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Surface organometallic chemistry: some fundamental features including the coordination effects of the support

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Contents

Abstract

The study of the various kinds of reactions between organometallic complexes and the surfaces of inorganic oxides, metals or zeolites constitutes a new aspect of the coordination

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chemistry on surfaces. In this non-exhaustive and short review article, we would like to try to answer a few questions regarding this area of coordination (or organometallic chemistry) which may have some future impact in the field of catalysis. The questions that we would like to answer are the following:

Are the basic rules of molecular organometallic and coordination chemistry valid when one tries to apply them to surfaces? One can wonder whether or not the functionalities which are present at the surface of an oxide, M_xO_y (M–OH groups, strained M–O–M groups and M=O, aso) have a chemical reactivity which can be predicted on the basis of molecular chemistry. A few selected examples will be given about the reactivity of tin, rhenium or zirconium alkyls with the silanol groups of partially dehydroxylated silica.

Can we obtain reliable and precise informations when some selected tools of surface science and molecular organometallic chemistry are applied simultaneously to elucidate the structure of surface organometallic fragments? One can reasonably expect that the way the surface organometallic fragments coordinate to the surface can be rationalized on the simple rules of coordination chemistry (electron counting, formal oxidation state). A few examples will be given regarding the surface structure of silica-supported zirconium hydrides or rhodium allyls.

Is it possible that a well chosen surface organometallic fragment represents an intermediate in heterogeneous catalysis? If one can study the reactivity of a well chosen surface organometallic fragment, then one is in a position to demonstrate some elementary steps of heterogeneous catalysis. In this review we shall consider the surface reactivity of supported rhodium allyls or tin alkyls.

What kind of mobility can we expect from surface organometallic fragments? In sharp contrast with discrete ligands of molecular chemistry, surfaces of oxides obviously provide a so called "pool of oxygens" which binds the surface organometallic fragments in a localized manner. However, due to its almost infinite structure, such a "pool" is obviously responsible for surface mobility, which is also a key parameter in certain catalytic processes (sintering, diffusion processes, reconstructions, leaching,···). Examples will be given on the mobility of $Rh^I(CO)_2$ grafted onto a silica surface. The organometallic fragments are also mobile around the metal carbon bonds and this phenomenon can be evidenced by solid-state nuclear magnetic resonance (NMR) and can have applications in molecular separations and on the reactivity of the organometallic complexes. In each case, the role of the support as a coordinating ligand is a key factor of this chemistry.

Keywords: Dehydroxylated silica; Heterogeneous catalysis; Organometallic complexes; Zirconium alkyls

1. Introduction

During the past 40 years or so, homogeneous catalysis has considerably progressed, due to the relatively high level of understanding reached by molecular organometallic chemistry. In fact, these two sciences have progressed in parallel, resulting in new concepts which makes it possible to predict, in several cases and for a given reaction, what will be the best homogeneous catalyst (the metal, its oxidation state, its ligands and the reaction conditions) [1].

In contrast, the heterogeneous catalysis, which is much more important from an industrial point of view, has progressed probably more slowly and even now, remains a highly empirical science with a huge potential [2]. One reason for this situation is the difficulty in characterizing, at an atomic level, the surfaces before, during and after the catalytic reactions. This resulted in the great development of physico–chemical methods which, often, do not take into account the diversity of the sites on the surface and their low concentrations. As a consequence, and up to now, only a few elementary steps are really well understood at the molecular and atomic level (e.g. ammonia synthesis, CO oxidation,···). As the reaction mechanisms are not known, it is not always possible to have a predictive approach.

One of the objectives of surface organometallic chemistry is to determine if the concepts developed for homogeneous catalysis by the molecular organometallic chemistry can be applied to heterogeneous catalysis [3–5]. Is it possible to synthesize or construct, on a surface, "active sites" with a uniform distribution on all the solid and in a high concentration? In order to achieve this goal, a possible strategy is to assume a mechanism coming from the knowledge of molecular chemistry. Then one should design the equivalent coordination sphere on the surface. In order to achieve well defined active sites, it is appropriate to react selective organometallic molecules with surfaces of oxides, metals, zeolites, etc. One of the reasons for choosing organometallic complexes is because the coordination sphere of the catalyst can already be partially constructed. Therefore, the first step of surface organometallic chemistry is to try to understand at an atomic and molecular level, what happens when an organometallic complex reacts with a surface and what is (are) the surface and gaseous reaction product(s). In a second step, the concept of molecular organometallic chemistry can be transposed to the supported complexes whose structure is "relatively" well defined; perhaps, the reactivity of surface organometallic fragments can be tentatively predicted on the basis of what is already known in molecular (coordination and organometallic) chemistry.

Such a strategy leads first to the study of the grafting reaction of several organometallic complexes onto several surfaces (in most cases oxides but also zeolites, metals, carbons,···) in order to determine the basic rules which govern this new chemistry. We will present the fundamental tools of this chemistry in three parts: (i) the reactivity of the organometallic complex with the surfaces; (ii) the structure of the resulting surface species and (iii) the reactivity of this grafted complex, especially with the remaining ligands of the surface.

2. Basic rules governing the reactivity of organometallic complexes with some surfaces

Depending on the nature of the surface (oxides, zeolites or metals, variously treated), the nature of the reactions will differ considerably. Indeed, the grafting sites will not be the same. For oxides or zeolites, which will be described in this review, the reaction can occur not only with the hydroxyl groups but also with more or less strained M–O–M bridges resulting from the dehydroxylation process, or even with the M=O double bonds with certain metals in a high oxidation state.

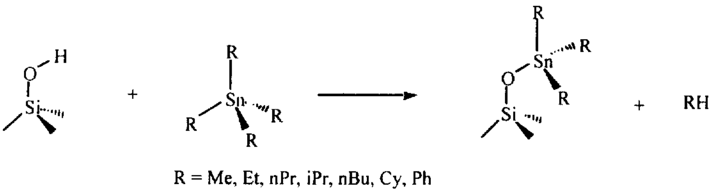
In many cases, the reaction occurs with the hydroxyl groups of the oxide surface, as they are present in large amounts, even after dehydroxylation at relatively high temperatures (below 700 °C). These hydroxyl groups have a behaviour quite comparable to that of the corresponding hydroxyl groups of organic or organometallic chemistry. This allows a transposition of the corresponding basic rules of the molecular chemistry to the reaction of the organometallic complex with the hydroxyl groups of the surface. Some of these rules are listed below:

- Nucleophilic attack to one (or more) ligand(s) of the organometallic complex by the OH groups [6].
- Electrophilic attack of one (or more) ligand(s) of the organometallic complex by the OH groups [7].
- Oxidative addition of the OH group on the metal center of the organometallic complex [8].
- Acid–base behaviour of the OH group.
- Electrophilic cleavage of M–C bonds of the organometallic complex by the OH groups.
- Abstraction by the surface OH groups of hydrogen atoms bonded to the metal (having an hydride character).

