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On the Origins and Development of “Surface Organometallic Chemistry”

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1.1 The Basic Concept

The basic concept is the intuition that, whether homogeneous or heterogeneous, catalysis is primarily a process controlled by a molecular phenomenon since it implies the catalyzed transformation of molecules into other molecules. It follows that on the surface of metals or metal oxides, sulfides, carbides, nitrides usually involved as heterogeneous catalysts, the relevant surface species and the mechanism of their mutual reactions must be of molecular character, as occurs in homogeneous or enzymatic catalysis.

This was the basic assumption developed in the early 1960s by Bond [1] and Ugo and Carrà [2] in a rather preliminary way to support the so-called “molecular approach to heterogeneous catalysis.”

To establish the validity of this “intuition” it was first necessary to evidence clear relationships between the two areas of homogeneous and heterogeneous catalysis, which are a priori very distinct from one another. The first was historically close to *molecular chemistry* and the second to *surface science* and in particular to the approach based on solid-state physics of surface states.

Already at the beginning of 1960s a different evolution of the two areas was emerging. During 1960–1970 there was a considerable parallel development of homogeneous catalysis and molecular organometallic chemistry that were progressing in a kind of “win-win” success story in terms of fundamental understanding by organometallic chemistry of the chemical steps in homogeneous catalysis. Most catalytic cycles proposed in homogeneous catalysis were, at least at first glance, rationalized by the simple elementary steps that were discovered in parallel in organometallic chemistry. In the same period, progress made in the fundamental understanding of the factors and mechanisms controlling heterogeneous catalysis, a discipline of great interest for industry, was emerging more slowly. Certainly, the fantastic physicochemical tools of surface sciences were developing less rapidly and in other directions [3]. The use of single-crystal surfaces as model catalysts supported by the development of the application of new

techniques that can monitor surface structure and dynamics of molecular intermediates and species on surfaces made, particularly since the late 1970s, a major contribution to the understanding of surface chemistry involved in heterogeneous catalysis. But they could not take easily into account the evidence that the surface of a real heterogeneous catalyst was indeed "heterogeneous," and thus the single-crystal approach could not account completely for the complexity of real surface states and above all with the very small number of "active sites," a concept proposed by Burwell and Taylor as early as 1937 [4]. The intrinsic "heterogeneity" of a surface was a crucial point that needed to be considered and solved (Figure 1.1). Not only the molecules entering the catalyst had to pass through a considerable number of diffusion processes in the pore system to reach the "region" of the active site (e.g., a particular atom or aggregates of atoms) but once they were close to the active site the situation was even more complex. In fact in a metal particle the surface heterogeneity is governed by the nature and properties of various surface atoms in different crystallographic positions (e.g., edges, faces, corners, kinks, steps) and, in principle, there was no simple reason why they should behave in the same way to activate the incoming, first "physisorbed" and then "chemisorbed", molecule.

Besides, the structure, nature and reactivity of the chemisorbed molecule could not be unambiguously identified because the physical tools used could not lead easily to a complete understanding of the "quasi molecular" character of surface chemisorbed species and move precisely to the definition of the elementary steps occurring during the molecular transformations taking place on the surfaces.

The molecular approach to heterogeneous catalysis was thus a link for the validation of the experimental evidences obtained from work on single crystals by the various physicochemical tools of surface science. In fact at the beginning of 1970s there was an increased acceptance of the "organometallic character of surface intermediates involved in heterogeneous catalysis": When a molecule(s) react(s) on a surface to make product(s), bonds are broken and/or made. If one excludes

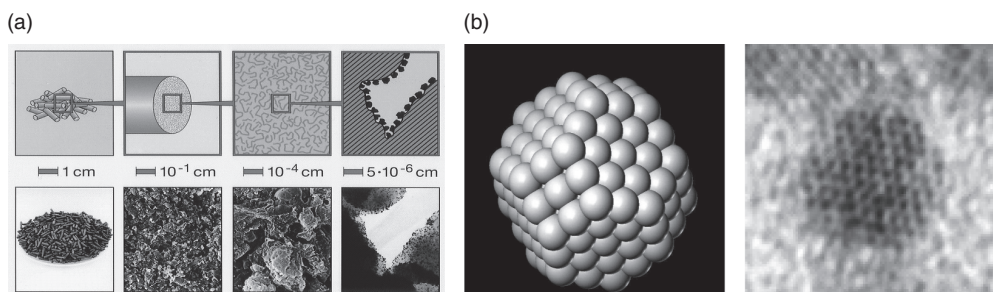


Figure 1.1 (a) Real heterogeneity of a catalyst from the centimetric level to the nanoscale (atomic) level; (b) a cubo-octahedral model of a metal particle and an electron microscope view of a platinum particle covered with n-octylsilyl fragments). (Unpublished results with permission of the Fritz Haber Institute, Berlin.)

electron transfer reactions or ones that are eventually free radical, there is an interaction with bond formation with surface atoms, the so-called active sites, to generate a “surface organometallic intermediate” and/or “transition state” that could be seen as a hybrid “molecule/surface” species. Such a concept of a hybrid species was investigated and studied with the concepts and tools of both molecular and surface science, but finally it was clear that this hybrid species should be considered as a “surface organometallic fragment” [5] (Scheme 1.1). Behind this simple concept a scientific approach slowly emerged that pushed toward the utilization of the tools of organometallic or coordination molecular chemistry, in particular molecular models of surface species, associated with those existing in surface science to characterize these hybrid entities.

