

# Surface organometallic chemistry on metals: controlled hydrogenolysis of Me<sub>4</sub>Sn, Me<sub>3</sub>SnR, Me<sub>2</sub>SnR<sub>2</sub>, MeSnBu<sub>3</sub> and SnBu<sub>4</sub> (R = methyl, *n*-butyl, *tert*-butyl, neopentyl, cyclohexyl) onto metallic rhodium supported on silica

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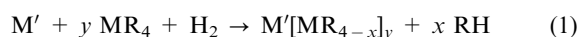
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Received (in Montpellier, France) 24th May 2004, Accepted 12th August 2004  
First published as an Advance Article on the web 17th November 2004

The controlled hydrogenolysis of Me<sub>x</sub>SnR<sub>4-x</sub> (0 ≤ *x* ≤ 4; R = methyl, *n*-butyl, *tert*-butyl, neopentyl, cyclohexyl) onto Rh/SiO<sub>2</sub> is followed by quantitative and qualitative analysis of evolved gases. Only MeH and RH are detected in the evolved gases. There is hydrogenolysis of the Sn–C bonds without any C–C bond hydrogenolysis, leading to formation of grafted organometallic fragments. Using various organotin compounds, Me<sub>x</sub>SnR<sub>4-x</sub>, it has been possible to determine the regioselectivity of the hydrogenolysis of the Sn–C bonds. The initial selectivity is inversely proportional to the steric bulk of the alkyl group: *t*Bu < Np < Bu. The formation of a five-coordinate tetraalkyl tin on the surface, Rh–SnMe<sub>x</sub>R<sub>4-x</sub> (symmetry *D*<sub>3h</sub>), in which the bulkiest group, *e.g.*, R, is away from the surface could explain these results. This surface five-coordinate tin species could eliminate an alkyl group, generally a methyl group, thus decreasing the steric bulk around the tin, into the equatorial plane of *D*<sub>3h</sub>, via a concerted hydrogen transfer-elimination mechanism to give Rh–SnMe<sub>x-1</sub>R<sub>4-x</sub>. Then, in the successive steps of the hydrogenolysis, the bulkiest group, R, would be eliminated.

## Introduction

The reaction between homoleptic tetraalkyl metals of group 14 (M = Sn, Ge) and silica- or alumina-supported group 8 metals M' (M' = Rh, Ru, Ni, ...) in the presence of molecular hydrogen, leads to a metallic surface covered with organometallic fragments, as in eqn (1).<sup>1,2</sup>



These new kinds of materials, generated by the “surface organo-metallic chemistry on metals” route<sup>1</sup> are interesting in several respects: (i) they represent a new family of compounds in which a metallic surface is covered *via* covalent metal-metal bond(s) by an organometallic “molecule”, which can play the role of a ligand as in classical molecular chemistry;<sup>3</sup> (ii) once the organometallic complex is grafted on the metallic surface, it can be transformed into various species including “adatoms” or “surface alloys”. A careful control of the hydrogenolysis conditions has allowed us to prepare a series of such supported organometallic complexes.<sup>4-6</sup> In particular, the selective hydrogenolysis of SnBu<sub>4</sub> on silica-supported rhodium, platinum or nickel catalysts was carried out at different temperatures for various coverage of the metallic particles. Analysis of the evolved gases has shown that the hydrogenolysis proceeds by a stepwise cleavage of the Sn–alkyl bond.<sup>4,6-9</sup> At *ca.* 150 °C, the naked tin adatoms are located on the surface of the catalyst and at higher temperature (about 400 °C), the tin atoms move inside of the metallic particle. The various species obtained were fully characterized by various physical techniques: electron microscopy (TEM-EDAX),<sup>4,6</sup> <sup>117</sup>Sn Mössbauer,<sup>10,11</sup> magnetic measurements,<sup>12</sup> XPS and EXAFS.<sup>4,6,7,13-15</sup>

In most systems that have been studied so far, the catalytic properties of the starting metal are considerably improved by the presence of the organometallic fragment itself, the adatoms or the surface alloy.<sup>16,17</sup> Extremely high chemo-, regio- or stereoselectivities can be obtained with catalysts prepared by such a route.<sup>14,16,18-29</sup> Besides, the loss of catalytic activity with time on-stream can be considerably lowered, for example, in the case of isobutane dehydrogenation<sup>25</sup> or *n*-hexane conversion,<sup>30</sup> with Pt–Sn catalysts prepared by the organometallic route.

Such improvement in catalytic performance justifies a systematic and careful approach to all the steps of catalyst preparation and in particular the hydrogenolysis step of the organometallic compound. For this reason the systematic study of reaction (1) with various tin alkyl complexes, Me<sub>x</sub>SnR<sub>4-x</sub>, was investigated. This article reports our results concerning the hydrogenolysis reaction of these compounds on rhodium metallic surfaces supported on silica.

