

Evidence for new surface organotin and germanium complexes with functional groups grafted at the surface of Pt and Rh

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Abstract

It has been previously demonstrated that reaction of organometallic compounds with group VIII metallic surfaces can lead to grafted organometallic fragments with well defined structures. The presence of remaining alkyl groups on the catalytic surface was demonstrated by various physical and chemical techniques (EXAFS, Magnetic measurements, I.R. spectroscopy, Mössbauer, Thermoreduction, etc.). Surface organometallic complexes with an average formula $M_x[M'R_x]_y$ ($M = \text{Rh, Pt, Ni}$; $M' = \text{Sn, Ge, Si, Se}$; $R = \text{Me, Et, Bu}$) were proposed. The impact of the presence of these alkyl groups on the selectivity and activity for various catalytic reactions is a subject of important investigations. In this work, we demonstrate that organometallic fragments with functional groups can also be grafted on a platinum or rhodium surface. We will describe the synthesis of $R_xM'R_{4-x}^f$ ($M' = \text{Sn or Ge}$; $R = \text{H or Bu}$ and $R^f = (\text{CH}_2)_3\text{OH}, (\text{CH}_2)_3\text{OMe}, (\text{CH}_2)_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OMe}, \text{ or } (\text{CH}_2)_4\text{OH}$) and the kinetics of the reaction under atmospheric pressure of hydrogen with the silica supported platinum or rhodium catalysts. In every case, the hydrogenolysis of the organometallic complexes is not total and some organometallic fragments with functional groups remain on the surface. With $R^f = (\text{CH}_2)_3\text{OH}$, $M = \text{Rh}$, $M' = \text{Sn}$, on average, the grafted organometallic fragment can be formulated as: $\text{Rh}_s[\text{SnBu}_{0.4}\text{R}_{0.4}^f]_y/\text{SiO}_2$. With $R^f = (\text{CH}_2)_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OMe}$, $M = \text{Rh, Pt}$, $M' = \text{Sn}$, on average, the grafted organometallic fragment can be formulated as: $\text{Pt}_s[\text{SnBu}_{0.6}\text{R}_{0.5}^f]_{0.43}/\text{SiO}_2$ or $\text{Rh}_s[\text{SnR}_{0.6}^f]_{0.6}/\text{SiO}_2$. With $(\text{CH}_2)_3\text{OMe}$, $M = \text{Rh, Pt}$, $M' = \text{Sn}$, there is formation of a grafted organometallic fragment which can be formulated on average as: $\text{Rh}_s[\text{H}_x\text{SnR}_{0.9}^f]_{0.9}/\text{SiO}_2$ and $\text{Pt}_s[\text{H}_x\text{SnR}_{1.2}^f]_{0.9}/\text{SiO}_2$. With $R^f = (\text{CH}_2)_4\text{OH}$, $M = \text{Rh, Pt}$, $M' = \text{Ge}$, an average formula can be obtained as: $\text{Pt}_s[\text{Ge}(\text{H})_x\text{R}_{1.0,6}^f]_{0.6}/\text{SiO}_2$, $\text{Rh}_s[\text{Ge}(\text{H})_x\text{R}_{0.9}^f]_{0.6}/\text{SiO}_2$. Catalytic properties of these new material is under investigation. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Surface organotin; Pt; Rh

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1. Introduction

Selective catalytic hydrogenation on metals is more and more involved in the synthesis of fine chemicals. Hydrogen is in fact a cheap and non-polluting reactant, but high selectivity are difficult to achieve on simple heterogeneous metallic catalysts. It is therefore necessary to use modified catalysts.

Surface organometallic chemistry on metals is a new field of chemistry devoted to the study of the reactivity, at a molecular level, of organometallic complexes with metallic surfaces [1]. In some cases, the metallic surface is covered by surface organometallic fragments which can govern the selectivity of this new kind of material in catalysis.

In previous publications [2–4], we have demonstrated that the selective hydrogenolysis of $\text{Sn}(n\text{-C}_4\text{H}_9)_4$ on rhodium, nickel or platinum catalyst lead to a stable surface organotin fragment. The identification of the grafted organotin complex has been carried out by various analytical methods (EXAFS, RGN, EM, XPS, Magnetism, etc.). All these data are consistent with the formation of a surface complex with the following average formula: $\text{Rh}[\text{Sn}(n\text{-C}_4\text{H}_9)_x]_y/\text{SiO}_2$ ($1 < x < 3$; $0 < y < 0.8$). This solid was very active and selective for the hydrogenation of a α - β unsaturated aldehyde (citral) into the corresponding unsaturated alcohol (geraniol and nerol) [2]. This kind of surface reaction was extended to organogermanium complexes and a grafted organogermanium moiety was recently observed on rhodium surface [5].