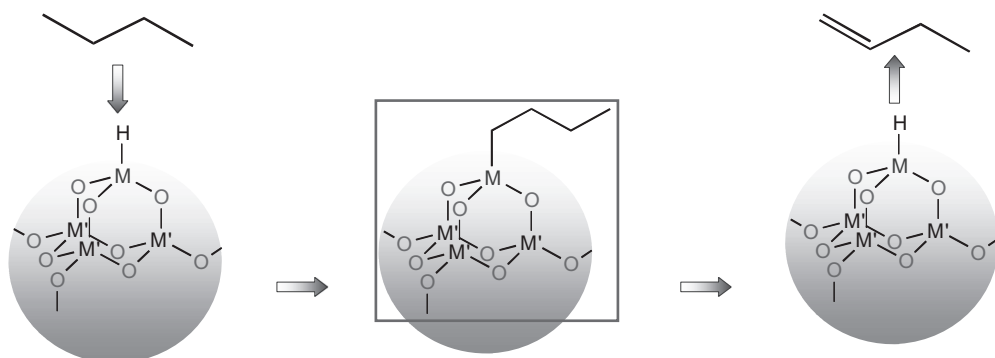
But what were the various evolutions after such “chemical intuitions” at the origin of the new field of chemical science called “surface organometallic chemistry”?

They came in the late 1970s/early 1980s from different intuitions and experimental overlap:

- the extension of concepts typical of coordination and organometallic chemistry to surface states;
- the use of “probes molecules on metallic surfaces;”
- the chemical and structural similarities between “molecular clusters and small metallic particles;”
- the close analogy between “supported molecular clusters and small supported metallic catalytic particles.”

These led progressively to the development of the new experimental field of “organometallic chemistry at surfaces” and its different applications, in particular:

- surface organometallic and coordination chemistry at surfaces,
- surface mediated organometallic synthesis,
- new supported heterogeneous/homogeneous metallic catalysts.



Scheme 1.1 When a molecule interacts with an active metal atom of the surface of a catalyst to give products there is an intermediate formation of a “surface organometallic fragment.”

1.2

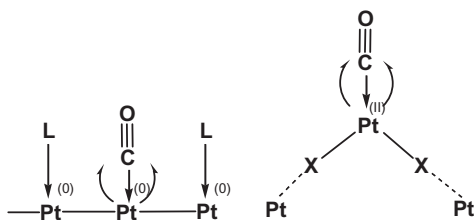
Use of Probe Molecules on Metallic Surfaces as Evidence of Coordination and Organometallic Chemistry at Metal Surfaces

The use of CO as a "chemical probe" of the nature of the molecular interactions with the surface sites of metallic catalysts [6] was the first clear experimental example of the transposition to surface science and in particular to chemisorption of the concepts of coordination chemistry [1, 2, 5]. In fact the "Chatt–Duncanson" model [7] of coordination of CO, olefins, etc. to transition metals appeared to be valid also for the interactions of such probes on metal surfaces. It could not fit with the physical approach to the surface states based on solid state "band gap theory" [8], which was popular at the end of 1950, but at least it was a simple model for the evidence of a localized process of chemical adsorption of molecules such as olefins, CO, H, olefins, dienes, aromatics, and so on to single metal atoms on the surfaces of metals or metal oxides [5].

One of the first clear pieces of experimental support to the molecular approach to chemisorption was the finding that a ligand L, in the Green formalism [9], behaves in the same way on a coordination metal complex and on a metallic surface since it could influence the π -back donation on an adjacent carbonyl without breaking metal–metal bonds, while a ligand X such as an halogen would break the metal–metal bonds, giving rise on the metallic surface to a kind of isolated "de-metallized" metal complex containing CO [e.g., $\text{Pt}^{\text{II}}(\text{CO})\text{X}_2$] (Scheme 1.2) [10].

In conclusion the experimental support given by the use of molecular probes to the molecular approach to chemisorption considered as a localized interaction of chemisorbed molecules with metal atoms on the surface of metals or metal oxides [2, 5] was at the origin of the development of a more precise experimental identification of surface species involved in some aspects of heterogeneous catalysis.

This approach allowed more precise identification of the nature of the bonds between many chemisorbed molecules and different kind of surface metallic sites (cations in zeolites or on the surface of metal oxides, metal atoms on the surface



Scheme 1.2 Evidence of the action of ligands L and X on a metal surface covered by a molecular probe such as CO, which may or may not lead to oxidation of metal atoms of the surface, close to the metal site of CO chemisorption, depending on the adsorbed ligands.

of particles even as metal alloys, metal complexes supported on various surfaces, etc.), and in particular it was a way to easily explain the electronic origin of the increased reactivity of a molecule when chemisorbed by coordinative interaction with metal atoms at a surface [2, 5].

1.3

Chemical and Structural Analogy between Molecular Clusters and Small Metallic Particles

This molecular picture of the surface states of chemisorbed molecules was consolidated by the analogy of the bonding of such molecules on molecular metal cluster and on small metal particles [11–13].

The family of large molecular metallic clusters developed since the early 1970s by Chini's group [14], by Lewis and Johnson [15] and so many others later on that we can not cite here, and the family of very large molecular metallic clusters first developed in the 1990s mainly by Schmidt [16] and Moiseev [17], were extremely good molecular models of metallic particles covered by chemisorbed molecules. The possible analogy between the increased reactivity and fluxional mobility of molecules "chemisorbed" on an ensemble of several metallic atoms, like a metal particle and what could be identified extremely well at molecular level for ligands in the coordination sphere of a molecular cluster, was initially nicely underlined by Ugo [5] and Muetterties [18].

The analogy between molecular clusters and metal particles was not an additional evidence of the similarity of bonding between metal–ligand and surface metal–adsorbed molecules. The metallic core of a molecular cluster frame could be also considered as a structural model of very small metallic particles [11, 14]. For instance, fascinating "giant molecular clusters" were made, for example, by Chini's group (Figure 1.2): as in the case of 38 Pt atoms covered by 44 carbonyls in a dianionic molecular cluster [19]. Such a cluster approaches the size of small platinum particles found on a platinum metallic catalyst supported on alumina (usually these particles have a diameter of <1 nm). In addition, for particles of alloys of two or more metals some molecular bimetallic clusters could be suitable models. For instance, in the case of the large cluster $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}\text{H}_{6-n}]^{n-}$ (still made by Chini's group) [20] formal evidence was produced for an isolated island of a metal (Pt) integrated in the full cluster structure made by another metal (Ni).