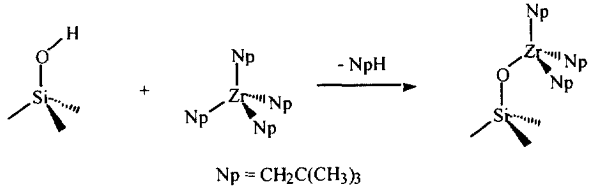
2.1. Reaction with hydroxyl groups

An example of electrophilic attack of a ligand coordinated to an organometallic compound by hydoxyl groups is the reaction of tetraalkyltin complexes with the surface of silica or alumina dehydroxylated at moderate temperatures (from 200–500 °C and denominated, respectively, $Al_2O_{3(200)}$ and $Al_2O_{3(500)}$) [9,10]. Various tetraalkyltin complexes were studied and all of them showed a comparable reactivity. The reaction was followed by infrared spectroscopy and analysis of the evolved gases, while the grafted organometallic fragments were characterized by several methods including solid-state ^{13}C and ^{119}Sn MAS NMR, microanalysis of the surface and the synthesis of molecular models. For all compounds, the reaction between the organometallic tin complex and the hydroxyl group can be described as an electrophilic cleavage of the Sn–C bond by the hydroxyl group of the surface. This extremely simple reaction is shown in Scheme 1. At moderate temperatures, and provided the silica is dehydroxylated at 500 °C, the cleavage of only one alkyl group occurs.

The electrophilic metal–carbon cleavage by the hydroxyl group was also observed with tetraneopentyl zirconium and $silica_{(500)}$ [11]. As above, the reaction was followed by infrared spectroscopy and analysis of the evolved gases while the grafted complex was characterized by the same methods as above and EXAFS [12]



Scheme 1.



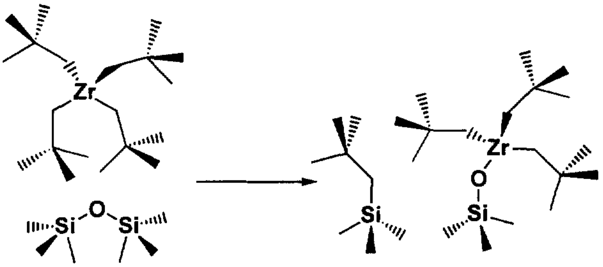
Scheme 2.

(Scheme 2). Interestingly, all the hydroxyl groups of silica$_{(500)}$ were instantaneously removed in this reaction.

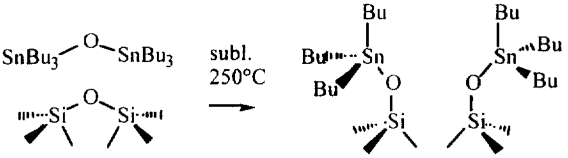
2.2. Reaction with highly strained ≡M–O–M≡ bridges

When the silica has been dehydroxylated at high temperatures (>800 °C), there is formation of highly strained ≡M–O–M≡ bridges, corresponding to the formation of cycles containing four atoms (two M atoms and two O atoms) and characterized in infrared spectroscopy by two bands at 888 and 908 cm^{-1} [13]. These strained bridges are highly reactive and can be opened by reaction with organometallic complexes. A typical example is the reaction of tetraneopentyl zirconium with a silica$_{(1000)}$ [14]. During this reaction, which is depicted in Scheme 3, one neopentyl ligand is transferred to a silicon atom of a strained ≡Si–O–Si≡ bridge, leading to the formation of a very strong Si–C bond, which cannot be broken by reaction with water or HCl. The remaining trisneopentyl zirconium fragment is grafted to the other silicon atom via an oxygen atom. A quite similar reaction was observed with trimethylethoxysilane on a silica$_{(600)}$, the resulting Si–C bonds being not easily cleaved, even under boiling water [15].

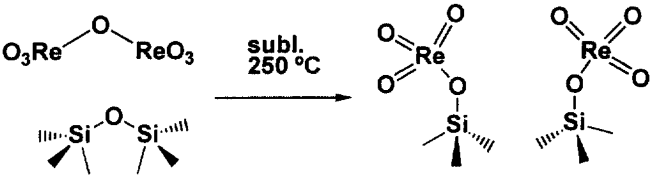
Another example of the reactivity of these strained bridges can be found in the chemistry of tin. Indeed, $Bu_3Sn–O–SnBu_3$ reacts with the surface of a silica$_{(1000)}$, leading to the formation of two $≡Si–O–SnBu_3$ grafted species by opening of the ≡Si–O–Si≡ bridges (Scheme 4) [16]. However, what is the most interesting is that this reaction proceeds not only with the ≡Si–O–Si≡ bridges of the four-membered cycles but also with less strained bridges having six and even eight-membered rings.



Scheme 3.



Scheme 4.



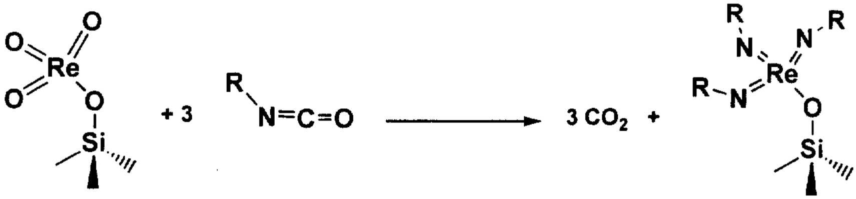
Scheme 5.

Such a result could have implications in the modification, by organometallic chemistry, of zeolites, as these materials contain eight-membered rings in their framework.

Similar results were obtained with Re_2O_7 instead of $Bu_3Sn-O-SnBu_3$: there is opening of the ≡Si–O–Si≡ bridges and, depending on the reaction temperature, four-membered rings or larger cycles can be opened [17] (Scheme 5).

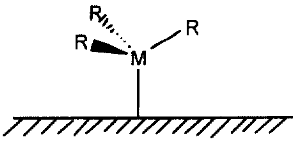
2.3. Reaction with metal oxo functionalities

When defined metal oxo are present on the surface, they can be transformed into imido species by reaction with alkyl or aryl isocyanate, leading to the formation of gaseous carbon dioxide. Such a chemistry could well be used in classical heterogeneous catalysis, to titrate surface metal oxo functionalities.



