Catalysis Science & Technology

Accepted Manuscript

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Perspective

Site isolated complexes of late transition metals grafted on silica: Challenges and chances for synthesis and catalysis

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th April 2014,
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

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Transition metal (TM) ions can be covalently attached to a silica surface by means of a M–OSi bond (grafting) to give site-isolated complexes. Acting as a ligand in such grafted species, the surface influences the electronic nature and the coordination number of the TM ion, in contrast to anchored complexes, in which a linker separates the metal ion and the surface and hence reduces their interaction. This perspective reviews general grafting strategies on an oxide surface and focuses on the peculiarity of silica-grafted catalysts of late TMs, which have a higher tendency to undergo aggregation into metal nanoparticles under reducing conditions than early TMs. Soft ligands (hydride, phosphines) and/or π-acceptors (CO) promote aggregation. In particular, silica-grafted hydride complexes of late TM ions are not stable and tend to undergo reductive elimination of silanol. The coordination chemistry background of this behaviour is discussed, and possible strategies to avoid aggregation are suggested.

Scope and aim

Most of the known and industrially applied processes make use of systems based on heterogeneous catalysts, namely supported nanoparticles. The active sites of these catalysts are complex entities from an atomic point of view, and their structure is generally little understood. As it is generally believed that the catalytic activity and selectivity can be optimised by tuning the structure of the active site, many efforts have been directed to prepare heterogeneous catalysts whose active sites have a well-defined structure and thus resemble their homogeneous counterparts.[1]

One approach starts from a supported heterogeneous catalyst and aims at its dispersion down to the atomic level on a surface with tailored features to achieve a well-defined reaction site. A single metal atom on a oxide surface represents the “simplest supported nanoparticle” and has been used as a model to investigate heterogeneous catalysts at the molecular level.

An alternative approach to site-isolated catalysts is the immobilization of a homogeneous complex on a surface. This strategy can be implemented in two alternative ways with very different implications and requirements depending on the junction between the surface and the ligand. If the metal complex interacts with the support via a linkage that involves one ancillary ligand, the surface atoms involved in the bond will interact poorly or not at all with the metal atom. Instead, if the metal is bound to a surface atom, the surface acts as a ligand and greatly affects the reactivity of the metal.

In this perspective, we use the word "grafting" to refer to the immobilization of a transition metal (TM) complex by means of a direct bond between the metal and a surface atom. Complexes of early transition metals have been extensively used for grafting onto oxide supports. Hard metal ions such as zirconium(IV) and titanium(IV) are highly oxophilic and give thus stable surface complexes by the interaction with the oxide ions of the surface.[2]

Late transition metals are less oxophilic and hence have a lower tendency to form stable surface organometallic species. Therefore, ions of late TMs have a larger tendency to aggregate than their congeners on the left part of the periodic table, which give more favourable interactions with the oxide support. Accordingly, oxide-supported nanoparticles of late transition metals are common and have been extensively studied in catalysis,[3] and will be not discussed here.

As we concentrate herein on site-isolated complexes of late transition metals grafted on silica, the accent will be put onto the factors that explain the tendency to aggregation and recapitulate the strategies to prevent it. The topic is introduced by a general overview of supported catalysts that is directed to the layman and encompasses nanoparticles, atomically disperse metals, and immobilised molecular species. Among the latter, grafted molecular species, on which the perspective is focused, are at the interface between coordination chemistry and surface science and are pivotal in the challenge of controlling the environment of a single metal atom. Therefore, our approach will be structural as in coordination chemistry rather than functional, that is, based on the catalytic application.

Supports

The most promising materials used for the immobilization of molecular catalysts are high surface area inorganic oxides,[4] of which the most used are silica,[5] alumina,[6] and zeolites.[7] Other metal oxides such as TiO_2, MgO, ZrO_2, CeO_2 have been used as supports too, but have been studied to a lesser extent.[8] Morphology (particle size, surface area, pore size), stability (thermal resistance, agglomeration), physico-chemical properties (concentration and type of hydroxo groups, hydrophobicity/-philicity) are the criteria for the classification and choice of a support.

A particularly important feature of inorganic oxides is their porosity, which varies from microporous materials, such as zeolites and aluminophosphates, to mesoporous silica.[9] The pore size influences the shape selectivity and the mass transfer properties of the catalyst.

Naturally occurring functionalities that act as donor atoms are hydroxyl groups, which react via exchange of the acidic proton with other molecular species (mostly metals of an organometallic precursor). The properties of the donor atoms can be tuned by varying the chemical and physical treatment of the oxide.[10] After a general introduction, the discussion of grafted complexes will be restricted to silica, the most used support.