Such a strong analogy between the electronic behavior of the metallic core of large molecular clusters and small metal particles was already suspected by Basset, Primet *et al.*, who had discovered already in 1975 [21] that the extent of "back donation" from the core of a metal particle to $[\text{NO}]^+$ (a ligand isoelectronic to CO) adsorbed Pt/alumina catalyst was particle size dependent as if the small particles were behaving as molecular clusters, since the extent of "back donation" on coordinated CO was shown clearly to be dependent on the size of the cluster in the series of molecular $[\text{Pt}_3(\text{CO})_{12}]_n^{2-}$ ($n = 1-5$, etc.) clusters made by Chini's group [22].

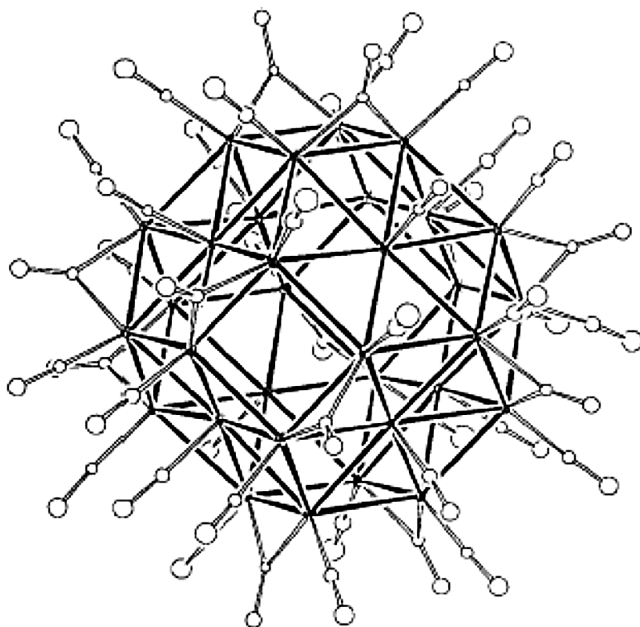


Figure 1.2 Structure of a Pt_{38} anionic molecular cluster [19]. (With the permission of G. Longoni.)

1.4

Analogy between Supported Molecular Clusters and Small Supported Catalytic Particles

In the mid-1970s it became tempting, on the basis of the above evidence for strong analogies between molecular cluster and small metallic particles, to try to "support molecular clusters" on inorganic surfaces with the objective of trying to keep on the metallic core of the molecular clusters intact as structure and size on the surface and then to investigate their chemical and catalytic behavior. There were two possible strategies:

1. Keep the molecular character of the cluster intact with most of its ligands left by grafting first specific ligands on a silica or other surfaces and then link the cluster to the surface by ligand exchange with the grafted ligands. This approach gave rise to the field of "supported molecular clusters" that has been developed by several groups, for instance by Grubbs and Pittman [23]. However, it was soon clear that such systems display quite complex, and not constant, behavior since in some instances the molecular clusters could leach from the support or simply decompose to give metal particles. Nonetheless, progressively, very small clusters of low nuclearity could be stabilized by this approach and lead to interesting surface chemistry [24, 25].

2. Decompose in a mild way the cluster after its adsorption on the surface of a metal oxide, to remove the ligands, and try to keep the size and possibly the structure of its metallic core as if the support by itself could “stabilize” a small metal particle with the same nuclearity of the metallic core of the original molecular cluster.

The second strategy, developed initially in the early 1980s mainly by Basset and Ugo [26, 27], subsequently proved to be at the origin of the development of what was defined as “surface organometallic chemistry” and, later, in other related topics such as “surface mediated organometallic synthesis,” in particular of metal cluster carbonyls and to the preparation of “new highly dispersed or even mono-centric supported metallic catalyst with unusual catalytic properties.” Regarding the preparation of new highly dispersed supported metallic catalysts with unusual catalytic properties, two fascinating observations made in about the same period suggested that very small metal particles could be, in some cases, obtained by decomposition of molecular metal clusters supported on metal oxides surfaces [28], giving rise to interesting new catalytic results:

1. The first, made by Ichikawa *et al.* [29], was the evidence that rhodium or iridium cluster carbonyls, when adsorbed on zinc oxide, titania, lanthanum oxides, zirconia or magnesia, could produce quite selectively ethanol by the Fischer–Tropsch synthesis. This was a timely discovery (metallic catalytic particles produced by traditional methods could not reproduce such selectivity) since it came at a period of geopolitical tension after the “Kippur war” in 1973, which caused the price of crude oil to increase enormously. Therefore, that period was characterized by intense research into selective Fischer–Tropsch catalysis.
2. The second observation was made by Basset, Ugo *et al.* [30], by thermally decomposing molecular metal cluster carbonyls adsorbed on the surface of alumina and various other oxides. The light character of Fischer–Tropsch type products, obtained by a simple heat treatment of several metal carbonyl clusters deposited on hydroxylated alumina, was of great interest. The hydrogen arose mainly from the hydroxylated support and the carbonyl ligands were responsible for the carbon atoms of the Fischer–Tropsch products. An in-depth analysis of such systems led to the discovery of the very complex chemical behavior of the molecular metal carbonyl cluster that was occurring by adsorption and thermal treatment of a molecular carbonyl cluster [e.g., $\text{Rh}_6(\text{CO})_{16}$] on a dehydroxylated or hydroxylated alumina surface (Figure 1.3) [26, 31].