It has been demonstrated [6] that platinum clusters embedded in micelles can be regio-selective in the hydrogenation of unsaturated fatty acids. The fatty acid molecule comprises a

hydrophobic alkyl chain and a hydrophilic carbonyl group at the end and it is known to form a kind of “Langmuir–Blodgett” film. It is thus reasonable to expect that the carboxyl groups of the fatty acid solubilized by the micelle are located at the hydrophilic layer of the micelle, far away from the metallic surface. Under these conditions, the C=C bond of the 10-undecenoic acid is always placed closer to the platinum surface than the C=C bond of the 2-undecenoic acid. On platinum cluster embedded in polyethylene glycol monolaurate, the initial rate of hydrogenation of 10-undecenoic acid was 5 times that of 2-undecenoic acid. In order to synthesize stable supported metallic systems surrounded by hydrophobic–hydrophilic layers, we have tried to graft via a covalent bond an organometallic fragment with hydrophilic head onto a metallic surface.

In this work, we demonstrate that some surface organometallic fragment with functional groups can be stabilized at the surface of platinum or rhodium. We will describe the synthesis of $\text{R}_x\text{M}'\text{R}_{4-x}^f$ ($\text{M}' = \text{Sn}$ or Ge ; $\text{R} = \text{H}$ or Bu and $\text{R}^f = (\text{CH}_2)_3\text{OMe}$, $(\text{CH}_2)_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OMe}(\text{CH}_2)_3\text{OH}$ or $(\text{CH}_2)_4\text{OH}$) and the kinetics of the interaction under atmospheric pressure of hydrogen with silica-supported platinum or rhodium catalysts. In every case, the hydrogenolysis of the organometallic complexes is limited and some functional groups remain on the surface.

2. Results and discussion

We shall describe successively the synthesis and characterization of the starting metallic cat-

Table 1
Characterization of silica supported Rh and Pt catalyst

Sample	M loading (%)	M ($\mu\text{mol/g}$)	H_2 adsorbed ($\mu\text{mol/g}$)	M_s ($\mu\text{mol/g}$)	D (M_s/M) (%)
Rh/SiO ₂	1.19	116	122	94	80
Pt/SiO ₂	1.33	68	71	39	58

alyst, the synthesis of functionalized tin and germanium alkyls and their grafting on Pt and Rh surface.

2.1. Synthesis and characterization of silica supported Pt and Rh catalysts

Pt/SiO₂ catalyst (1.33%) and Rh/SiO₂ catalyst (1.19%) were prepared according to a classical method of exchange and reduction (see Section 4).

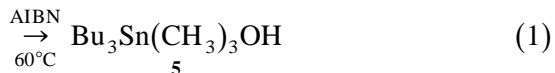
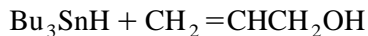
Chemisorption of H₂ was used to determine the dispersion of the metal (number of surface metal atoms per total number of metal atoms M_s/M) (see Section 4). The isotherms of chemisorption for H₂ were measured at 25°C under hydrogen pressures ranging from 0 to 200 mbar. Blank experiments performed under the same conditions with the pure silica indicate that the amount of hydrogen adsorbed is negligible. The accepted stoichiometries of 1.8 H/Pt_s and 1.3 H/Rh_s are assumed for an equilibrium pressure of 150 [7–9]. The values obtained are reported in Table 1.

For both cases, a rather narrow distribution of metallic particle size has been observed by electron microscopy, with an average metallic particles diameter (*d*) of 1.2 nm for Rh/SiO₂ and 2 nm for Pt/SiO₂. These values correspond roughly to a dispersion (*D*) of 0.8 and 0.5 for Rh and Pt, respectively (using the general formula $D = 1/d$ [10]), in good accordance with the values obtained by hydrogen chemisorption.

2.2. Synthesis of the functionalized organometallic compounds

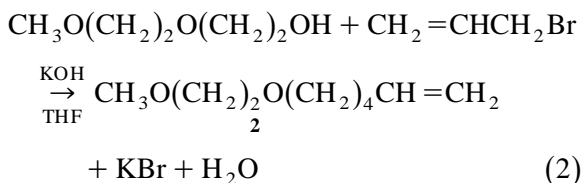
2.2.1. Bu₃Sn(CH₂)₃OHI

This product is obtained by hydrostannation of allylic alcohol according to an already published procedure [11] (for more details see Section 4).

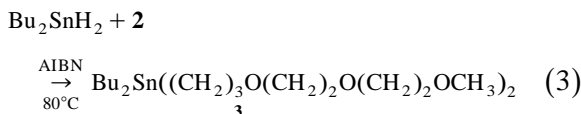


2.2.2. Bu₂Sn((CH₂)₃O(CH₂)₂O(CH₂)₂OCH₃)₂**3**

This polyethered olefin was made in several steps. First, the olefin diether **2**, was synthesized [12] (for more details see Section 4).

