickly removed by desorption or by washings with a solvent.

Thermal Stability of the Grafted Organometallic Species (3). The sample studied in Figures 7 and 13 by infrared spectroscopy has been prepared by grafting ((−)-menthyl)Me$_2$SnH at 60 °C in situ on a silica pellet previously treated at 500 °C. According to the results presented above, in this case, $\equiv$Si$-$O$-$Sn(menthyl)Me$_2$ (**3**) surface organometallic fragments are formed. The infrared spectrum 13b′ shows the ν(CH) (2960, 2929, 2876, and 2847 cm^{-1}) and δ(CH) vibration bands (1459, 1446, 1387, and 1369 cm^{-1}) of the alkyl groups bonded to tin in these species. In this case (2.3 wt % Sn), silanol groups are still present on the surface since the ν(OH) vibration bands of free (3747 cm^{-1}) and interacting (3698 cm^{-1}) silanols appear (spectrum 13b). The thermal decomposition under vacuum of $\equiv$Si$-$O$-$SnR$_3$ fragments (R = Me, *n*-Bu) has already been precisely studied.[29,37,38] It was found that two reactions occurred at temperatures higher than 150 °C: (i) a reaction with the remaining surface silanol groups leading to the formation of ($\equiv$Si$-$O)$_n$SnR$_{4-n}$, $n = 2-4$, with liberation of an alkane, RH; (ii) for R = *n*-Bu, a β-H elimination followed by a reductive elimination of hydrogen with formation of 1-butene and ($\equiv$Si$-$O)$_2$Sn$^{\mathrm{II}}$. We did not study here the thermal decomposition mechanism of the $\equiv$Si$-$O$-$Sn(menthyl)Me$_2$ (**3**) species in detail. However it can be seen that the intensity of the ν(CH) and δ(CH) bands of the surface species is kept after thermal treatments at 100 and 150 °C (spectra c′ and d′ in Figure 13) while it dramatically decreased after a thermal treatment at 200 °C (spectrum e′). This shows that the menthyl and methyl groups bonded to tin in **3** disappear under vacuum in the 150−200 °C temperature range. This result agrees with the fact that other species than trialkylmono(siloxy)tin(IV) were formed during the grafting of ((−)-menthyl)Me$_3$Sn on silica at temperatures higher than 160 °C. At these temperatures, once formed on the silica surface, **3** can decompose into other surface tin species.

In conclusion, the mono(siloxy) surface organometallic fragments $\equiv$Si$-$O$-$Sn(menthyl)Me$_2$ (**3**) formed upon grafting ((−)-menthyl)Me$_3$Sn or ((−)-menthyl)Me$_2$SnH onto silica appear to be thermally stable up to 150 °C under vacuum and they start to decompose into other surface tin species above 160 °C.

Conclusion

It has been shown that the grafting of ((−)-menthyl)Me$_3$Sn on a partially dehydroxylated silica(500) forms a well-defined chiral $\equiv$Si$-$O$-$Sn((−)-menthyl)Me$_2$ (**3**) species with evolution of methane. The selectivity of this reaction reaches 85% if the reaction is conducted at temperatures lower than 160 °C. The other surface species is very likely to be $\equiv$Si$-$O$-$SnMe$_3$ (**4**), associated with the formation of menthane. For higher reaction temperatures, other tin species are formed leading to a less defined surface. The grafting of ((−)-menthyl)Me$_2$SnH on silica at temperatures lower than 80 °C leads also to compound **3** which represents more than 95% of the grafted tin if the reaction of the trialkyltin hydride in excess with the surface organometallic fragments is avoided. To our knowledge, species **3** is the first well-defined chiral surface organostannic compound. It is thermally stable up to 160−200 °C. Studies are now in progress in order to graft such chiral organometallic fragments on the external surface of a mordenite and on other adsorbents in an attempt to perform enantiomeric separations.

OM9708844

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