The carbonyl cluster $\text{Rh}_6(\text{CO})_{16}$ was initially stable as such on the completely dehydroxylated alumina surface. But as soon as hydroxyl groups were generated (e.g., by adding traces of water) it decomposed to give various surface transformations. First, the cluster structure was disrupted, with breakage of the core cluster frame, into $(\text{Al-O-})(\text{Al-OH})\text{Rh}^{\text{(I)}}(\text{CO})_2$, $\text{Rh}^{\text{(I)}}$ monoatomic species sigma and π -bonded to the oxygens atoms of the alumina surface, with formation of molecular

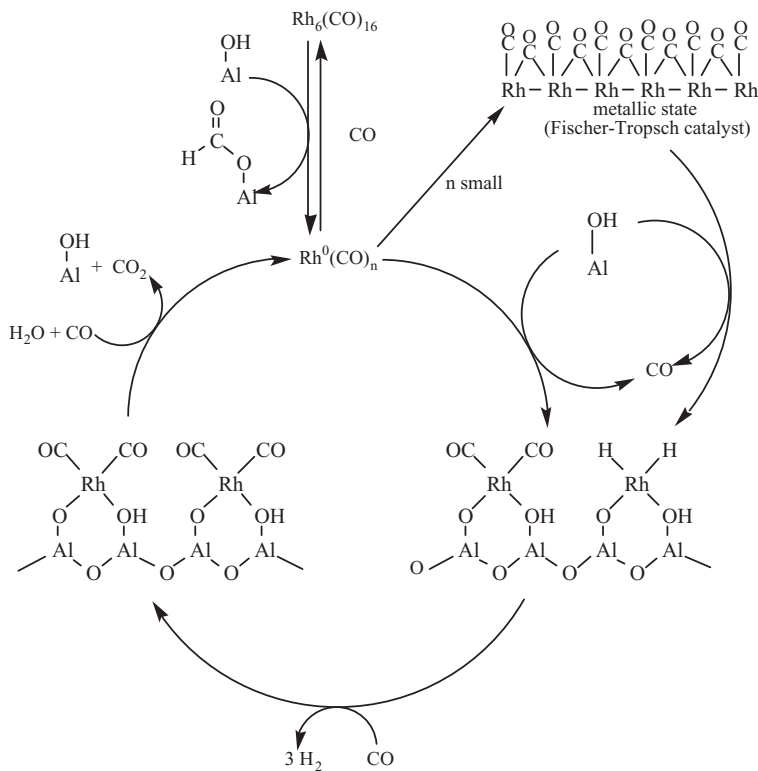


Figure 1.3 Behavior of $\text{Rh}_6(\text{CO})_{16}$ on a hydroxylated alumina surface.

hydrogen. The pseudo-molecular nature of such $\text{Rh}^{(I)}$ surface species was suggested by its typical infrared spectrum and later confirmed by other more sophisticated spectroscopic and physicochemical techniques. The molecular metallic cluster could eventually reform, depending or not on the presence of water and of an excess of CO . Otherwise it could transform into small metallic particles of rhodium of higher nuclearity covered with CO . These small particles of rhodium were in fact responsible of the Fischer–Tropsch synthesis. The simultaneous water-gas shift reaction was the result of redox processes involving $\text{Rh}^{(0)}$, $\text{Rh}^{(I)}$ and $\text{Rh}^{(III)}$. Interestingly the small particles of metallic rhodium were also disrupted into the above $\text{Rh}^{(I)}$ dicarbonyl species by action of surface hydroxyl groups (Figure 1.3). Most important, these results showed that a rich surface chemistry could occur when adsorbing molecular metal carbonyl cluster on the surface of an oxide, but also they showed that it was quite impossible to transform molecular carbonyl clusters into small metallic particles having the same nuclearity. Such a process of aggregation of the original metal core of the molecular cluster into larger metallic cores was challenging since it was observed that one could also preserve the chemical composition of bimetallic particles, starting from bimetallic clusters but

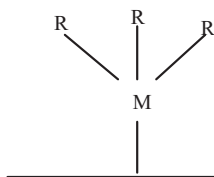
at the same time, unambiguously, the bimetallic particles were much larger than the metallic core of the starting bimetallic molecular cluster.

Such aggregation of metallic particles occurs not only during the step of decomposition of the original molecular metal cluster but also during a catalytic reaction. This was first evidenced by Basset *et al.* for the Fischer–Tropsch synthesis carried out under mild conditions, catalyzed by metal particles that originated from the anionic cluster $[\text{HFe}_3(\text{CO})_{11}]^-$ supported on alumina via a kind of ion-pair interaction with the surface [32]. The selective formation of light hydrocarbons at the beginning was due to the very small size of the iron metallic particles generated by decomposition of the original cluster. The shift of the reaction products to hydrocarbons of higher molecular weight to obtain the distribution of hydrocarbons typical of a classical Fischer–Tropsch catalysts was related to the increase with time of the size of the metallic particles.

1.5 Foundation of Surface Organometallic Chemistry

At the beginning of the 1970s the representation of surface molecular intermediates was extremely simplified and really a “cartoon representation,” mainly owing to the relatively low level of direct experimental evidence of their structure and reactivity and consequently of the nature of the bonds between the molecular intermediate linked to the surface and the surface metallic atoms. Although IR spectroscopy gave, early on, some useful direct information [33], for instance on the possible molecular species (mainly metal carbonyls) present at the surface of some highly divided metal oxides, surface scientists were reluctant to draw chemical bonds between molecular surface species in particular organometallic fragments and some well-known functionalities present at the surface of the oxides ($\equiv\text{Si}-\text{OH}$, $\equiv\text{Si}-\text{O}-\text{Si}\equiv$, $\text{Al}-\text{OH}$, etc.). In general the surface was represented by a simple straight line (Scheme 1.3).

Progressively, in the 1970s–early 1980s, structural evidence of a coordinative bonding between the surface atoms and the grafting atoms of organometallic surface species as well as the coordination number of the atoms of a metal surface or of metal atoms encapsulated into the surface of a metal oxide became known, lead to a direct understanding of the nature of the coordinative bonding to the metal surface and of the real structure of some molecular surface species. This is mostly owing to a much experimental characterization of surface organometallic



Scheme 1.3 Initial description of a surface organometallic fragment.