## Experimental

### Catalyst preparation

The preparation of the monometallic catalyst has been described elsewhere.<sup>31</sup> The silica support (Aerosil 200 m<sup>2</sup> g<sup>-1</sup>) was purchased from Degussa. The Rh was grafted onto silica by cationic exchange between [RhCl(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> ions and surface [≡Si–O]<sup>–</sup>[NH<sub>4</sub>]<sup>+</sup> groups. The surface complex obtained was decomposed by calcination at 400 °C in a flowing nitrogen–oxygen mixture (5 : 1), reduced in flowing H<sub>2</sub> at 400 °C and then kept at 25 °C under dry air. The Rh and Cl loadings were 1.1% and 0.06% (wt), respectively. The particle size distribution of the Rh/SiO<sub>2</sub> catalyst has been determined by CTM

**Table 1** Synthesis of  $\text{Me}_x\text{SnR}_{4-x}$  derivatives from  $\text{R}_3\text{SnCl}$ 

R	R'	M <sup>a</sup>	T/°C	t/h	% Yield <sup>b</sup>	Bp/°C (torr)	Ref.
<i>n</i> Bu	Me	MgBr	25	3.5	89	125 (12)	33–37
Me	<i>n</i> Bu	MgCl	0	1	23	121 (760)	33–37
Me	<i>t</i> Bu	Li	25	4.5	26	110 (760)	34, 36–41
Me	Np	Li	40	2	37	27 (2.3)	36, 37, 41, 42
Me	Cy	MgBr	40	4	33	41 (1)	34, 38–40, 43

<sup>a</sup> solvent  $\text{Et}_2\text{O}$ ; <sup>b</sup> yld after purification.

analysis. The average value for the detectable particles is 1.4 nm. Assuming that the particles have a cubooctahedral shape,<sup>32</sup> the dispersion ( $D$  = surface rhodium atoms/total rhodium atoms) is close to 0.75.

### Preparation of the organotin compounds

The three organotin families, namely  $\text{Me}_x\text{SnBu}_{4-x}$  ( $0 \leq x \leq 4$ ),  $\text{Me}_3\text{SnR}$ , and  $\text{Me}_2\text{SnR}_2$  ( $\text{R}$  = methyl, *n*-butyl, *tert*-butyl, neopentyl, cyclohexyl) were prepared by reacting the corresponding organomagnesium or organolithium reagent with tin alkyl chloride or dichloride. Experimental conditions are given in Tables 1 and 2. Characterization of the organotin compounds is given in Table 3. <sup>13</sup>C NMR data and particularly the relationship between the value of the coupling constants  $^1J(^{119}\text{Sn}-^{13}\text{CMe})$  and  $^1J(^{119/117}\text{Sn}-\text{C}_x)$  and the bulkiness of  $\text{R}$  have been used to determine the structures and the conformations of the tin compounds.

### Chemisorption measurements

The chemisorption measurements were carried out using conventional static volumetric equipment already described.<sup>31,44</sup> The vacuum ( $10^{-6}$  mbar) was achieved by means of a rotary pump and a mercury diffusion pump. A cold trap at liquid nitrogen temperature avoid the diffusion of mercury vapors into the reaction part of the apparatus. The equilibrium pressure was measured with a Schlumberger gauge (pressure range 0–1000 mbar, accuracy 0.1 mbar). The gas phase was extracted from the vessel and then analyzed by gas chromatography, *vide infra*.

### Reaction of $\text{Me}_x\text{SnR}_{4-x}$ with $\text{Rh}/\text{SiO}_2$

**Experimental procedure.** The reaction between organotin compounds and reduced Rh particles was performed in the same apparatus as described before.<sup>44</sup> A given amount (generally 800 mg, 87.1  $\mu\text{mol}$  of Rh) of the monometallic  $\text{Rh}/\text{SiO}_2$  catalyst was loaded in the reactor (r), reduced at 350 °C under  $\text{H}_2$ , treated under vacuum at the same temperature to remove the water formed and cool down to 25 °C under vacuum. Pure hydrogen is introduced into the reactor up to an equilibrium pressure of 30 mbar. The quantity of hydrogen adsorbed on the catalyst, at 25 °C under 30 mbar, is close to 42  $\mu\text{mol}$  of  $\text{H}_2$  indicating that 84  $\mu\text{mol}$  of Rh were at the surface of the particle. The dispersion  $D$  of the catalyst is then close to 0.77, in very good agreement with the dispersion measured by electron microscopy ( $D$  = 0.75). The desired amount of the organotin compound, corresponding to a molar ratio close to 0.5 of  $\text{Me}_x\text{SnR}_{4-x}$  introduced per surface

rhodium atom, is then carefully introduced in the reactor without any contact with air. The reaction is performed at 25 °C under molecular hydrogen (30 mbar). The gas evolved during the reaction was trapped at liquid nitrogen temperature in an other part of the apparatus, to avoid possible feedback of the gas on the catalytic surface and further hydrogenolysis. After the desired time of reaction ( $t_{\text{re}}$ ), the reactor was isolated and the cold trap was warm up to room temperature. The gas phase was then analyzed by GC (KCl/Al<sub>2</sub>O<sub>3</sub> column,  $T_{\text{inj}}$  = 190 °C,  $T_{\text{dec}}$  = 210 °C) and volumetric measurements, in order to determine the nature and the amount of gas evolved during the reaction. At the end of the reaction, the catalyst was washed under argon with heptane (10 cm<sup>3</sup>). The washings were analyzed by GC (DC 550 column,  $T_{\text{inj}}$  =  $T_{\text{dec}}$  = 250 °C) to determine the quantity of unreacted tin compound. The solid was then dried (100 °C, 24 h) to remove traces of solvent and elemental analyses were performed at the Laboratoire de Chimie Analytique du CNRS to measure the quantities of Rh and  $\text{Sn}_{\text{graft}}$  in the sample.