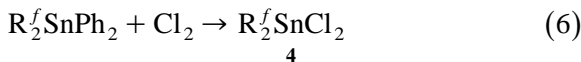
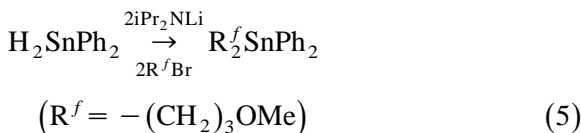
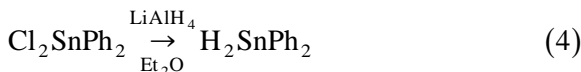


Then **3** was obtained by hydrostannation of **2** by Bu₂SnH₂

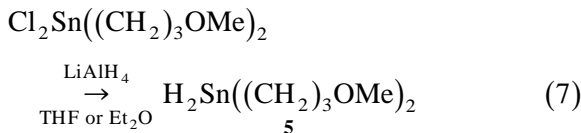


2.2.3. H₂Sn[(CH₂)₃OMe]₂**5**

We have first synthesized the corresponding dialkyl ether tin dichloride **4**, following the following successive steps (for more details see Section 4):



The reduction of **4** was then performed in Et₂O or THF, with LiAlH₄

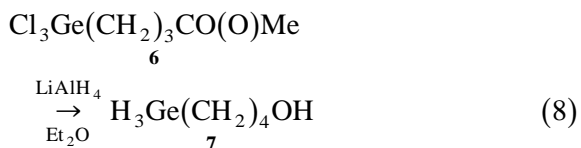


2.2.4. H₃Ge(CH₂)₄OH**7**

Cl₃Ge-(CH₂)₃-CO(O)CH₃ **6** was first synthesized using the insertion reaction of GeCl₂.dioxane into the carbon-halogen bond [13,14] of Cl-(CH₂)₃-CO(O)CH₃ (for more de-

Fig. 1. Kinetics of the hydrogenolysis of **1** on Rh/SiO₂, in propan-2-ol.

tails see Section 4). Then **6** was reduced by LiAlH₄ to give **7**



2.3. Reaction of **1**, **3**, **5** and **7** with silica supported Rh and Pt

2.3.1. Procedure

The reaction of organometallic compounds was performed in a ‘‘Schlenk’’ tube, under atmospheric pressure of hydrogen, in propan-2-ol or THF as solvent (see Section 4). Prior to the reaction, the monometallic catalyst was reduced under flowing hydrogen at 450°C and then introduced in the reactor without any contact with air. The kinetics of the reaction was followed by CPG analysis of the samples of either the gas or the liquid phase at a regular time interval (see Section 4).

2.3.2. Hydrogenolysis of Bu₃Sn(CH₂)₃OH (**1**) on Rh/SiO₂

The reaction was performed in propan-2-ol as solvent. The products observed during hydrogenolysis of **1** are mainly butane, small quantities of 1-propanol and traces of propane.

Butane comes from the hydrogenolysis of the Sn–Bu bond, propan-1-ol comes from the hydrogenolysis of the Sn–R^f bond and propane very likely comes from dehydroxylation of propanol.

The variation of the concentration with time of reagent and products observed during the hydrogenolysis of **1** with silica supported Rh are reported on Fig. 1.

The reaction is fast. There is formation of a grafted organometallic fragment on the rhodium surface which can be formulated as: Rh_s[SnBu_xR^f_{x'}]_y/SiO₂. At the end of the reaction, the total amount of **1** fixed (Sn_{fix}) is measured by the difference between the amount introduced and the amount remaining in solution. The value obtained is 0.80 Sn_{fix}/Rh_s. This value is in rather good agreement with the total amount of tin present on the surface after 18 h of reaction, measured by elemental analysis (Sn_{fix}/Rh_s = 0.79) (see Section 4).

In Fig. 2, the amount of butane and (propan-1-ol + propane) formed is represented as a function of the amount of **1** fixed during the reaction of **1** on Rh/SiO₂.

As can be seen in Fig. 2, the amount of butane and (butan-1-ol + propane) formed per mole of **1** remains constant with the metallic coverage. This means that there is simultaneously hydrogenolysis of the R and R^f frag-

Fig. 2. Mole of butane and (propan-1-ol + propane) per mol of **1** fixed during the reaction of **1** on Rh/SiO₂ in propan-2-ol.

ments. The average formula of the grafted organometallic fragment does not depend on the coverage. On average, the grafted organometallic fragment can be formulated as: $\text{Rh}_s[\text{SnBu}_{0.4}\text{R}^f_{0.4}]_y/\text{SiO}_2$ for $0 < y < 0.8$.

At the end of the reaction, the following structures are in good qualitative agreement with the amount of evolved ligands (Scheme 1).

The respective proportions of each species are tentatively given in bracket.