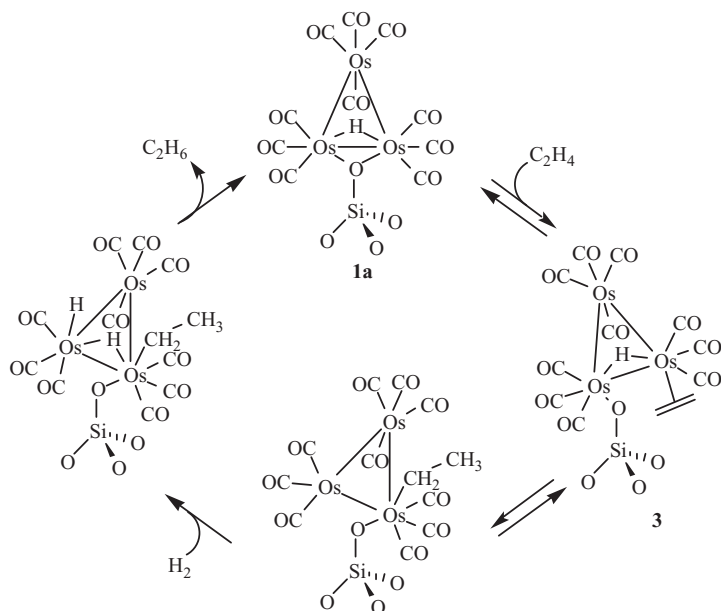
complexes using chemical and physical tools (in particular, surface microanalysis, *in situ* IR, *in situ* EXAFS and *in situ* solid state NMR) [32], an increased understanding of the metal–ligand interaction via coordinative bonds [5] and to the rapid development of new tools in surface science (e.g., EXAFS and solid-state NMR) [34].

In parallel the proposal that the surface of a metal oxide behaves as a ligand of a surface organometallic molecular species arose from different observations, made particularly by Basset and Ugo in the late 1970s–early 1980s:

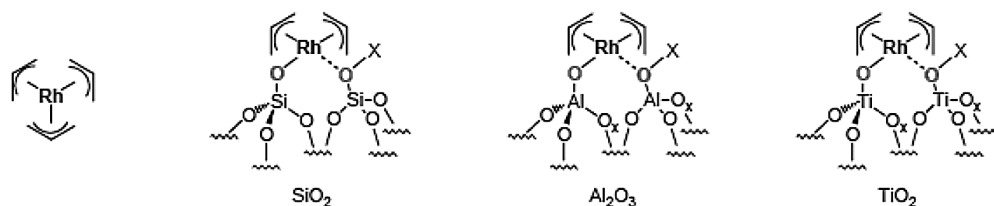
1. During the chemisorptions of $\text{Ru}_3(\text{CO})_{12}$ or $\text{Os}_3(\text{CO})_{12}$ on silica, the first step with the surface silanols was to produce a covalent bonding with the silica surface by oxidative addition of the silanol group to the metal–metal bond of the clusters. The nature of surface molecular species $[\equiv\text{Si-O})(\text{M}_3(\mu\text{-H})(\text{CO})_{10}]$ covalently linked to the silica surface (M = Ru, Os) was clearly defined and structurally characterized by a series of physical and chemical techniques, including mass balance taking into account the evolution of two molecules of CO and one molecule of hydrogen [27, 33, 35].

These were, without doubt, the first surface organometallic species fully characterized both structurally and in terms of reactivity. For instance the Os cluster anchored to the surface of silica or alumina could be disaggregated thermally to produce carbonyl $\text{Os}^{(II)}$ species incapsulated into the surface. As in the case of $\text{Rh}^{(I)}$ carbonyl species incapsulated into the silica surface [26] it was shown that these $\text{Os}^{(II)}$ surface species recombine under particular conditions ($\text{H}_2\text{O} + \text{CO} + \text{heat}$) to regenerate the original cluster $\text{Os}_3(\text{CO})_{12}$. Final decomposition of these $\text{Os}^{(II)}$ surface species to metallic osmium particles occurs only under conditions more difficult than those necessary to generate rhodium metallic particles [33]. Starting from these evidences, the chemistry of these molecular surface organometallic species was clearly parallel to their well-known organometallic chemistry in solution [36].

2. The silica supported cluster $[(\mu\text{-O-Si}\equiv)\text{Os}_3(\mu\text{-H})(\text{CO})_{10}]$ and its molecular analog $(\mu\text{-O-C}_6\text{H}_5)\text{Os}_3(\mu\text{-H})(\text{CO})_{10}$ are catalysts in the heterogeneous and homogeneous phase, respectively, for ethylene hydrogenation [37]. The cluster frame was kept intact thanks to the ligand character of the surface oxygen, which could become $\mu\text{-}_2$ or $\mu\text{-}_1$ in the various elementary steps of the catalytic cycle (Scheme 1.4). This was the first example of a true catalytic cycle with a molecular cluster linked at the surface of an oxide. It was also a clear example that stabilization of a molecular cluster frame by surface oxygen's acting as ligands can lead to a surface chemistry and a chemical behavior of the molecular surface species well described as traditional organometallic chemistry. On the above evidence, Basset and Ugo in the early 1980s proposed for this new field of surface science the definition "surface organometallic chemistry," where the surface is acting as a ligand of traditional organometallic species [28, 36, 38]. After a few years



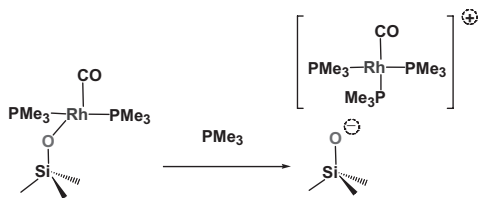
Scheme 1.4 Catalysis with a silica supported grafted osmium cluster (while keeping the molecular cluster intact).



Scheme 1.5 Silica, alumina and titania surface oxygens behaving as ligands in the “M.L.H. Green formalism” [9] after reaction of $^3\eta$ -tris(allyl)rhodium with a partially dehydroxylated surface [39].