An example of the amount of RH evolved, related to the amount of Sn fixed at the end of the reaction (after 80 h) as a function of time is given in Fig. 1, for  $\text{Me}_2\text{SnBu}_2$ . Only MeH and RH are formed. We can see in Fig. 1 that the reaction, at 25 °C under about 30 mbar of hydrogen, proceeds with a reaction rate decreasing with increasing reaction time. After *ca.* 80 h, the reaction stops. We checked that when hydrogen is replaced by helium, the Sn–C bond cleavage is stopped.

**Determination of the role of silica on the adsorption properties of the hydrocarbons.** During the hydrogenolysis of  $\text{Me}_x\text{SnR}_{4-x}$ , the hydrocarbons that are formed, especially R–H, are susceptible to physisorb/desorb on the silica support at different rates. Fig. 2 reports the evolution of the desorption, at 25 °C, of several hydrocarbons physisorbed on silica at –198 °C. Whereas the desorption of methane was almost instantaneous, the desorption of butane, isobutane and neopentane was somewhat slower although complete after one hour. This means that over a time scale of one to several hours, we can compare the quantities of these gaseous hydrocarbons evolved for the same series  $\text{Me}_3\text{SnR}$  or  $\text{Me}_2\text{SnR}_2$ . In the case of cyclohexane, only a part of the initial quantity introduced was found in the gas phase; the rest stayed irreversibly adsorbed on the silica even after 6 h (of 22.5  $\mu\text{mol}$  introduced, 20  $\mu\text{mol}$  were recovered). Therefore, both the amounts of cyclohexane given off and the regioselectivity based on this quantity cannot be considered to be correct.

## Results

### Hydrogenolysis of $\text{Me}_x\text{SnR}_{4-x}$ derivatives on $\text{Rh}/\text{SiO}_2$

Results obtained from the hydrogenolysis of  $\text{Me}_x\text{SnR}_{4-x}$  ( $\text{R}$  = Me, Bu, *t*Bu, Np, Cy) compounds on  $\text{Rh}/\text{SiO}_2$  after about 80 h are given in Table 4. The quantities of tin grafted (determined by elemental analysis) onto the silica-supported rhodium surface for the series of  $\text{Me}_x\text{SnR}_{4-x}$  derivatives were found to be almost the same as that initially introduced:  $\text{Sn}_{\text{intr}}/\text{Rh}_s = \text{Sn}_{\text{graft}}/\text{Rh}_s$ . Furthermore, only MeH and RH were given off.

**Table 2** Synthesis of  $\text{Me}_x\text{SnR}_{4-x}$  derivatives from  $\text{R}_2\text{SnCl}_2$ 

R	R'	M <sup>a</sup>	T/°C	t/h	% Yield <sup>b</sup>	Bp/°C (torr)	Ref.
<i>n</i> Bu	Me	MgBr	25	3	72	90 (8.5)	33–37
Me	<i>t</i> Bu	Li	25	7.5	52	28 (1)	35, 39
Me	Np	Li	40	5	68	58 (1.3)	41, 42
Me	Cy	MgBr	40	4	77	78 (1)	35

<sup>a</sup> solvent  $\text{Et}_2\text{O}$ ; <sup>b</sup> yld after purification.

**Table 3**  $^{13}\text{C}$  NMR chemical shifts and coupling constants of the methyl and  $\text{C}_\alpha$  of the R moieties in the  $\text{Me}_x\text{SnR}_{4-x}$  derivatives

Compound	$\delta$ Me	$^1J^{119}\text{Sn-Me}$ , $^1J^{117}\text{Sn-Me/Hz}$	$\delta$ $\text{C}_\alpha$	$^1J^{119}\text{Sn-C}_\alpha$ , $^1J^{117}\text{Sn-C}_\alpha/\text{Hz}$	$\delta$ $^{119}\text{Sn}$	$\theta^\circ$
$\text{Me}_4\text{Sn}$	-9.1	340, 321	—	—	0	109
$\text{Bu}_4\text{Sn}$	—	—	8.7	313, 299		
$\text{Me}_3\text{SnBu}$	-10	317, 303	10.8	368, 352	-0.7	
$\text{Me}_3\text{SnNp}$	-8.3	316, 302	31.2	368, 351	-14	
$\text{Me}_3\text{SnCy}$	-11.7	302, 289	25.7	409, 390	-4.2	
$\text{Me}_3\text{SntBu}$	-12.1	293, 283	21.2	n. d. <sup>a</sup>	18.7	
$\text{Me}_2\text{SnBu}_2$	-11.5	300, 287	10.2	350, 330	-2.3	106
$\text{Me}_2\text{SnNp}_2$	-6.6	297, 284	32.0	346, 331		105
$\text{Me}_2\text{SnCy}_2$	-14.0	272, 262	25.5	371, 354		103
$\text{Me}_2\text{SntBu}_2$	-14.4	250, 239	24.8	388, 377		101
$\text{MeSnBu}_3$	-12.8	284, 272	9.4	330, 315	-5.8	

<sup>a</sup> Not determined, literature value:  $J = 437 \text{ Hz}$  <sup>35, 39</sup>  $\theta = \text{Me-Sn-Me}$  angle calculated from:  $^1J(^{119}\text{Sn-}^{13}\text{CMe}) = 10.5 \theta - 810$ .