3. Structure of the surface-grafted organometallic fragments

The determination, this time at a molecular and atomic level, of the structure of a grafted organometallic complex is a key step for the understanding of the rules governing the stability and reactivity of these species. Up to ca. 10 years ago, most of the work published in the literature did not describe the chemical bond between the organometallic fragment and the surface. Due to the lack of techniques available,



Scheme 6.

it was not really possible to have a sufficient knowledge of the structure of the grafted surface species (Scheme 6).

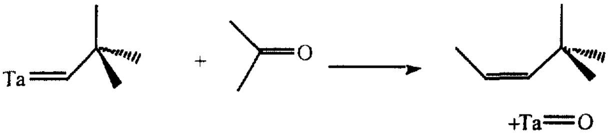
A variety of tools can now be applied to shed some light on the determination of the chemical nature of the bond between the metal atom of the organometallic fragment and the surface. For this purpose, the concepts developed by Green and Hoffmann [18] concerning the calculation of the number of electrons surrounding the metal in a molecular complex is very useful, even on surfaces. By combining this rule with the highest number of physico–chemical characterizations, the structure of the grafted organometallic fragment can now be obtained with a reasonable degree of confidence. These physico–chemical characterizations include surface microanalysis, infrared spectroscopy, solid-state NMR, EXAFS, XANES, XPS and Mössbauer spectroscopy. It is not the purpose of this review to describe these techniques. In an extremely naive approach we can say that EXAFS will give the number and the distance of first neighbours of the metal atom; XPS and Mössbauer will give indications about the oxidation state of some metal; infrared spectroscopy will allow to determine what type of hydroxyl groups are consumed during the grafting reaction; ^{13}C solid-state NMR will give information about the nature and mobility of the ligands around the metal atom, while metal solid-state NMR will allow the determination of the coordination number of the metal atom. We will present here examples of structures determined in this way. The examples displayed here are interesting as the support acts as a ligand, ensuring additional interactions with the grafted organometallic fragment.

3.1. Structure of a zirconium alkyl supported on silica

As previously mentioned, one can easily obtain a zirconium trisneopentyl on a silica$_{(500)}$. The zirconium is linked to the surface of silica by only one Si–O–Zr bond. EXAFS data gave an O–Zr distance of 0.195 nm and three Zr–C bonds of 0.221 nm. Even if the zirconium is highly oxophilic, it cannot react with the surface due to the high steric crowding of the three neopentyl ligands. Solid-state NMR of this surface-complex allows the observation of the peaks of the methyl and of the carbon directly bonded to zirconium, even if this late signal is very broad due to the interactions with the d orbitals of the metal. The zirconium is formally 10 electrons, if we count the surface oxygen ligand as donating three electrons.

3.2. Structure of a tantalum alkylidene complex

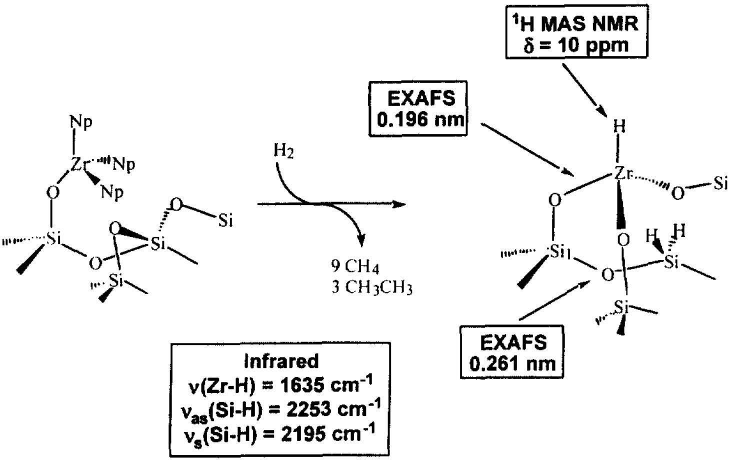
When the Schrock carbene $TaNp_3(=CHCMe_3)$ reacts with a silica$_{(500)}$, two species are formed: one in which the tantalum is linked to one oxygen atom of the silica and a second one in which the tantalum is linked to two oxygens of the silica. Both structures contain a carbene ligand, as evidenced by the pseudoWittig reaction with acetone, which gives, quantitatively, the corresponding olefine.



3.3. Structure of the zirconium hydride supported on silica

We have described above the reaction of tetraneopentyl zirconium with the hydroxyl groups of a silica$_{(500)}$. The grafted organometallic fragment present on the surface is then ≡Si–O–ZrNp$_3$ and it has been fully characterized [11]. By heating at 150 °C under hydrogen, this supported complex undergoes a reaction, as evidenced by infrared spectroscopy, which shows the disappearance of the ν(C–H) bands, characteristic of the neopentyl ligands [19]. Simultaneously, new bands, attributed to ν(Si–H) and ν(Zr–H) vibrations, appear while the gaseous phase shows the appearance of ethane and methane (three ethane and nine methane molecules per grafted zirconium complex), arising from the hydrogenolysis of the evolved neopentane by the resulting zirconium complex.

The spectroscopic data for the surface zirconium complex are summerized in Scheme 7. The most important data are EXAFS, which show that the zirconium atom is surrounded by four oxygen atoms: three atoms at 0.196 nm corresponding to a σ Zr–O bond, and one atom at 0.264 nm corresponding to a very weak bond which is likely a π bond [12]. Infrared spectroscopy also gives other important data, as it shows that the silicon hydride is present as a dihydride [12]. By taking into

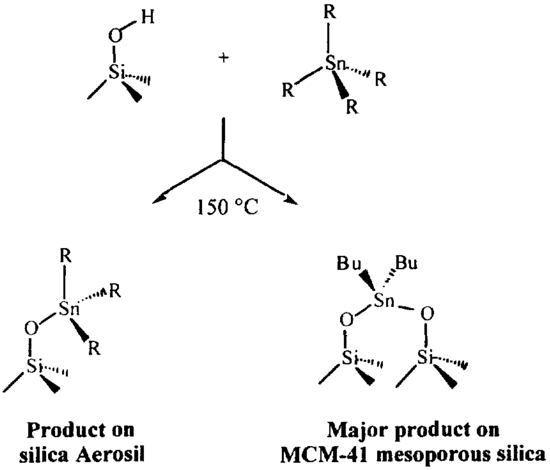


Scheme 7.

account these results, it is necessary to postulate for the zirconium hydride a structure similar to that depicted in Scheme 7, in which the zirconium(IV) d^0 is surrounded by 14 electrons. We consider here the surface oxygen atoms as three-electron donors as the $p\pi$–$d\pi$ interaction most certainly occurs with a zirconium that has a d^0 configuration. Molecular modelling studies show that such a structure can be achieved on the silica surface, the silicon atoms being at a reasonable distance from the zirconium. The obtention of this structure, in which the zirconium atom is highly electrophilic, is easily explained by the cleavage of two $\equiv$Si–O–Si$\equiv$ bridges by the zirconium hydride. Note that, in this structure, the third $\equiv$Si–O–Si$\equiv$ bridge acts as a π-ligand for the zirconium.