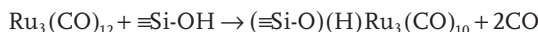
this concept was accepted by surface scientists since it was clearly shown that on the surface of metal oxides surface oxygen could coordinate organometallic fragments quite well. For instance, several types of other organometallic (for instance, $^3\eta$ -allyl derivatives [39] as reported in Scheme 1.5) were fully characterized, showing that the surface of an oxide could also behave as a chelating ligand. Interestingly, the surface can even behave as an anionic ligand, allowing for instance the formation of a cationic surface organometallic species of Rh (Scheme 1.6) [40].

3. Simultaneously, it was shown that the OH groups of basic surfaces such as magnesia or alumina could behave as nucleophiles toward CO coordinated to



Scheme 1.6 Surface of silica behaving as an anionic ligand toward $[\text{Rh}(\text{CO})(\text{PMe}_3)_3]^+$ [40].

a molecular cluster frame. For instance, by adsorption on alumina the cluster $\text{Fe}_3(\text{CO})_{12}$ was transformed into $[\text{HFe}_3(\text{CO})_{11}][\text{Al}]^+$ [41], an anionic cluster originated by an ionic interaction with a Lewis acid site of the alumina, while $\text{Ru}_3(\text{CO})_{12}$ [as with $\text{Os}_3(\text{CO})_{12}$] was subject to oxidative addition in the case of the more acidic OH silanol groups of the surface of silica [35].



However, when $\text{Ru}_3(\text{CO})_{12}$ was adsorbed on the surface of a basic metal oxide such as the decarbonated surface of magnesia, a similar nucleophilic attack was demonstrated to occur with formation of the anionic $[\text{HRu}_3(\text{CO})_{11}]^-$ species on the magnesia surface [42].

This significant, and in some ways unexpected, difference in behavior between the surface OH groups of silica and those of alumina and in particular of magnesia toward the same family of metal cluster carbonyls showed unambiguously the broader aspect of this new area of surface chemistry where the surface of the metal oxide was behaving not only as a ligand but also as an electron donor, whose properties were related to acidic or basic nature of the surface oxygen or hydroxyl groups, or even as an anionic site.

Owing to such richness of the surface organometallic chemistry, and to the basic concept of considering the surface of a metal oxide as a donor or acceptor coordination sphere, this new discipline produced the study of a huge variety of surface organometallic (and coordination) species, taking into account many surfaces. Nevertheless, these surfaces were mostly limited to metal oxides such as silica, alumina, titania, magnesia, or even zeolitic materials, etc. Surface organometallic species investigated were those of main group elements, transition metals, lanthanides and actinides [38, 43]. The concept of "surface organometallic chemistry" was confirmed in the 1980–1990s by the definition of a series of structural characteristics of the surface organometallic species by various physicochemical, spectroscopic and chemical evidences [44].

Structural evidences of the nature of surface organometallic species were confirmed in a few cases by the synthesis and structural characterization of molecular models (in particular using silanolate ligands) of surface organometallic

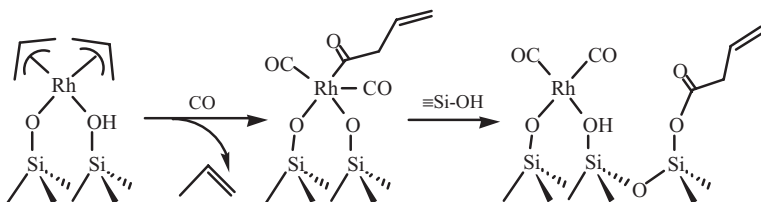
species [45]. By this latter approach their chemical behavior was also investigated.

The field of surface organometallic chemistry was largely unexplored before the basic work initially done by Basset and Ugo at the end of the 1970s, even though pioneering work by Ballard and Yermakov had already given some beautiful examples in the field of surface linked organometallic species [46] mainly with the objective of obtaining new heterogeneous catalyst for olefins polymerization, without taking into consideration in detail the organometallic chemistry occurring on the surface. Today “surface organometallic chemistry” is a well defined and accepted field of surface science and huge varieties of new surface organometallic species have been characterized since the early 1980s.

1.6

From Organometallic Surface Chemistry to the Elementary Steps Occurring on Surfaces and Stabilization by the Surface of Rather Unstable Molecular Species

One of the questions raised by the identification and characterization of surface organometallic species was: Can the elementary molecular steps involved in catalytic cycles typical of homogeneous catalysis be considered valid also when organometallic fragments linked to the surface of a metal oxide are involved in heterogeneous catalytic process? Initially, these elementary steps were found to be the same as those in homogeneous molecular chemistry (see for instance Scheme 1.4) but, progressively, owing to a profound understanding of various aspects of organometallic surface chemistry and in particular of the reactivity of surface organometallic species, it appeared that the surface was acting as a “non innocent” system of ligands. One of the first answers arose in the case of the reaction of CO with the bis- $^3\eta$ -allyl rhodium fragment attached to silica via a Si–O–Rh bond (Scheme 1.7) [39]. Carbonyl groups could insert into the Rh($^3\eta$ -allyl) bond to form an allylic acyl ligand that could then reductively eliminate on the surface oxygens. It was shown thus that such reductive elimination could take place only with the help of the other silanol groups located closely on the surface. Such behavior was new with respect to the known organometallic molecular chemistry in solution. It

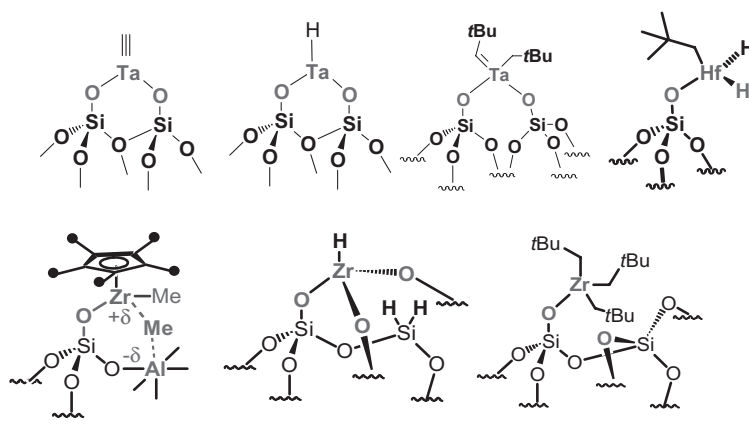


Scheme 1.7 Elementary steps occurring in the reaction of CO on a silica surface with supported $^3\eta$ -allyl rhodium.

thus appears that in surface organometallic chemistry we may have cooperative effects related to the surface topology that can not be present in molecular chemistry performed in solution.