2.3.3. Hydrogenolysis of $\text{Bu}_2\text{Sn}((\text{CH}_2)_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OCH}_3)_2$ (**3**) on Rh and Pt / SiO_2

The reaction is performed in propan-2-ol as solvent. The products observed during hydrogenolysis of **3** are mainly butane, polyether $((\text{CH}_3)(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OCH}_3)$ and traces of propane. Butane comes from the hydrogenolysis of Sn–Bu bond, polyether comes from the hydrogenolysis of the Sn– R^f bond ($\text{R}^f = (\text{CH}_2)_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OCH}_3$) and C_3H_8 comes probably from the hydrogenolysis

Fig. 4. Kinetics of the hydrogenolysis of **3** on Pt/ SiO_2 .

of the C–O bond of the polyether ($\text{C}_3\text{H}_7\text{–OR}$) to give C_3H_8 and ROH.

The reagent (**3**) cannot be detected by GPC. The amount of products observed during the hydrogenolysis of **3** with silica supported Rh and Pt are reported on Figs. 3 and 4.

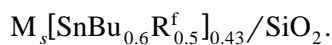
On Rh/ SiO_2 (Fig. 3), the reaction is fast at 25°C. The total amount of tin present on the surface after 25 h of reaction, measured by elemental analysis (see Section 4) is $0.52 \text{ Sn}_{\text{fix}}/\text{Rh}_s$. In Fig. 3, we can see that the total amount of butane and polyether evolved after 25 h of reaction at 25°C is close to $1 \text{ C}_4/\text{M}_s$ and $0.65 \text{ R}^f\text{H}/\text{M}_s$. If we relate these values to the total amount of tin fixed, there is evolution of about 2 mol of butane, 1.25 mol of polyether and 0.15 mol of propane per fixed organotin fragment. At the end of the reaction, there is no remaining butyl group, but there is still about 0.6 ligand with functional groups on the metallic surface. On average, the grafted organometallic fragment can be formulated as: $\text{M}_s[\text{SnR}^f_{0.6}]_{0.6}/\text{SiO}_2$

Fig. 3. Kinetics of the hydrogenolysis of **3** on Rh/ SiO_2 .

Scheme 2.

Scheme 3.

On Pt/SiO₂ (Fig. 4), the reaction is slow at 25°C but the rate can be improved by increasing the temperature to 50°C. In these conditions and after 120 h of reaction, the total amount of tin present on the surface, measured by elemental analysis (see Section 4) is 0.43 Sn_{fix}/Pt_s. The total amount of butane evolved is 1.4 C4/Sn_{fix}, there is no formation of propane and the amount of polyether is 1.5 R^fH/Sn_{fix}. There is formation of a grafted organometallic fragment which can be formulated on average as:



At the end of the reaction, we could propose that the following species coexist on the surfaces (Schemes 2 and 3).

Fig. 6. Amount of CH₃(CH₂)₂OMe formed during the hydrogenolysis of **5** on Rh/SiO₂ and Pt/SiO₂.

2.3.4. Hydrogenolysis of H₂Sn(CH₂)₃OMe(**5**) on Rh and Pt / SiO₂

This particular reaction was performed in THF as a solvent. It has been demonstrated previously that dialkyltinhydride (H₂SnBu₂) can react at 100°C on the silica surface [15]. In our case, in THF at 25°C, **5** reacts only slowly with the silica surface, without hydrogenolysis of R^f as shown in Fig. 5. In presence of M/SiO₂ (M = Pt or Rh), **5** reacts faster than in the presence of silica (Fig. 5). The total amount of **5** introduced (Sn_{int.}/M_s = 1) is fixed on the surface in less than 3 h. This value is in rather good agreement with the total amount of tin

Fig. 5. Kinetics of the hydrogenolysis of **5** on SiO₂, Rh/SiO₂ and Pt/SiO₂.

Fig. 7. Amount of CH₃(CH₂)₂OMe formed, related to the amount of **5** fixed during the reaction of **5** on M/SiO₂.

Scheme 4.

present on the surface after 18 h of reaction, as measured by elemental analysis ($\text{Sn}_{\text{fix}}/\text{M}_s = 1.03$ and 0.94 for respectively Rh and Pt) (see Section 4).

Since the reaction was performed under hydrogen (see Section 4), it was not possible to measure the amount of hydrogen formed. The only product observed during reaction of **5** with M/SiO_2 is $\text{CH}_3(\text{CH}_2)_2\text{OMe}$ which comes from the hydrogenolysis of the $\text{Sn}-\text{R}^f$ bond (Fig. 6).

In Fig. 7, we represent the amount of R^fH formed, related to the amount of **5** fixed during the reaction of **5** on M/SiO_2 .

The amount of R^fH formed per fixed amount of **5** remains constant with the metallic coverage (Fig. 6). This means that the average formula of the grafted organometallic fragment does not depend on the coverage.

The amount of R^fH evolved is higher in the presence of Rh ($\text{R}^f\text{H}/\text{Rh}_s = 1.0$) than in the presence of Pt ($\text{R}^f\text{H}/\text{Pt}_s = 0.7$). If we assume that only 10% of **5** reacts on the silica surface without hydrogenolysis of R^f , we can conclude that there is formation of a grafted organometallic fragment on the metallic surface which can

Scheme 5.