### Selectivities in the hydrogenolysis of the tin-carbon bonds

To obtain kinetics information about the reactivity of the Sn-Me bond compared to the Sn-R ( $\text{R} = \text{Bu}$ ,  $t\text{Bu}$ ,  $\text{Np}$  and  $\text{Cy}$ ) bond, starting with  $\text{Me}_x\text{SnR}_{4-x}$ , we report in Table 5 the respective amounts of MeH and RH evolved after  $t = 1$  and 80 (f) h of reaction ( $[\text{MeH}]_t$  and  $[\text{RH}]_t$ ), relative to the total amount of Me or R initially present in the complexes. Therefore, the regioselectivity ( $\mathcal{R}_t$ ) in the hydrogenolysis of the tin-carbon bonds was calculated from eqn. (2):

$$(\mathcal{R}_t) = \frac{[\text{MeH}]_t}{[\text{RH}]_t} \quad (2)$$

The obtained values of  $\mathcal{R}_t$  for  $t = 1$  or 80 h are reported in Table 5.

The regioselectivity taken after 1 h of reaction ( $\mathcal{R}_{1h}$ ) is related to the rate at which the respective Sn-C bonds break. The final regioselectivity ( $\mathcal{R}_f$ ), taken after about 80 h of reaction, gives the formula of the stable products of the hydrogenolysis reaction.

From the values in Table 5, it is obvious that Sn-C bond hydrogenolysis is always faster for the Sn-Me bond than for the Sn-R bond. It can be observed that increasing the number of Bu groups in the starting complexes decreases both the rate of Sn-Me and Sn-Bu bond hydrogenolysis. Relatively comparable kinetics are obtained when  $\text{R} = \text{Bu}$ ,  $t\text{Bu}$  and  $\text{Np}$ , while the hydrogenolysis rate of both Sn-Me and Sn-R bonds are strongly depressed when  $\text{R} = \text{Cy}$ .

### Discussion

#### Possible structures obtained after about 80 h at 25 °C under 30 mbar $\text{H}_2$

In general, after *ca.* 80 h of reaction (Table 4), there is little difference in the amounts of introduced tin and that actually

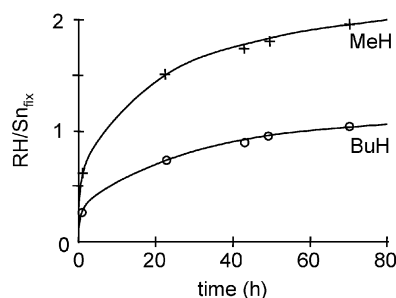
fixed and there are still alkyl groups covalently bonded to the grafted tin complexes. Irrespective of the tin complex used, only methane and hydrocarbons corresponding to the cleavage of the Sn-R bonds are observed in the gas phase.

Concerning the percentage of Sn-Me bonds cleaved, the following observations can be made. (i) in the case of  $\text{Me}_3\text{SnNp}$ ,  $\text{Me}_2\text{SnMe}_2$ ,  $\text{Me}_2\text{SnBu}_2$ ,  $\text{Me}_2\text{SnCy}_2$ ,  $\text{Me}_2\text{SnNp}_2$ , and  $\text{Me}_2\text{SntBu}_2$  all the methyl groups are cleaved. This gives rise to a relatively well-defined surface species  $\text{Rh}_s(\text{SnR}_x)_y$ , (ii) For the derivatives  $\text{Me}_3\text{SnBu}$ ,  $\text{Me}_3\text{SntBu}$  and  $\text{Me}_3\text{SnCy}$ , about 2.5 equiv. of methane per mole of fixed tin is given off, to give as the final surface species  $\text{Rh}_s(\text{SnR}_{0.5}\text{Me}_{0.5})$ . Concerning the percentage of Sn-R bonds cleaved, the following results were obtained. (i) There is little difference between Bu,  $t\text{Bu}$  or  $\text{Np}$ ; about half of the Sn-R bonds are cleaved.

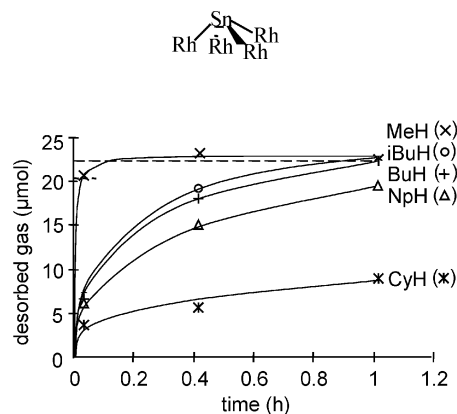
Even when taking into account adsorption phenomena,  $\text{Me}_2\text{SnCy}_2$  gives the highest final regioselectivity. The Sn-Cy bond seems to be the least sensitive to hydrogenolysis.

In the following sections we present the surface structures. There are a few cases for which only one organometallic compound is present on the surface: tin monobutyl or fully dealkylated tin atoms. In the other systems, the average formulae do not correspond to a single well-defined species. For these, we have postulated the most likely structures present at the end of the reaction and we have indicated, below these structures, the respective proportions.

**$\text{Me}_4\text{Sn}$ .** In this case it must be noted that the amounts of tin introduced and grafted were such that the ratio  $\text{Sn}_{\text{intr}}/\text{Rh}_s = 0.8$ , and  $\text{Sn}_{\text{graft}}/\text{Rh}_s = 0.7$ . As expected, only methane was given off. The final species presented no methyl groups and can then be formulated without any ambiguity as  $\text{Rh}_s(\text{Sn})_{0.7}$ .