3.4. *Structure of tin complexes grafted onto various supports*

As mentionned above, various tetraalkyltin compounds were reacted with the surfaces of oxides or zeolites. The reaction proceeds at 150 °C when the supports are dehydroxylated from 200–500 °C [9]. The resulting grafted tin complexes were characterized by determination of the evolved gases during the grafting reaction, chemical analysis (carbon, tin, and at least one element of the support for calibration), infrared spectroscopy (presence of the ν(C–H) bands characteristics of the alkyl ligands), molecular models, and ^{13}C CP-MAS and ^{119}Sn MAS NMR. ^{119}Sn MAS NMR gives very useful information about the coordination sphere of tin. The ^{119}Sn chemical shift is highly sensitive to the coordination sphere of tin and can vary over more than 500 ppm for tin(IV) complexes. For example, for the same organotin fragment, –O–SnR_3, grafted on different supports and in which the tin is tetracoordinated, the ^{119}Sn chemical shift varied from +100 ppm (for $\equiv$Si–O–SnR_3 supported on silica) [9] to +150 and +175 ppm, respectively, for $\equiv$Ga–O–SnR_3 and $\equiv$P–O–SnR_3 grafted on cloverite [20,21] and to more than +250 ppm for $\equiv$M–O–SnR_3 (M = Si, Al) grafted on Y zeolite [22]. These studies also show that different species were obtained, depending on the nature of the support. Even for supports with the same chemical composition, different results are obtained. For example, for Aerosil silica, which can be considered as spheres of ca. 10–20 nm in diameter, the reaction of SnBu_4 leads to the formation of $\equiv$Si–O–SnBu_3 only (Scheme 8) [9], while on the MCM-41 mesoporous silica, in which the hydroxyl groups are located inside channels of ca. 2–3 nm in diameter, the reaction is not so selective and leads to variously substituted tin butyl fragments ($\equiv$Si–O)$_x$SnBu_{4-x} ($x = 1$–3), the major product (more than 70% of tin) being the species bonded to the surface via two $\equiv$Si–O bonds (Scheme 8) [23]. The explanation of such a reactivity difference between these two kinds of silicas is probably related to the different arrangment of the hydroxyl groups in these materials. Indeed, it has been reported that on mesoporous silica most of the hydroxyl groups were hydrogen-bonded to one another, the amount of free hydroxyl groups being small [24,25]. The presence of such interactions reflects the proximity of the hydroxyl groups, rendering their successive reactions with the same butyl tin fragments more easy than on dehydroxylated Aerosil silica. This effect may also be depicted more simply as follows: on Aerosil silica, the surface is convex, leading to hydroxyl groups

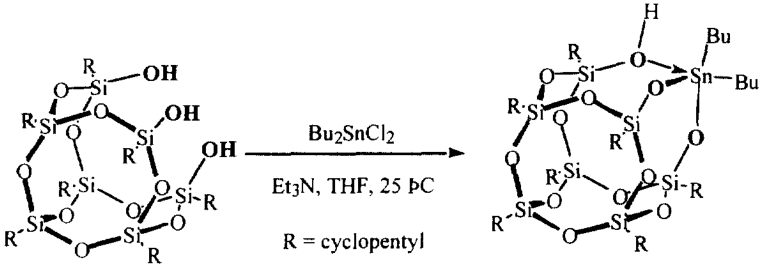


Scheme 8.

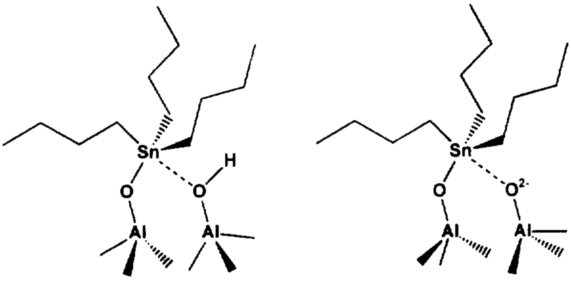
pointing to divergent directions while on MCM-41, the surface is concave and so the hydroxyl groups point to convergent directions. Naturally this is only a very naive and oversimplified picture of the surface.

A molecular model of the $(\equiv Si{=}O)_2SnBu_2$ surface species was made by reaction of dibutyl dichloride tin with a silsesquioxane (Scheme 9) [26]. The corresponding product was fully characterized and showed a particular behaviour. The remaining hydroxyl group of the silsesquioxane was bonded to tin via van der Waals interactions. This interaction, which was not strong, had no effect on the ^{119}Sn chemical shift (−34 ppm, a value quite comparable to that found for $(RO)_2SnR_2$ complexes in which tin is teracoordinated). So, it cannot be excluded that such an interaction exits on silica. Even if it is not the case, this complex can be considered as an intermediate during the thermolysis of the surface species (see later).

On alumina, the behaviour was completely different from that observed on silica or zeolites [10]. While the ^{119}Sn NMR showed only the presence of tetracoordinated tin, the spectra obtained after reaction with various aluminas showed, in addition to a signal at ca. +80 ppm and attributed to a tetracoordinated tin species, numerous



Scheme 9.



Scheme 10.

signals at ca. −200 ppm corresponding to tin in a pentacoordinated environment. These peaks were reproducible from one alumina to another and were attributed to species in which tin was linked to the surface via two bonds, as represented in Scheme 10. The high number of resonances was ascribed to the high number of grafting sites (there are five types of hydroxyl groups and the fifth ligand can be an oxygen atom, O^{2-}, or an hydroxyl group, leading to a high number of possibilities.

3.5. Grafting reaction of $Rh(\eta^3\text{–}C_3H_5)_3$ on oxide surfaces

The reaction between $Rh(\eta^3\text{–}C_3H_5)_3$ [27] (in toluene solution) and the surface of $silica_{(200)}$ takes place readily, at room temperature to give a material with a deep yellow colour while one equivalent of propene is evolved [28].