Fig. 8. Kinetics of the hydrogenolysis of **7** on Rh/SiO_2 and Pt/SiO_2 .

be formulated on average as: $\text{Rh}_s[\text{H}_x\text{SnR}_{0.9}^f]_{0.9}/\text{SiO}_2$ and $\text{Pt}_s[\text{H}_x\text{SnR}_{1.2}^f]_{0.9}/\text{SiO}_2$.

At the end of the reaction, the following species probably coexist on the surfaces, with the respective proportions tentatively given in brackets (Schemes 4 and 5).

2.3.5. Hydrogenolysis of $\text{H}_3\text{Ge}(\text{CH}_2)_4\text{OH}$ (**7**) on Rh and Pt / SiO_2

This reaction was performed in propan-2-ol as solvent. It has been demonstrated previously that alkylgermaniumhydride (H_3GeAd , $\text{Ad} = \text{Adamantyl}$) does not react at 25°C on the silica surface, but readily reacts on the rhodium surface [5]. We found that **7** does not react in propan-2-ol with the silica surface at 25° , but reacts quickly in the presence of M/SiO_2 ($\text{M} = \text{Pt}$ or Rh) as seen in Fig. 8. The total amount of **7** fixed on the metallic surfaces after about 15 h

Scheme 6.

Scheme 7.

of reaction was found to be 0.6 for both rhodium and platinum.

Here also, since the reaction was performed under 1 atm of hydrogen (see Section 4), it was not possible to measure the amount of hydrogen formed. The only product formed during reaction of **7** with M/SiO_2 is butan-1-ol which is observed in small amount and only in the presence of Rh/SiO_2 . Butan-1-ol comes from the hydrogenolysis of the $Ge-R^f$ bond but the amount formed is too small ($0.1/Rh_s$) to explain the amount of grafted organometallic fragment ($1/Rh_s$). We must conclude that **7** reacts on the metallic surface by selective cleavage of one or more $Ge-H$ bonds, as demonstrated previously [5]. We can propose that there is formation of a grafted organometallic fragment on the metallic surface which can be formulated on average as: $M_s[Ge(H)_x R_{x'}^f]_{0.6}/SiO_2$ with $0 < x < 2$; $M_s = Rh$, $x' = 0.9$ and $M_s = Pt$, $x' = 1$.

At the end of the reaction, the following species seem to coexist on the surfaces, with the respective proportions tentatively given in brackets (Schemes 6 and 7).

3. Conclusion

It has been demonstrated that reaction of organometallic compounds with group VIII metallic surfaces can lead to grafted organometallic fragments with well defined structures [1,2,4,5,16–18]. The presence of remaining alkyl groups on the catalytic surface was demonstrated by various physical and chemical

techniques (EXAFS, Magnetic measurements, I.R. spectroscopy, Mössbauer, Thermoreduction, etc.). Surface organometallic complexes with an average formula $M_s[M'R_x]_y$ ($M = Rh, Pt, Ni$; $M' = Sn, Ge, Si, Se$; $R = Me, Et, Bu$) were proposed. The impact of the presence of these alkyl groups on the selectivity and activity for various catalytic reactions is a subject of important investigations. In this work, we demonstrate that organometallic fragments with functional groups can be grafted on a platinum or rhodium surface. In Table 2, we summarize the results obtained on platinum and rhodium surfaces, using tin or germanium complexes.

In every case, the value of $x'(R^f/M')$ is greater than 0. This result means that organometallic fragments with functional groups remain on the catalyst surface.

In the case of organotin complexes, the extent of hydrogenolysis of the organic groups is greater on rhodium than on platinum. This is in accordance with the general assumption that hydrogenolysis reaction is deeper on rhodium surface than on platinum surface.

There is also, but to a small extent, reaction of the functional group with the metallic surface, leading to unfunctionalized ligand and formation of water in the case of OH or an alcohol in the case of ester.

Table 2
Recapitulation of the stoichiometry of the various solids $M_s[M'R_x R_{x'}^f]_y$

We never observed products resulting to a C–C bond breaking of the ligand. Clearly, the presence of hydride rather than butyl group allow to obtain higher values of $x'(R^f/M')$.

These solids can be compared to colloidal dispersions of metal clusters embedded in the micelles. Toshima and Takahashi [6] have found that on colloidal dispersion of platinum clusters (2.5 nm in average diameter) surrounded by nonionic surfactant polyethylene glycol monolaurate, the hydrogenation of 10-undecenoic acid is faster than that of 2-undecenoic acid. We will then investigate in a forthcoming work, the possible regioselective hydrogenation of polar molecules.