**Fig. 1** Amount of MeH and BuH evolved, related to the amount of Sn fixed at the end of the reaction (after 80 h), as a function of time for  $\text{Me}_2\text{SnBu}_2$ .



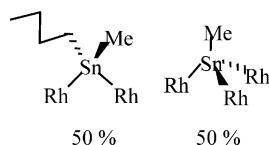
**Fig. 2** Evolution of the desorption, at 25 °C, of hydrocarbons previously physisorbed (22.5  $\mu\text{mol}$ , dashed line) on silica (800 mg) at  $-196^\circ\text{C}$ .

**Table 4** Results obtained from the hydrogenolysis of  $\text{Me}_x\text{SnR}_{4-x}$  ( $\text{R} = \text{Me}, \text{Bu}, \text{tBu}, \text{Np}, \text{Cy}$ ) compounds on  $\text{Rh}/\text{SiO}_2$  after about  $t_{\text{re}}$ 

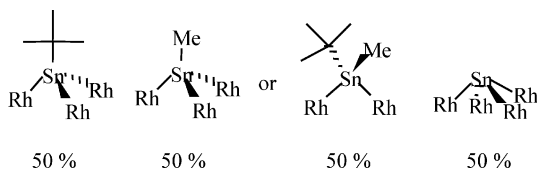
$\text{Me}_{4-x}\text{SnR}_x$	$t_{\text{re}}/\text{h}$	$\text{Sn}_{\text{intr}}/\text{Rh}_s$	$\text{Sn}_{\text{graft}}/\text{Rh}_s$	$\text{MeH}/\text{Sn}_{\text{graft}}$	$\text{RH}/\text{Sn}_{\text{graft}}$	Grafted tin species
$\text{Me}_4\text{Sn}$	80	0.8	0.7	4	—	$\text{Rh}_4[\text{Sn}^\circ]_{0.7}$
$\text{Me}_3\text{SnBu}$	80	0.7	0.7	2	0.5	$\text{Rh}_5[\text{SnMeBu}_{0.5}]_{0.7}$
$\text{Me}_3\text{SntBu}$	80	0.5	0.4	2.6	0.6	$\text{Rh}_5[\text{SnMe}_{0.4}\text{tBu}_{0.4}]_{0.4}$
$\text{Me}_3\text{SnNp}$	80	0.5	0.45	3	0.6	$\text{Rh}_4[\text{SnNp}_{0.4}]_{0.45}$
$\text{Me}_3\text{SnCy}$	80	0.5	0.5	2.2	0.5 <sup>a</sup>	$\text{Rh}_5[\text{SnMe}_{0.8}\text{Cy}_{0.5}]_{0.5}$
$\text{Me}_2\text{SnBu}_2$	80	0.5	0.5	1.9	1	$\text{Rh}_5[\text{SnBu}]_{0.5}$
$\text{Me}_2\text{SntBu}_2$	80	0.5	0.4	1.4	1	$\text{Rh}_5[\text{SnMe}_{0.4}\text{tBu}]_{0.4}$
$\text{Me}_2\text{SnNp}_2$	80	0.5	0.4	1.9	1	$\text{Rh}_5[\text{SnNp}]_{0.4}$
$\text{Me}_2\text{SnCy}_2$	80	0.5	0.4	2	0.6 <sup>a</sup>	$\text{Rh}_5[\text{SnCy}_{1.4}]_{0.4}$
$\text{MeSnBu}_3$	90	0.5	0.5	1	2.3	$\text{Rh}_4[\text{SnBu}_{0.7}]_{0.5}$
$\text{SnBu}_4$	70	0.5	0.3	—	2.2	$\text{Rh}_5[\text{SnBu}_{1.8}]_{0.3}$

<sup>a</sup> Increased by 25% to take into account irreversible adsorption on the surface.

**$\text{Me}_3\text{SnBu}$ .** Here, the ratios  $\text{Sn}_{\text{intr}}/\text{Rh}_s$  and  $\text{Sn}_{\text{graft}}/\text{Rh}_s$  both equal 0.7. The amount of methane and butane evolved at equilibrium was approximately 3 and 0.5, giving a surface rhodium-tin species with the average formula  $\text{Rh}_5[\text{SnMeBu}_{0.5}]_{0.7}$ . One should notice that the amount of methane evolved is quite high, probably because the molecule has three very unbulky fragments that can approach the surface quite easily.

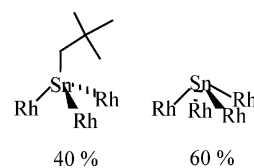


**$\text{Me}_3\text{Sn}(\text{tBu})$ .** The ratios  $\text{Sn}_{\text{intr}}/\text{Rh}_s$  and  $\text{Sn}_{\text{graft}}/\text{Rh}_s$  were respectively 0.5 and 0.4. Only methane and isobutane are formed. The amounts of methane and isobutane evolved with time were greater than that observed for  $\text{R} = \text{butane}$  (Table 4). The final stoichiometry of the surface species was  $\text{Rh}_5(\text{SnMe}_{0.4}\text{tBu}_{0.4})_{0.4}$ . There are two possible formulations in agreement with the proposed stoichiometry, shown below.