The formation of a chemical bond between rhodium and silica via an oxygen atom of the surface was concluded on the basis of Raman spectroscopy. The corresponding spectrum showed bands at 447, 481 and 505 cm^{-1} attributed to ν(Rh–O) vibrations of the grafted species. The presence of two allyl ligands remaining bonded to rhodium was demonstrated by the evolution of two equivalents of propene when the grafted species was treated with H_2SO_4.

Dufour et al. [7] studied the reaction of $Rh(\eta^3\text{–}C_3H_5)_3$ with variously treated silicas. The same stoichiometry of this reaction was observed regardless of the degree of dehydroxylation or the porosity of the silica sample. Thus, it seemed likely that the reaction resulted in a single product. However, the amount of rhodium which could be grafted onto the surface was sensitive to the degree of dehydroxylation of the silica, consistent with the varying availability of surface –OH groups. The formation of propene was demonstrated to occur using a surface proton. Thus, when quantitatively deuterated silica was used, the gaseous product was exclusively propene–d_1 [7,29].

$$\equiv Si-O-D + Rh(\eta^3-C_3H_5)_3 \rightarrow \underset{\mathbf{1}}{\equiv Si-O-Rh(\eta^3-C_3H_5)_2} + C_3H_5D$$

Product **1** was also tentatively characterized by IR bands at 1496 (w), 1462 (m), and 1391 cm^{-1} (m), which were assigned to $\delta(CH_2)$ and ν(C–C–C) modes of the allyl ligands. Changes in the vibrational spectrum in the O–H stretching region indicated that the rhodium complex likely interacted with the O–H groups on the surface of the silica. After reaction with $Rh(\eta^3\text{-}C_3H_5)_3$, the intensity of the ν(O–H) band at 3746 cm^{-1} decreased, while the band due to hydrogen-bonded silanols changed in shape and position. An intriguing feature of the spectrum of silica after reaction with $Rh(\eta^3\text{-}C_3H_5)_3$ was the formation of a sharp band of weak intensity at 3636 cm^{-1}. During experiments in which increasing amounts of $Rh(\eta^3\text{-}C_3H_5)_3$ were added to the sample, an increase of its intensity was observed, thus it was likely due to a hydroxyl group coordinated to rhodium. A band of similar frequency had also been previously reported for an hydroxyl group coordinated to a metal center [30].

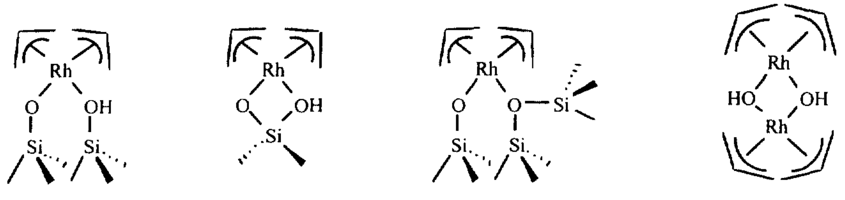
When ^2H-enriched silica (obtained by partial exchange of the surface silanol with D_2O) was used, two sharp bands were obtained at 3636 and 2683 cm^{-1}. These bands had the expected isotopic frequency ratio for H/D substitution.

Isotopic labelling experiments were also carried out using ^{18}O-enriched silica (obtained by partial exchange of the surface silanols with $H_2{}^{18}O$). Moreover, two sharp bands appeared at 3635 and 3625 cm^{-1}. The frequency of these sharp bands corresponded to a calculated isotopic $\nu(^{16}OH)/\ \nu(^{18}OH)$ ratio of 1.003 as opposed to the theoretical value of 1.006.

The grafted bis(allyl)rhodium fragment eluded attempts at NMR characterization for some time. In the solid state, the low mobility of π-bound allyl ligands rendered them difficult to observe, even using CP-MAS techniques [31]. Recently, ^{13}C and ^1H spectra of **1** were reported, using ^{13}C-enriched $Rh(\eta^3\text{-}C_3H_5)_3$ as a starting material [32]. The H–C correlation supported the assignment of the grafted species as a bis(π-allyl) fragment.

On silica, the formation of a complex with a coordinated hydroxyl group was effectively observed. Molecular modelling of the surface complex was performed [7] using bond lengths and bond angles identical to those in the model compound, $[Rh(\mu\text{-}OH)(\eta^3\text{-}C_3H_5)_2]_2$ [33]. The $Rh(\eta^3\text{-}C_3H_5)_2$ fragment could be accommodated on the (100) surface of β-cristobalite to give **1a** and **1c** and on the (111) surface to give **1b** without steric complications.

In summary, it has been shown that the surface organometallic fragment **1** is a well-defined surface complex. Three microenvironments were proposed for **1** on the silica surface (Scheme 11), based on the known structure of a molecular analogue, **1′** [33], IR evidence [7], and theoretical calculations [34].



1a **1b** **1c** **1′**

Scheme 11.

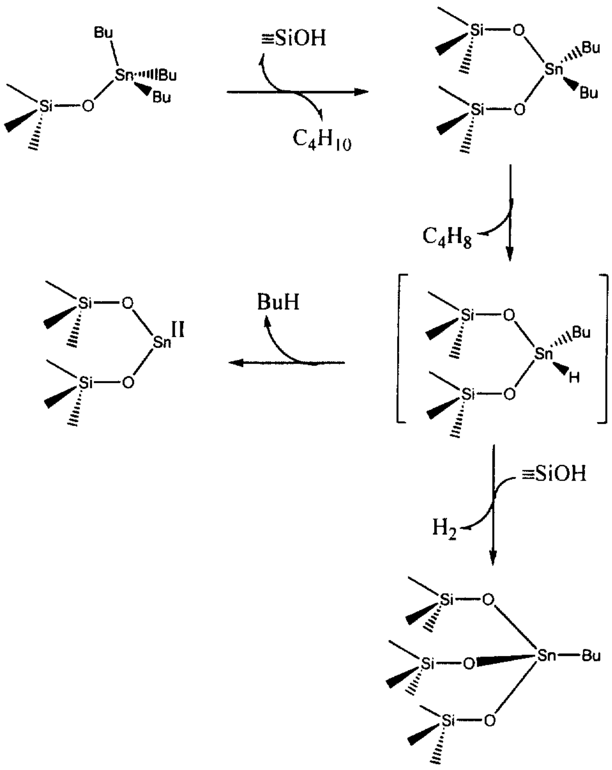
4. Reactivity of the surface-grafted organometallic fragments

The grafted organometallic fragments can undergo further reactions with the support or with other molecules. Those reactions can be, in some cases, considered as elementary steps of heterogeneous catalysis. We shall present here only few examples of such reactions, taken from the tin and rhodium chemistry.