4. Experimental

4.1. General procedures

All experiments with metal complexes were carried out under atmosphere of purified argon ("Air Liquide 'U'"), deoxygenated and dehydrated by passing through deoxo catalyst and molecular sieve 4 Å), using standard Schlenk techniques. Solvents other than Et₂O and THF were refluxed over P₂O₅, distilled under nitrogen and kept under argon over 4 Å molecular sieves. Et₂O and THF were refluxed over Na/benzophenone and distilled under nitrogen just before use. Commercially available reagents were used as received.

¹H and ¹³C NMR spectra were recorded at 100 or 200 MHz, ¹¹⁹Sn NMR spectra were recorded at 300 MHz, using Bruker spectrometers. All NMR measurements were performed in C₆D₆, unless otherwise specified. ¹H and ¹³C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane, using the residual hydrogen signal of the solvent as reference. ¹¹⁹Sn NMR chemical shift are reported in parts per million, using tetramethyltin as internal standard. Abbreviations used in the description of NMR data are follows: s, singlet; d, doublet; t, triplet; q, quadruplet; qu, quintu-

plet; m, multiplet. For ¹³C NMR, coupling constants $J^n\text{Sn-C}$ (n = distance from Sn to C expressed in number of carbon atoms) are given in brackets.

Infrared spectra were recorded on Nicolet 550 spectrometer.

Gas phase chromatography analysis are performed on Delsi IGC 120FL and capillary column JW DB-5 (25 m × 0.25 mm, PN₂ = 3 bars) or Shimadzu GC-14A with capillary column Alltech AT-1, GC14A and KCL/Al₂O₃ (30 m × 0.32 mm, PN₂ = 1 bar).

Elementary analysis of Pt and Rh on silica. Prior to the elementary analysis, the bimetallic samples are first washed with alcohol in order to remove the unreacted organometallic compound and then treated at 350°C under flowing hydrogen in order to remove all the remaining groups. Analysis of platinum, rhodium and tin in the samples are achieved after treatment with HNO₃ + HCl and then HF. After dissolution of the solid, quantitative analysis is carried out by atomic absorption.

Electron microscopy (EM) analysis of monometallic catalysts is performed on Jeol 100MX.

Gas adsorption measurements are carried out at room temperature using conventional Pyrex volumetric adsorption equipment. The vacuum (10⁻⁶ mbar) is achieved with a liquid nitrogen trapped mercury diffusion pump. The equilibrium pressure is measured with a Texas Instrument gauge (pressure range 0–1000 mbar with an accuracy of 0.1 mbar). The catalyst sample is placed in a Pyrex flow-through cell to enable reduction in flowing hydrogen at 500°C. After reduction, the cell is sealed and the sample is outgassed at 530°C for 2 h under vacuum before gas chemisorption measurements.

The reaction between organometallic complexes (M'R_xR_{4-x}^f; M' = Sn or Ge) and monometallic catalysts (M/SiO₂, M = Rh, Pt) is performed at room temperature in a close glass reactor in the presence of one atmosphere of hydrogen. Prior to the reaction, the desired amount of catalyst (0.5 g) is reduced at 450°C

under flowing dry hydrogen during 3 h. After cooling down at room temperature under hydrogen, the reduced catalyst is introduced always under hydrogen, into a Schlenk tube. The freshly distilled butan-2-ol (5 ml) and known amounts of tetradecane and isobutane (internal standards) are introduced in the Schlenk tube which is then closed under 1 atmosphere of hydrogen. We verify that there is no reaction between the solvent and the monometallic catalyst. After 30 min of stirring, the amount of $M'R_xR_{4-x}^f$ corresponding to $1 M'R_xR_{4-x}^f/M_s$ is added. The variation of the $MR_xR_{4-x}^f$ concentration and the amount of R-H (butane) or R^fH evolved are then followed by GPC analysis of the liquid and the gas phase. It has been verified that isobutane is never formed during the reaction of $MR_xR_{4-x}^f$ with silica supported rhodium or platinum. In this study, the hydrogen used for the reduction of the samples and for the reaction in the closed reactor is fully deoxygenated and dehydrated by flowing through deoxo and zeolite traps.

4.2. Rh/SiO₂ and Pt/SiO₂ preparation

The preparation of the monometallic catalysts has been described elsewhere [9,19]. The silica support Aerosil 200 m² g⁻¹ was purchased from Degussa. The platinum and rhodium salts, [Pt(NH₃)₄](OH)₂ and [RhCl(NH₃)₄]Cl₂ were purchased from STEM Chem. The [Pt(NH₃)₄](OH)₂ salt was used as received, but the rhodium salt is exchanged to [RhCl(NH₃)₄](OH)₂ by passing through an ionic exchange resin IRA 400. The platinum and rhodium complexes are grafted onto the silica surface by the reaction with Si-OH groups of the silica surface in ammoniacal solution (pH 10). This ionic exchange is achieved by stirring the slurry of silica and salts for 10 h. After filtration, the surface complex obtained is decomposed by calcination under a mixture of nitrogen/oxygen (5/1) at increasing temperatures from 25 to 400°C (1°C nm⁻¹). The solid obtained is then reduced under flowing hydrogen at 400°C for 4 h and then stored at room temperature in air.