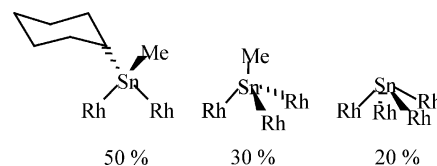


**$\text{Me}_3\text{SnNp}$ .** The ratios  $\text{Sn}_{\text{intr}}/\text{Rh}_s$  and  $\text{Sn}_{\text{graft}}/\text{Rh}_s$  were respectively 0.5 and 0.45. Neopentane and methane were given off, this time in greater quantities than those obtained for  $\text{R} = \text{tBu}$  (Table 4). Furthermore, all the methyl groups were found to be hydrogenolyzed, thus leading to a final surface species stoichiometry of  $\text{Rh}_5(\text{SnNp}_{0.4})_{0.45}$ . Since all the methyl groups have been eliminated the structure of the surface compounds

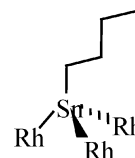
is simple:



**$\text{Me}_3\text{SnCy}$ .** Both the ratios  $\text{Sn}_{\text{intr}}/\text{Rh}_s$  and  $\text{Sn}_{\text{graft}}/\text{Rh}_s$  were 0.5. The quantity of cyclohexane evolved is low compared to that of methane (Table 4). Taking into account the amount of cyclohexane irreversibly adsorbed onto the silica surface, the effective amount of cyclohexane given off is then 0.5  $\text{Cy}/\text{Rh}_{\text{graft}}$  and the stoichiometry of the final surface species could be  $\text{Rh}_5(\text{SnMe}_{0.8}\text{Cy}_{0.5})_{0.5}$ . A simple, and probably oversimplified, interpretation of the data can be illustrated by the structures depicted below.



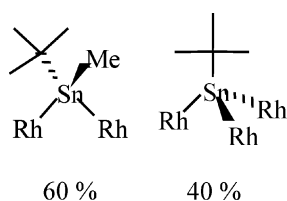
**$\text{Me}_2\text{SnBu}_2$ .** As in the previous case, the ratios  $\text{Sn}_{\text{intr}}/\text{Rh}_s$  and  $\text{Sn}_{\text{graft}}/\text{Rh}_s$  were 0.5. All the methyl groups were eliminated with one butyl group remaining. The stoichiometry of the final surface species was calculated to be  $\text{Rh}_5[\text{SnBu}]_{0.5}$ , which can be depicted as:

**Table 5** Results obtained from the hydrogenolysis of  $\text{Me}_x\text{SnR}_{4-x}$  ( $\text{R} = \text{Me}, \text{Bu}, \text{tBu}, \text{Np}, \text{Cy}$ ) compounds on  $\text{Rh}/\text{SiO}_2$  after about 1 h

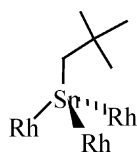
$\text{Me}_{4-x}\text{SnBu}_x$	$\text{MeH}_{1\text{h}}/\text{Me}$	$\text{RH}_{1\text{h}}/\text{R}$	$\text{MeH}_f/\text{Me}$	$\text{RH}_f/\text{R}$	$\mathcal{R}_{1\text{h}}$	$\mathcal{R}_f$	$\text{MeH}_{1\text{h}}/\text{MeH}_f$	$\text{RH}_{1\text{h}}/\text{RH}_f$
$\text{Me}_4\text{Sn}$	1	—	1	—	—	—	1.00	—
$\text{Me}_3\text{SnBu}$	0.56	0.47	0.67	0.5	1.2	1.3	0.84	0.94
$\text{Me}_2\text{SnBu}_2$	0.53	0.25	0.95	0.5	2.1	1.9	0.56	0.50
$\text{MeSnBu}_3$	0.16	0.12	0.92	0.75	1.3	1.2	0.17	0.16
$\text{SnBu}_4$	—	0.03	—	0.5	—	—	—	0.06
$\text{Me}_2\text{SnNp}_2$	0.58	0.33	0.95	0.5	1.8	2.0	0.61	0.66
$\text{Me}_2\text{SntBu}_2$	0.68	0.33	0.70	0.5	2.0	1.4	0.97	0.66
$\text{Me}_2\text{SnCy}_2$	0.22	<0.05	1.0	0.3	<4	3.3	0.22	<0.17



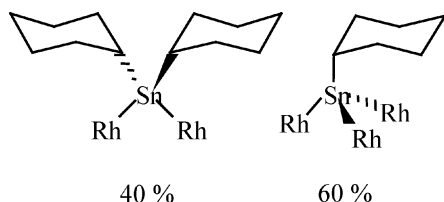
**Me<sub>2</sub>Sn(*t*Bu)<sub>2</sub>.** The ratios Sn<sub>intr</sub>/Rh<sub>s</sub> and Sn<sub>graft</sub>/Rh<sub>s</sub> were 0.5 and 0.4, respectively. The stoichiometry of the final surface species was calculated to be Rh<sub>s</sub>[SnMe<sub>0.6</sub>(*t*Bu)<sub>0.4</sub>], which could be depicted as:



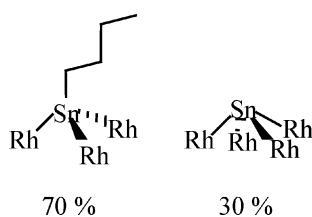
**Me<sub>2</sub>SnNP<sub>2</sub>.** The ratios Sn<sub>intr</sub>/Rh<sub>s</sub> and Sn<sub>graft</sub>/Rh<sub>s</sub> were 0.5 and 0.4, respectively. The results for methane and neopentane evolution were identical to those obtained for the dibutyl analogue. Thus, the final surface stoichiometry is quite similar, Rh<sub>s</sub>(SnNP)<sub>0.4</sub>.