4.1. Thermolysis under vacuum of ≡Si–o–SnBu$_3$ fragments grafted on silica

We have shown above that tetrabutyl tin reacts at 150 °C with the silanol groups of silica (Aerosil Degussa) dehydroxylated at moderate temperatures (from 200–500 °C) with the formation of a ≡Si–O–SnBu$_3$ surface species. This surface complex, which has been fully characterized (see above) can undergo further reactions when it is heated under vacuum at temperatures up to 500 °C [23,35]. The observed reactions are summarized in Scheme 12.

The grafted complex can react with the surface silanol groups by the same mechanism as for the grafting reaction, leading then to $(\equiv SiO)_{x+1}SnR_{3-x}$ (x = 1, 2, 3) multigrafted species. Simultaneously, butane is evolved. However,



Scheme 12.

$\equiv$Si–O–SnBu$_3$ can also react by another mechanism, and this way will be preferred if the density of the remaining OH groups on the surface is small, i.e. if the silica has been dehydroxylated at 500 °C rather than at 200 °C: one of the butyl ligands of the grafted complex undergoes a β-H elimination with formation of butene-1 (detected in the gaseous phase) and possibly a surface tin hydride (which is probably highly unstable and has never been observed). This tin hydride could react with a silanol group or with an other alkyl ligand of the complex. In the first case, there is hydrogen evolution while in the second case butane is evolved while tin is reduced to the +II coordination state. This pathway has been confirmed by Mössbauer spectroscopy, which detected the presence of tin(II) in a sample of $\equiv$Si–O–SnBu$_3$ heated under vacuum at 500 °C.

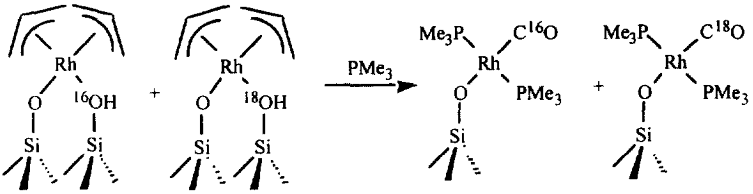
4.2. *Interaction of* $(\equiv SiO)(\equiv SiOH)Rh(\eta^3\text{-}C_3H_5)_2$ *(1) with* H_2

The reactivity under hydrogen of bis-allyl rhodium complexes grafted on silica, has been studied "in situ" using qualitative and quantitative analytical techniques such as gas phase chromatography, mass spectroscopy, volumetry, electron microscopy and IR spectroscopy. The reaction of **1** with hydrogen leads to the quantitative regeneration of the hydroxyl groups of the surface, the loss of the allylic groups, as propane and hexanes, and the formation of numerous metallic particles detected by electron microscopy. In the literature, the formation of a rhodium hydride complex was proposed on the basis of an infrared band at 2048 cm^{-1} [28]. We observed that this band remained at the same frequency whether the sample was exposed to hydrogen or deuterium and whether the silica was deuterated or not, proving that it cannot be assigned to an Rh–H band [36]. In contrast, labelling of the starting silica with $H_2{}^{18}O$ resulted in a shift of the band at 2048 cm^{-1} to 2005 cm^{-1}. On the other hand, this band completely disappeared after exposure to oxygen at room temperature with formation of carbon dioxide, supporting its attribution to a ν(Rh–CO) band. Further studies showed that the coverage of rhodium by CO was less than 1% [36]. The formation of carbon monoxide during the reduction under hydrogen of **1** was explained by the formation of allylic alcohol, the oxygen coming from the support. This assumption was supported by the results of reaction of **1** with PMe$_3$ on silica$_{(200)}$, which almost exclusively gave propene, $\equiv$SiORh(PMe$_3$)$_3$, as surface product and allylic alcohol [29]. This alcohol is further decarbonylated by $\equiv$SiORh(PMe$_3$)$_3$ with the evolution of ethane and formation of $\equiv$SiORh(CO)(PMe$_3$)$_2$. A similar decarbonylation reaction was reported between allylic alcohols and ClRh(PPh$_3$)$_3$, yielding ClRh(PPh$_3$)$_2$(CO) [37].

With a partially labelled ^{18}O surface, the reaction of **1** with PMe$_3$, afforded, in this case, two carbonyl peaks at 1957 and 1915 cm^{-1}, corresponding to the isotopically different products of Scheme 13 [38].

4.3. *Interaction of* $(\equiv SiO)(\equiv SiOH)Rh(\eta^3\text{-}C_3H_5)_2$ *(1) with Lewis bases*

When **1** is prepared on a silica surface dehydroxylated at 550 °C (**1**$_{550}$), only a few hydroxyl groups remain after grafting. In this case, the predominant species is

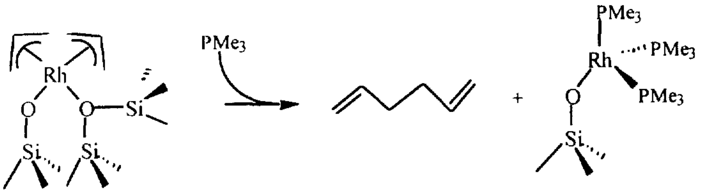


Scheme 13.

believed to be **1c**, whose reactivity towards Lewis bases resembles that of molecular analogues [39]. For example, when $\mathbf{1}_{550}$ is exposed to PMe$_3$ or CO, 1,5-hexadiene is formed by reductive elimination of two allyl ligands from the coordination sphere of Rh (Scheme 14).

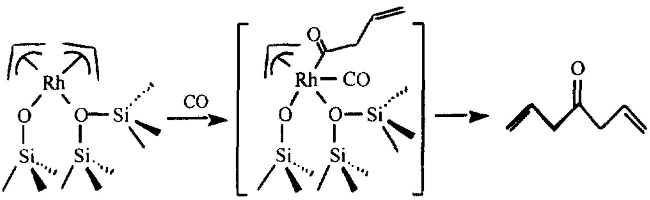
The organometallic product, which, in the case of L = PMe$_3$, is ≡SiORh(PMe$_3$)$_3$, was characterized by ^{31}P MAS NMR and elemental analysis. It was prepared independently by reaction of CH$_3$Rh(PMe$_3$)$_3$ with silica [29]. It can also be considered as a "surface" analogue of the Wilkinson's catalyst.