4.3. Bu₃Sn(CH₂)₃OH 1

Synthesis of **1**: 3.70 g of tributylstannane (12.7 mmol, 1 eq.) are added under argon to 1.45 g of allylic alcohol (24.9 mmol, 2 eq.) and to 0.12 g of AzoIsoButyroNitril (AIBN). The mixture is heated at 60°C during 135 min. After this time, the infrared band attributed to the tin hydride (1803 cm⁻¹) has totally disappeared. The allylic alcohol in excess is removed under vacuum. The residue is distilled under reduced pressure to obtain 3.1 g of **1**. The yield is 70%.

Characterization of **1**: boiling point: 142°C/3 mmHg (expected: 175°C/12 mmHg). Infrared Spectra (pure): 3330, 2957, 2925, 2872, 2855, 1464, 1373, 1069, 1050, 1012, 689, 668, 595 cm⁻¹. ¹H NMR (C₆D₆): 3.33 (2H, q, *J* = 5.9 Hz, became triplet by exchange with D₂O), 1.2–1.8 (m, 15 Hz), 0.7–1.1 (m, 17 Hz). ¹³C NMR: 4.6 (*J*¹Sn-C = 289 Hz), 9.1 (*J*¹Sn-C = 300 Hz), 13.9, 27.8 (*J*³Sn-C = 52 Hz), 29.7 (*J*²Sn-C = 20 Hz), 30.4 (*J*²Sn-C = 36 Hz), 66.1.

4.4. Bu₂Sn((CH₂)₃O(CH₂)₂O(CH₂)₂OCH₃)₂ 3

Synthesis of CH₃(O(CH₂)₂)₂OCH₂CH = CH₂ **2**: 5.6 g (0.1 mol, 2 eq.) of KOH and 6 g (0.05 mol, 1 eq.) of CH₃(O(CH₂)₂)₂OH are dissolved in 50 ml of THF. The solution is heated to reflux and 9.1 g (0.075 mol, 1.5 eq.) of Br(allyl) are added slowly. The solution is maintained to reflux during 4 h and then cooled down to room temperature. The THF is removed under reduced pressure and the residue is dissolved into 40 ml of water. The aqueous phase is extracted by ether. The organic phase is dried on MgSO₄ and ether is evaporated and we obtain a pale yellow liquid. This liquid is distilled under reduced pressure and we obtain 6.55 g (82% yield) of **2**.

Characterization of **2**: boiling point: 89°C/16 mmHg (expected: 100°C/25 mmHg). Infrared Spectra (pure): 3081, 2981, 2875, 1649, 1456, 1351, 1200, 1111, 1029, 996, 927, 852 cm⁻¹.

^1H NMR (C_6D_6): 6.01 (1H, m), 5.36–5.47 (1H, dq, $J_{trans} = 17.3$ Hz, $J_q = 18$ Hz), 5.18–5.25 (1H, dq, $J_{cis} = 10.4$ Hz, $J_q = 1.5$ Hz), 4.01 (2H, dt, $J_d = 5.2$ Hz, $J_t = 1.5$ Hz), 3.51–3.72 (8 H, m), 3.32 (3 H, s). ^{13}C NMR (C_6D_6): 58.6, 69.9, 70.8, 70.9, 72.0, 72.2, 115.9, 135.6.

Synthesis of $\text{Bu}_2\text{Sn}[(\text{CH}_2)_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OCH}_3]_2$ **3**: 2.755 g (11.7 mmol, 1 eq.) of Bu_2SnH_2 are added under argon to 3.76 g (23.4 mmol, 2 eq.) of **2** and a small quantity of AIBN. The mixture is heated at 80°C under argon during 4 h. After this time, the Sn–H infrared band has disappeared. The mixture is cooled down and then distilled. We obtain 2.82 g (44% yield) of a light liquid.

Characterization of **3**: Infrared spectra (pure): 2954, 2923, 2871, 1457, 1353, 1200, 1112, 1029 cm^{-1} . ^1H NMR (C_6D_6): 3.46–3.56 (12 H, m), 3.30–3.39 (8 H, m), 3.13 (6 H, s), 1.76–1.91 (4 H, m), 1.25–1.68 (8 H, m), 0.81–1.01 (14 H, m). ^{13}C NMR (C_6D_6): 5.3 ($J^1\text{Sn}-\text{C} = 315$ at 300 Hz), 9.1 ($J^1\text{Sn}-\text{C} = 320$ at 306 Hz), 13.9, 27.5 ($J^2 = 18$ Hz), 27.7 ($J^3 = 53$ Hz), 29.6 ($J^2 = 20$ Hz), 58.6, 70.6, 70.9, 71.0, 72.3, 74.8 ($J^3 = 57$ Hz). ^{119}Sn NMR: -8.2 . Elemental analysis: expected for $\text{C}_{24}\text{H}_{52}\text{O}_6\text{Sn}$: C, 51.90; H, 9.36; O, 17.28; obtained: C, 51.35; H, 9.03; O, 17.38.