**Me<sub>2</sub>SnCy<sub>2</sub>.** The ratios Sn<sub>intr</sub>/Rh<sub>s</sub> and Sn<sub>graft</sub>/Rh<sub>s</sub> were 0.5 and 0.4, respectively. Table 3 shows the amounts of methane and cyclohexane given off with time. In the case of cyclohexane, silica adsorbs irreversibly 25% of the cyclohexane evolved during the reaction. Because of this, the observed 0.5 mole of cyclohexane per mole of fixed tin corresponds to the quantity of gas given off, measured in the gas phase. This value can be estimated to be 0.6 mole of cyclohexane per mole of fixed tin actually evolved. Nevertheless, there was less cyclohexane evolved than for butane, isobutane and neopentane. Consequently, the final surface stoichiometry could be estimated as Rh<sub>s</sub>[Sn(Cy)<sub>1.4</sub>]<sub>0.4</sub>.

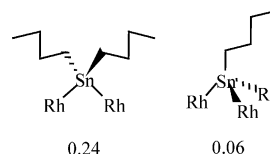


**MeSnBu<sub>3</sub>.** After 90 h of reaction, the totality of the tin complexes introduced, Sn<sub>intr</sub>/Rh<sub>s</sub> = 0.5, was grafted onto the surface. The amounts of methane and butane given off correspond to the hydrogenolysis of 1 methyl and 2.3 butyl groups, respectively. The final surface rhodium species thus has the average formula Rh<sub>s</sub>(SnBu<sub>0.7</sub>)<sub>0.5</sub>. As in the previous case one can propose the following mixture of surface species in which one has simultaneously surface "adatoms" as well as a mono-butyltin fragment.



**SnBu<sub>4</sub>.** At 25 °C, SnBu<sub>4</sub> reacted slowly on Rh/SiO<sub>2</sub>. After 70 h, the ratios Sn<sub>intr</sub>/Rh<sub>s</sub> and Sn<sub>graft</sub>/Rh<sub>s</sub> were 0.5 and 0.3, respectively, and, on average, 2.2 butyl groups were lost. The calculated stoichiometry of the final supported surface rhodium species is thus Rh<sub>s</sub>(SnBu<sub>1.8</sub>)<sub>0.3</sub>. This is in agreement with the previous results.<sup>4</sup> From the average formula it is possible to

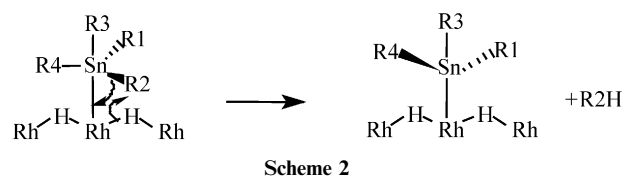
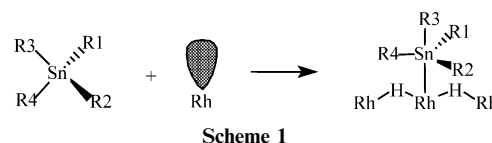
propose for the surface organometallic fragments the two following structures with their respective proportion: Rh<sub>s</sub>(SnBu<sub>2</sub>)<sub>0.24</sub> and Rh<sub>s</sub>(SnBu)<sub>0.06</sub>. We have deliberately eliminated the tributyl fragment due to its bulkiness and to the fact that at low coverage it is easily hydrogenolyzed to its less alkylated form.