In the case of the reaction with CO, the organometallic product is [≡SiORh(CO)$_2$]$_2$ [40,41]. The fact that the product is a dimer, while the starting complex, **1c**, is monomeric has important implications on the mobility of surface organometallic fragments (vide infra). Insertion of CO into the metal–allyl bond is also observed: in addition to 1,5-hexadiene, traces of 1,6-heptadien-4-one are also detected. We suggest that this product is formed by reductive elimination from an (allyl)(acyl)rhodium intermediate (Scheme 15).



1c

Scheme 14.



1c

Scheme 15.

Reductive elimination of 1,6-heptadien-4-one was also observed in the reaction of molecular bis(allyl)nickel complexes with CO [42]. Homogeneous (alkyl)(acyl)Rh^{III} complexes such as $[RhR(C(O)(\acute{R})(CO)(Cl)L_2]$ are unstable and rapidly eliminate ketones [43].

In summary, when few surface hydroxyl groups are present, the reactivity of **1** towards Lewis bases is similar to the reactivity of molecular analogs. This point is additionally illustrated by comparison with the chemistry of the molecular compound, $[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$.

Addition of CO induces the $\eta^3 \rightarrow \eta^1$ shift of the allyl ligand, followed by reductive elimination of 1,5-hexadiene or CO insertion and reductive elimination of 1,6-heptadien-4-one [41] (Scheme 16).

By increasing the surface hydroxyl concentration (using $\text{silica}_{(200)}$ or a low Rh coverage on a $\text{silica}_{(400)}$), the proportion of species **1a** and **1b** increases with respect to **1c**. Reaction with Lewis bases no longer produces 1,5-hexadiene. Instead, propene is the major product. We propose that it is formed by the electrophilic attack of a surface proton on a σ–allyl ligand (Scheme 17).

The proposed mechanism is supported by an experiment in which the surface hydroxyl groups were partially deuterated by exchange with D_2O. The amount of monodeuterated propene liberated by the reaction of **1** with L, was equal to the amount of deuterium incorporated into surface silanol groups. The coordination of L forces a π–allyl ligand of **1** to adopt a σ–allyl configuration, which in general renders the metal–carbon bond susceptible to electrophilic cleavage [44].

The elimination of propene and coordination of L to Rh is followed by the $\eta^3 \rightarrow \eta^1$ shift of the second allyl ligand (Scheme 18). In the case of $L = PMe_3$, we observed IR bands at 3072 and 1612 cm^{-1}, which are characteristic of a σ–allyl group, coordinated to a metal atom [46]. These bands are assigned respectively to the ν(=C–H) and ν(C=C) modes of **2**. The $\eta^3 \rightarrow \eta^1$ shift was inferred in the reaction

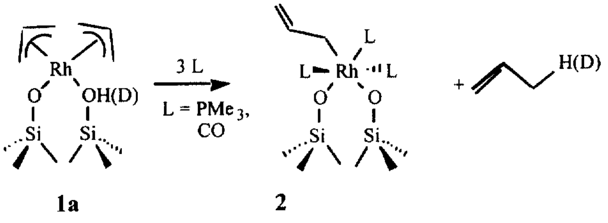
$$[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2 + CO \rightarrow Rh(\eta^1\text{-}C_3H_5)(\eta^3\text{-}C_3H_5)(CO)Cl + CO$$

$$\rightarrow [Rh(C(O)C_3H_5)(\eta^3\text{-}C_3H_5)(CO)Cl] \qquad [Rh(\eta^1\text{-}C_3H_5)_2(CO)_2Cl]$$

$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$

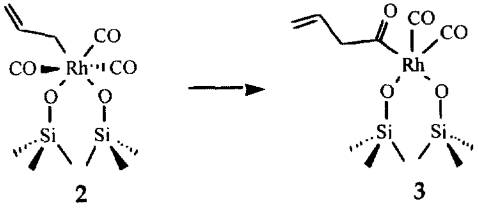
$$[Rh(CO)_2Cl]_2 + C_3H_5\text{-}CO\text{-}C_3H_5 \qquad [Rh(CO)_2Cl]_2 + C_6H_{10}$$

Scheme 16.

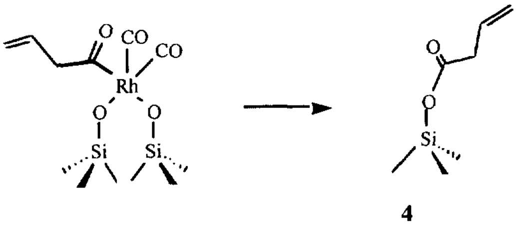


1a **2**

Scheme 17.



Scheme 18.



Scheme 19.

of **1** with CO (Scheme 18). However, rapid insertion of CO into the Rh–C bond, which gives an acyl complex [ν(C=O) 1692 cm^{-1}], prevents the characterization of a σ–allyl complex comparable with **2**.

The acylrhodium complex (**3**) undergoes reductive elimination of the acyl ligand with a siloxy ligand coordinated to Rh to give the silyl ester of 3-butenoate which was extracted from the surface as the methyl ester with both $(CH_3)_2SO_4$ and CH_3I, and identified by GC (Scheme 19).

In molecular chemistry, this type of intramolecular reductive coupling is a viable final step in ester synthesis [45].

5. Mobility of the surface-grafted organometallic fragments

An organometallic complex grafted onto the surface of an oxide can exhibit at least two types of mobility:

- One of them is the mobility of the organometallic fragment itself versus the oxygen atoms of the surface. Its proof and its explanation by the coordination chemistry concepts should give new insights about some important processes in heterogeneous catalysis such as the sintering or the formation of metallic particles during the reduction of a catalyst prepared by impregnation.
- The second deals with the conformational mobility of the alkyl chains of the grafted organometallic fragments. Such a mobility will be governed by van der Waals or hydrogen-type interactions between the alkyl ligands of the organometallic fragment and the oxygen atoms or the hydroxyl groups of the surface.

We will give here one example of each of these two types of mobility, the rhodium carbonyls on silica and the tributyl tin fragments grafted onto silica.