Although the surface of the various inorganic oxides involved in surface organometallic chemistry show functional surface groups like OH^- or O^{2-} with chemical and donor properties quite close to those of some coordination donor spheres encountered in organometallic molecular chemistry, a special stabilization of usually rather unstable organometallic species may occur. In fact the rigidity of the coordination sphere produced by the surface, together with a low surface mobility of organometallic surface species (when compared to solution), allows the stabilization of organometallic species that could not be easily detected in traditional molecular organometallic chemistry (Scheme 1.8). Typical examples are the silica-supported $(\equiv\text{Si}-\text{O})_2\text{Ta}^{\text{III}}(\text{H})$, or $(\equiv\text{Si}-\text{O})_3\text{Zr}^{\text{IV}}(\text{H})$ species, formally eight electron species that are extremely electron deficient [43]. Progressively, it appeared in the late 1990s that some of these surface organometallic species (for instance surface carbynes) could even be stable at extremely high temperatures, suggesting that at the relatively high temperatures usually required by "classical" heterogeneous catalysis" reaction intermediates may still maintain a "surface organometallic character."

In conclusion it has become clear that the surface of an inorganic oxide does not behave only as a classical ligand and a classical homogeneous reaction medium but in particular cases it can also behave as a highly specific and often complex system of new kinds of ligands or as a reaction medium behaving quite differently from what is known in solution chemistry. It is now accepted that surface organometallic chemistry is not only a simple extension of the well-known organometallic chemistry in solution but it also has some specific and new characteristics.



Scheme 1.8 Selected examples of thermally stable surface organometallic fragments [43].

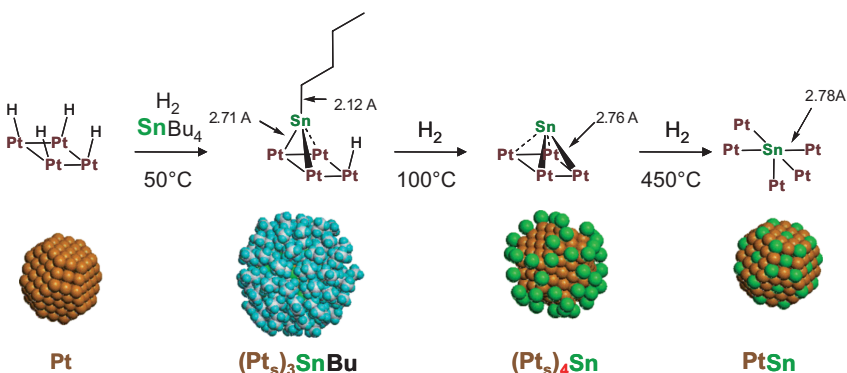
1.7

From Surface Organometallic Chemistry on Oxides to Surface Organometallic Chemistry on Metals

Basset and Candy discovered (in almost the same period) that organometallic compounds react with metallic surfaces, that is the surface of supported or unsupported metallic particles, much faster than with oxides surfaces. This interesting observation resulted in the development of surface organometallic chemistry on metals [47]. Organometallics of several metals (TM, MGE) react selectively with the surface of metals through the formation of several types of surface structures: “grafted organometallic fragments,” “adatoms” or bimetallic alloys.

Scheme 1.9 gives a typical example, describing all the steps of the reaction of a tetra-alkyl tin with silica-supported platinum particles. This scheme is also valid for group VIII metal particles. As in surface organometallic chemistry on oxides, the surface organometallic fragments are stable over a wide range of temperatures before being decomposed into adatoms and finally into surface or bulk alloys.

This led *inter alia* to a “clean” preparation of bimetallic catalysts. The improvement of bimetallic catalyst in terms of catalytic activity, selectivity, stability, life time and eventually regenerability has often been attributed in the past to modification of the active surface metal atom by the second additive. Using surface organometallic chemistry on metals has afforded drastic improvements, allowing rationalization of the effect of the second metal in terms of mechanistic understanding. In particular, the concept of “site isolation”, that is the full surrounding of a catalytically active metal atom by a catalytically inactive metal, allows very selective catalytic reactions. Surface characterization at an atomic scale level allows an easy interpretation of the reasons for the enhanced selectivity [47, 48].



Scheme 1.9 Steps in the reaction of (tetra-butyl)tin with silica supported platinum particles.

1.8

From Surface Organometallic Chemistry to Surface-Mediated Organometallic Synthesis

The specific characteristics of a surface such as silica, if considered as a new reaction medium, were confirmed by the unusual selectivity and easy reactivity shown in so-called surface-mediated organometallic synthesis.

The evidence, produced already in the early 1980s, that monometallic surface species like Os^(II) or Rh^(I) carbonyl fragments, incapsulated into the surface of silica or alumina, may have the necessary mobility to react with each other, since they return quite easily under a CO atmosphere to the original clusters Os₃(CO)₁₂ and Rh₆(CO)₁₆ respectively [26, 27, 31], was the origin of so-called surface mediated organometallic synthesis.