4.5. $\text{H}_2\text{Sn}[(\text{CH}_2)_3\text{OMe}]_2$ **5**

Synthesis of $\text{H}_2\text{Sn}[(\text{CH}_2)_3\text{OMe}]_2$ **5**: 2.75 g (8.2 mmol, 1 eq.) of $\text{Cl}_2\text{Sn}[(\text{CH}_2)_3\text{OMe}]_2$ are dissolved in 50 ml of ethylic ether. This solution is added dropwise to a suspension of 0.5 g (13.2 mmol, 1.6 eq.) of LiAlH_4 in 50 ml of ether. The solution is let under reflux during 2 h and then cool down at 0°C . 50 ml of pentane are added and the solution is hydrogenolysed with 10 ml of water. The solution is filtered and dried on MgSO_4 and the solvents are removed. The residue is distilled to give 1.51 g (69%) of **5**.

Characterization of **5**: boiling point: $42^\circ\text{C}/0.1$ mmHg. Infrared (pure): 2980, 2920, 2862, 2823, 1837, 1117, 713 cm^{-1} . ^1H NMR (C_6D_6): 4.90

(2H, s), 3.22–3.38 (8H, m), 1.87 (4H, qu, $J = 6.5$ Hz), 1.14 (6H, t, $J = 7.0$ Hz), 0.90 (4H, t, $J = 7.9$ Hz). ^{13}C NMR (C_6D_6): 4.5 ($J^1\text{Sn}-\text{C} = 393$ and 376 Hz), 28.0 ($J^2 = 25$ Hz), 75.2 ($J^3 = 49$ Hz).

4.6. $\text{H}_3\text{Ge}(\text{CH}_2)_4\text{OH}$ **7**

Synthesis of $\text{Cl}_3\text{Ge}-(\text{CH}_2)_3-\text{CO}_2\text{CH}_3$ **6**: 1.89 g (13.8 mmol, 1 eq.) of methyl-4-chlorobutyrate are added to a suspension of 3.21 g of GeCl_2 .dioxane (13.8 mmol, 1 eq.) in 15 ml of anhydrous dichlorobenzene under argon. The mixture is heated at 110°C during 24 h. After cooling down to room temperature, the unreacted GeCl_2 .dioxane (0.57 g) is filtered and the dichlorobenzene is evaporated. The yellow residue is distilled under low pressure and 500 mg of **6** are obtained.

Characterization of **6**: boiling point: $64^\circ\text{C}/0.2$ mmHg. ^1H NMR (C_6D_6): 3.26 (s, 3H), 1.79 (t, 2H, $J = 6.7$ Hz), 1.45–1.63 (m, 2H), 1.22 (t, 2H, $J = 8.5$ Hz). ^{13}C NMR (C_6D_6): 18.0, 30.7, 33.5, 50.6, 171.1.

Synthesis of $\text{H}_3\text{Ge}-(\text{CH}_2)_4-\text{OH}$ **7**: 2.05 g (15 mmol, 1 eq.) of methyl-4-chlorobutyrate are added to a suspension of 3.21 g of GeCl_2 .dioxane (13.8 mmol, 1 eq.) in 15 ml of anhydrous dichlorobenzene under argon. The mixture is heated at 110°C during 70 h. After cooling down to room temperature, the unreacted GeCl_2 .dioxane (0.50 g) is filtered and the dichlorobenzene is evaporated. The light residue (expected to be almost 40% of **6**) is dissolved in 10 ml of ether and directly reduced by dropwise addition of LiAlH_4 in ether (18 mmol, 3 eq.). After addition, the reflux is maintain during 4 h and then 10 ml of water are added slowly. The aqueous phase is extracted by 3×20 ml of ether. The organic phase is dried on MgSO_4 and traces of ether are evaporated. The residue is distilled under low pressure to give 378 mg of **7** (17% yield).

Characterization of **7**: boiling point: $74^\circ\text{C}/10$ mmHg. Infrared spectroscopy: 3605, 3468, 2977, 2933, 2866, 2064 cm^{-1} . ^1H NMR (C_6D_6):

3.71 (t, 3H, $J = 3.4$ Hz), 3.52 (t, 2H, $J = 5.9$ Hz), 2.39 (s, 1H disappeared by exchange with D_2O), 1.52 (m, 4H) 0.93 (m, 2H). ^{13}C NMR (C_6D_6): 8.0, 24.4, 35.5, 62.0. Elemental analysis: expected for $C_4H_{12}OGe$: C, 32.30; H, 8.08; obtained: C, 31.45; H, 7.88.

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