5.1. Influence of surface hydroxyl groups on the mobility of surface (≡SiO)(≡SiOX)Rh(CO)$_2$ (X=H or Si≡) organometallic fragments

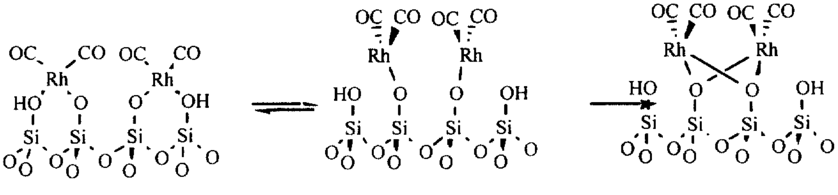
The surface hydroxyl groups influence the chemistry of **1** and the fate of organometallic products by direct participation in the coordination sphere of rhodium.

The initial rhodium complex formed by the reaction of **1** with CO is monomeric, with a formula (≡SiO)(≡SiOX)Rh(CO)$_2$ (X=H or Si≡), as shown by the presence of two ν(CO) bands in the IR spectra, and six ν(CO) bands in the presence of a ^{12}CO/^{13}CO mixture [41]. Over the course of several minutes, the monomer dimerizes (Scheme 20).

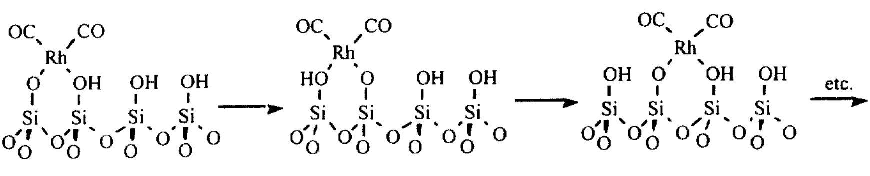
During this reaction, the ν(CO) bands shift and a third ν(CO) band appears at higher frequency, typical of non-planar dicarbonylrhodium dimers. A probable structure for the dimer contains bridging siloxy ligands [40], as in the molecular complex [Rh(CO)$_2$(μ-OSiMe$_3$)]$_2$. Dimerization requires surface migration of Rh^I(CO)$_2$ fragments, a process which has been demonstrated on oxide surfaces during the formation of zerovalent Rh clusters [47,52]. The presence of surface hydroxyl groups is thought to be crucial for the mobility of the dicarbonylrhodium fragments [48]. The mechanism of mobility probably involves the migration of surface protons and the reversible coordination of surface silanols to rhodium (Scheme 21).

The facile exchange of alkoxy ligands, –OR, on rhodium in the presence of R′OH, already reported [49], supports such a mechanism.

Finally, in the presence of H$_2$, the surface dimers [Rh(CO)$_2$(μ-OSi≡)]$_2$ are reduced to zerovalent rhodium atoms which can also migrate to form CO-covered metal particles.



Scheme 20.



Scheme 21.

Non-coordinated OH groups facilitate the migration of surface organometallic species. The latter phenomenon makes bimolecular surface reactions possible, and may lead to the formation of higher nuclearity clusters. The principle of surface mobility has been used in the surface-mediated synthesis of rhodium clusters [50,51].

This surface mobility can also explain, at least in part, the leaching of the metal during catalysis. Indeed, replacement of the hydroxyl groups of silica by, for example, alcohols, will lead to species with no more bonds to the surface, which will then be evacuated in the catalytic solution.

5.2. *Mobility of the alkyl chains of* $\equiv Si{-}O{-}SnBu_3$

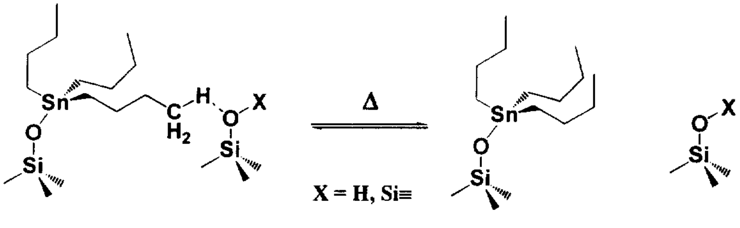
As described above, the ^{13}C CP-MAS NMR spectrum of $\equiv Si{-}O{-}SnBu_3$ shows some interesting features, one of them being the presence of two peaks at 11 and 13.4 ppm for the δ-carbon atom of the butyl chains [9]. We have performed a detailed study of this system by varying parameters such as the tin loading on the surface or the dehydroxylation temperature of silica. These results indicate that these two peaks correspond to two butyl chains:

- The peak at ca. 11 ppm corresponds to butyl chains interacting with the hydroxyl groups of the surface by their methyl groups.
- The peak at 13.4 ppm corresponds to free rotating butyl chains which are not interacting with the surface.

A study by ^{13}C CP-MAS NMR, at variable temperatures, has been made on this system. It shows that at 80 °C, only the peak at 13.4 ppm, corresponding to the methyl groups of the free rotating butyl chains, is observed, so the interaction with the surface has been suppressed [9] (Scheme 22).

6. Conclusion

In the course of this short review article, we have given examples of the reactions of zirconium, rhodium and tin complexes with the surface of inorganic oxides and zeolites. These reactions can be rationalized by using the basic rules of the organometallic and coordination chemistries. The structural determination of such surface organometallic fragments can be achieved if the tools of surface science and of organometallic chemistry are applied simultaneously. Rather precise determinations



Scheme 22.

of surface structures can then be made. The organometallic well-defined surface complexes can undergo reactions with the support (leading to multigrafted species) or with gaseous molecules, leading to a new coordination chemistry in which the support acts as a real ligand. Its effect is to dilute the organometallic species and to reduce their mobility, allowing, in some cases, the obtention and stabilization of extremely electron-deficient metal hydrides. With zirconium, the oxophilicity of these species is so high that they react with the siloxane bridges of the support, leading then to its partial reconstruction. A typical example is the obtention of $(\equiv Si{-}O)_3Zr{-}H$, by treatment under hydrogen of $\equiv Si{-}O{-}ZrNp_3$. This hydride can achieve both C–H and C–C bond activation of alkanes at low temperatures. The effect of the support can also favor some species. For example, the reaction of tetrabutyl tin with Aerosil $silica_{(200)}$ leads to the formation of monografted $\equiv Si{-}O{-}SnBu_3$, while $(\equiv Si{-}O)_xSnBu_{4-x}$ ($x=2, 3$) multigrafted species are obtained on a mesoporous MCM-41 silica. Good knowledge of the surface structures also allows good understanding of the reactions occurring with various substrates, so we can model the catalytic cycles, step by step. Examples of the mobility of the surface species in the presence or absence of a reagent were given, showing the conformational mobility of the butyl chains in $\equiv Si{-}O{-}SnBu_3$ and the migration of rhodium complexes on the silica surface. In all cases, the role of the support as a coordinating ligand is a key factor of this chemistry.

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