In fact, mainly by work carried out by Roberto and Ugo [49] and by Gates and his group [50], it was shown, in the early 1990s, that working under mild conditions of pressure (e.g., 1 atm of CO) and in a well-defined range of temperatures (room temperature up to 200 °C or even higher) a large series of metal carbonyl compounds, and in particular of metal carbonyl clusters of increasing nuclearity, could be easily obtained starting from various metallic salts supported on metal oxides, in particular silica, with yields and selectivity often better than those reported for the related synthesis in solution, which in any case often require to work under high pressure.

In this unusual and new synthetic approach the surface of the inorganic oxide does not behave as a new medium for dispersion of reagents but as a particular kind of ligand that by binding, in various ways, surface organometallic molecular fragments or species controls both the kinetic and the selectivity of the reactions taking place on the surface.

Such easy reactivity and selectivity working under rather mild conditions is probably favored by the lack of relevant solvation effects and by a controlled mobility and diffusion corresponding to few collateral reactions and consequently high selectivity.

The surface of metal oxides is characterized by specific surface sites such as acidic Brønsted centers (silica, alumina, etc.), Lewis acidic centers (alumina and magnesia highly dehydroxylated), strong basic centers (decarbonated magnesia, alumina) or very weak basic centers (silica). Therefore, according to the nature of the various surfaces, relevant acidic or basic activities can be introduced that can tune the surface syntheses and therefore may control the final reaction products. Neutral products, for instance high nuclearity metal carbonyl clusters of noble metals, are obtained working on the rather neutral surface of silica, but anionic high nuclearity metal carbonyl clusters are obtained on the very basic surface of decarbonated magnesia [49, 50]. Roberto and Ugo *et al.* [49] have also discovered that by adding a base such as K₂CO₃ or Na₂CO₃ to the silica surface it is possible to induce a high basicity of the surface, which behaves then like the surface of completely decarbonated and dehydroxylated magnesia. By working on a silica

surfaces of various basicity by addition of basic species under 1 atm of CO and temperatures from room temperature up to over 200 °C, a large series of neutral and anionic clusters of increasing nuclearity of Pt, Ir, Rh, Ru and Os have been synthesized [49, 51].

Notably, the role of the surface of the metal oxide is not merely that of another reaction medium but also that of allowing a specific reactivity, including yields and in particular selectivity.

The essential role of the silica surface was confirmed recently [51] by the report that reaction under 1 atm of CO of a mixture of Na_2PtCl_6 and CH_3COONa gives only a progressive reduction to metallic platinum upon increasing temperature, while reacting the same mixture of Na_2PtCl_6 and CH_3COONa supported on silica produces the cluster $\text{Na}_2[\text{Pt}_{15}(\text{CO})_{30}]$ in 75% yield at 25 °C under 1 atm of CO.

In addition, aided by profound knowledge of the nature and reactivity of some surface organometallic species, it was possible to identify the various steps and the nature of intermediates involved in the nucleation processes occurring on the surface in the selective growth of very large clusters such as for instance in the case of $[\text{Os}_5\text{C}(\text{CO})_{14}]^{2-}$ and $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ [52]. As this subject is treated in detail elsewhere in this book it is not covered here.

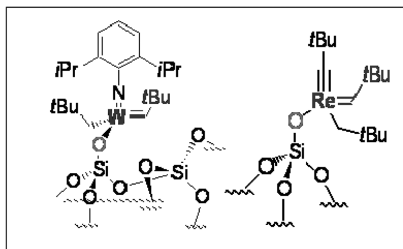
1.9

Single Metal Site Heterogeneous Catalysts and the Design of New Catalysts

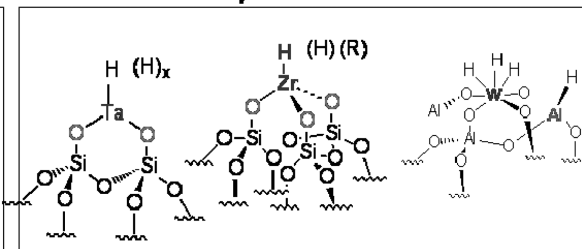
The development in the last 30 years of a profound knowledge of surface organometallic chemistry has been a springboard for the preparation and full characterization of single metallic surface sites, usually incapsulated into the surface of an inorganic oxide, opening thereby a new approach to the design of heterogeneous catalysts just as chemists involved in homogeneous catalysis are doing. This means conceiving a possible step by step molecular mechanism and designing the coordination sphere that could allow the desired catalytic reaction. For example, olefin metathesis was expected to require the stabilization of surface metallo-carbenes, polymerization of olefins of surface metal alkyls, alkanes activation of highly reactive surface metal hydrides, oxidation of surface oxo or peroxy or alkoxo metallic species, etc. (Figure 1.4).

This is a major achievement, mainly due to Basset and his group, in surface organometallic chemistry because it has been thus possible to prepare “single site” catalysts for various known or new catalytic reactions [53] such as metathesis of olefins [54], polymerization of olefins [55], alkane metathesis [56], coupling of methane to ethane and hydrogen [57], cleavage of alkanes by methane [58], hydrogenolysis of polyolefins [59] and alkanes [60], direct transformation of ethylene into propylene [61], etc. These topics are considered in detail in subsequent chapters.

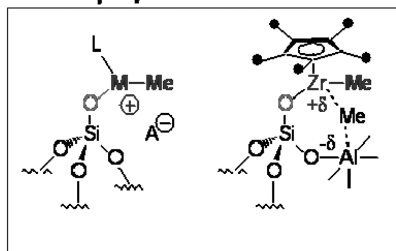
Olefin metathesis



Alkane chemistry



Olefin polymerisation



Oxidation

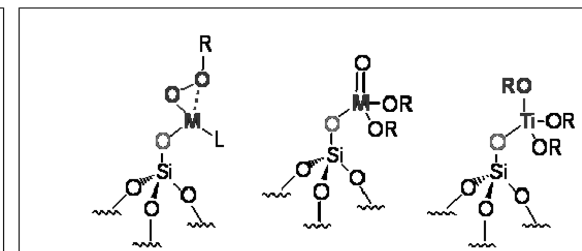


Figure 1.4 Expected intermediates in various reactions.

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