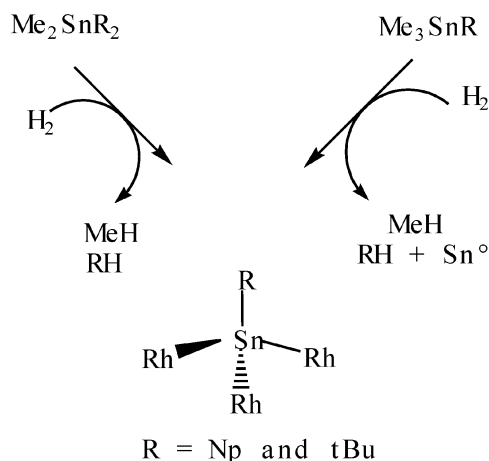


### Selectivities in the hydrogenolysis of the tin-carbon bonds

Only methane and hydrocarbons corresponding to the cleavage of the Sn–C bond present were observed. This implies that there was no cleavage of C–C bonds. This regioselectivity of the hydrogenolysis is probably governed by the difference in the Sn–C and C–C bond energies.<sup>45,46</sup> Accordingly, the introduced tin compound reacts exclusively by tin activation and not through C–H activation at the alkyl moiety. This is because a surface Rh–alkyl species would be expected to decompose either by β-H elimination or by hydrogenolysis of C–C bonds.<sup>47</sup> Based on geometry optimization procedures and electronic structure SCF(CI) calculations, it was demonstrated<sup>48</sup> that the first step involved in the interaction between Sn(CH<sub>3</sub>)<sub>4</sub> and the reduced Rh<sub>13</sub>H<sub>20</sub> cluster is a linear coordination of Sn(CH<sub>3</sub>)<sub>4</sub> with Rh, with simultaneous cancellation of unpaired spins. The sticking of Sn is helped by two CH<sub>3</sub> groups that are also involved in the adsorption, through coordination to adjacent Rh. This process weakens the Sn–C bonds and in a second step, a CH<sub>3</sub> group is evolved as CH<sub>4</sub>. In the intermediate structure thus generated, the Sn atom is coordinated to a Rh atom and three CH<sub>3</sub> groups. Moreover, in the literature, several examples report the ability of the tin atom to accommodate extra coordination.<sup>49</sup> The distortion that occurs on forming the five-coordinate intermediate from the starting material's original tetrahedral structure renders the alkyl groups bound to the tin more reactive.<sup>50</sup>

All these data and our results suggest that, firstly, the tin binds to supported rhodium *via* the dz<sup>2</sup> orbital to form a five-coordinate tin intermediate of D<sub>3h</sub> symmetry. Structural calculations support the fact that, in this intermediate shown in Scheme 1, the metallic surface, which plays the role of electron-donating coordinate, and the bulkiest group R3 are apicophilic.<sup>51</sup> Once grafted, the surface five-coordinate tin species can eliminate an alkyl group *via* a concerted hydrogen transfer-elimination mechanism,<sup>52</sup> as shown in Scheme 2. These two successive steps could account (i) for the simultaneous formation of different types of hydrocarbons, R1H, R2H and R4H in the gas phase and (ii) that the bulkiest R3, the furthest from the metallic surface, was still present after 80 h whatever the starting material (see Scheme 3).





Scheme 3

Concerning the kinetics of the reaction and the selectivity, there are a few points that deserve to be mentioned (Table 5). (i) The Sn–Me bond always reacts more rapidly than the Sn–Bu bond. (ii) The proportion of methane or butane given off after 1 h of reaction ( $\text{MeH}_{1\text{h}}/\text{Me}$  or  $\text{RH}_{1\text{h}}/\text{R}$ ) is proportional to the number of Sn–Me bonds in the starting compound. (iii) The proportion of methane or butane given off after 80 h of reaction ( $\text{MeH}_t/\text{Me}$  or  $\text{RH}_t/\text{R}$ ) is roughly independent of the number of Sn–Me bonds in the starting compound. Almost all the methyl groups and about half of the butyl groups have reacted after *ca.* 80 h.

This difference of reactivity between Sn–Me and Sn–Bu bonds can be easily explained by the higher steric constraints or cone angle of the Sn–butyl ligand with respect to Sn–methyl. During the first hour, tin-alkyl reactivity decreases with increasing steric bulk. Conversely, after 80 h there is no longer any steric effect observed.

## Conclusions

We have studied the hydrogenolysis of organometallic derivatives on a silica-supported rhodium metal surface. The compounds examined can be divided into three families of the following general formula: (i)  $\text{SnMe}_x\text{Bu}_{(4-x)}$ , where  $x = 0-4$ ; (ii)  $\text{SnMe}_3\text{R}$ , where  $\text{R} = t\text{Bu}, \text{Np}, \text{Cy}$ ; (iii)  $\text{SnMe}_2\text{R}_2$ , where  $\text{R} = t\text{Bu}, \text{Np}, \text{Cy}$ .

Our results indicate that:

(i) The  $\text{Me}_x\text{SnR}_{4-x}$  compounds react immediately on a 25 °C metallic surface and only with the metallic surface. After *ca.* 80 h, the reaction rate is very low and there are still alkyl groups bounded to the grafted tin. Generally, the remaining alkyl group is the bulkiest one.

(ii) During the first hour, as after 80 h, only methane and hydrocarbons corresponding to the cleavage of the Sn–C bond are observed. This implies that there is no cleavage of C–C bonds. This regioselectivity of the hydrogenolysis is probably governed by the difference in the Sn–C and C–C bond energies.<sup>45,46</sup>

(iii) The stoichiometry of the surface species after 1 h shows the presence of more alkyl groups than after 80 h of hydrogenolysis, which supports a step-wise hydrogenolysis of the Sn–C bond.

(iv) The first step of the reaction could form a five-coordinate tin intermediate, of  $D_{3h}$  symmetry, where the metallic surface plays the role of the electron-donating coordinate and the bulkiest R3 group is apicophilic.<sup>51</sup>

(v) Once grafted, the five-coordinate surface tin species can eliminate an alkyl group *via* a concerted hydrogen transfer-elimination mechanism.<sup>52</sup>

(vi) Among the alkyl groups studied ( $\text{R} = \text{Me}, \text{Bu}, t\text{Bu}, \text{Np}, \text{Cy}$ ), the Cy group is the most stable, since both the regioselectivity

tivities taken after 1 or about 80 h are the highest ( $\text{R}_{1\text{h}}$  or  $\text{R}_t$ ; Table 5) for the  $\text{Me}_2\text{SnCy}_2$  complexes.

Although the results are somewhat fragmented, the results from this systematic study of the hydrogenolysis of the Sn–C bond on Rh/SiO<sub>2</sub> has brought to light the importance of fivefold coordination and steric effects as determining factors.

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