From bulk metal to single atoms

In 1985, Boudart[11] classified supported metals into three categories according to the particle size (below 10 Å, between 10 and 50 Å, and above 50 Å). The structural effects are particularly marked in the range from 10 to 50 Å because parameters such as the number of exposed atoms, surface sites, coordination number, and nearest neighbours change more drastically than above 50 Å, where the crystallographic habit is fully developed and regular, and the surface structure and properties resemble those of bulk metal.

Recently, the third category concerning particles smaller than 10 Å (clusters) has developed enormously.[12] Differently from nanoparticles, which are an aggregation of up to 10^7 atoms and have a diameter up of to 10 nm, clusters consist of a molecular entity composed of 2 – 30 atoms. As opposed to nanoparticles, which have a continuous band of electronic energy levels and hence metallic character,[13] supported clusters possess a molecular nature with discrete energy levels. Hence, they are not considered metallic but metal-like or "molecular metals".[9,14] Additionally, as the particle size decreases, the metal-surface interactions gain in importance, and the nature of the support plays a major role.

Some industrial catalysts, such as those employed in the paraffin reforming to give aromatics, are composed of clusters of only few atoms, such as platinum supported on zeolite LTL, which has a particle nuclearity between 5 and 11 atoms and catalyses the alkane dehydrocyclization.[15] Clusters of two-three atoms of platinum on γ-Al_2O_3 have been observed by STEM in some industrial catalysts, too.[16] Subnanometric Pt_{8-10} clusters show activity in the oxidative dehydrogenation of propane up to 100 times higher than platinum nanoparticles even maintaining the high selectivity.[12b]

Much of the recent development of atomically dispersed metal on oxide supports involves noble metals such as palladium, platinum, and gold.[17] An inherent problem with noble metals on oxide surface is their tendency to undergo aggregation into entities of higher nuclearity, especially under catalytic conditions.[18] Thus, under hydrogenation conditions, the fragment $[Ir(C_2H_4)_2]$ supported on zeolite aggregates into Ir_4 clusters to an extent that depends on the composition of the gas phase, but no significant effect on the catalytic performance was observed.[19] In general, however, the catalyst nuclearity influences its reactivity: Single atoms of rhodium are effective for ethene oligomerization, whereas small clusters are more active in ethene hydrogenation.[17d] The effect of the particle size on the reactivity and selectivity is a general trend and has been observed, for instance, in the trimerization of acetylene based on Pd supported on MgO.[20]

To avoid aggregation, an atomically disperse supported late TM species must be stabilized by ligands – besides the surface itself that acts as ligand by virtue of its hydroxyl groups. For instance, an organometallic precursor can be chemisorbed on the support. Thus, $[Ir(acac)(C_2H_4)_2]$, $[Rh(acac)(CO)_2]$ and $[Ru(acac)_2(C_2H_4)_2]$ react with the hydrogen form of zeolite Y (HY) to give supported complexes containing the $[Ir(C_2H_4)_2]$,[21] $[Rh(CO)_2]$, or $[Ru(C_2H_4)_2]$[22] fragments, respectively.

Supported complexes

Complexes can be supported on a surface either via a non covalent or via a covalent attachment.[23] The *immobilization via noncovalent attachment* exploits hydrogen bonding or, more rarely, Van der Waals interactions, which are extremely weak and give systems that are prone to leaching. The interaction with the surface of sulfonic or phosphonic acid substituted phosphine ligands has been used for immobilization by hydrogen bonding.[24] Another noncovalent immobilization method exploits the electrostatic interactions of the support with a charged complex[25] or with its counterion.[26] Alternatively, organometallic molecules can be physically immobilised in the cavities of a zeolitic framework ("ship-in-a-bottle")[27] or entrapped in ordered inorganic networks, such as polysiloxane matrices, environmentally benign organopolymers,[28] or via a supramolecular network.[29]

The *immobilization via a covalent attachment* can occur according to two general schemes. In one of these, the linkage to the surface is made via a linker, method called anchoring,[10] whereas the second approach uses a directed surface–metal bond. We refer to it as "grafting".

Covalent attachment: Anchoring vs. grafting

Many attempts have been done to establish a nomenclature to define and discriminate between different bonding modes. IUPAC recommendations states: "… *deposition involving the formation of a strong bond (e.g., covalent bond) between the support and the active element is usually described as grafting or anchoring. This is achieved through a chemical reaction between functional groups (e.g., hydroxyl groups) on the surface of the support and an appropriately selected inorganic or organometallic compound of the active element*".[30]

According to this definition, no differences exist between grafting and anchoring. The nomenclature used throughout this text refers to the proposed[10] differentiation between molecular complexes directly bonded to the surface by means of a metal–oxygen bond (where oxygen is an atom originally pertaining to the surface), defined as grafting, and molecular complexes connected to the surface via linkers or spacers. In the latter case, which is defined as anchoring, the linker can be connected either to the metal or to a ligand of the complex (Figure 1).

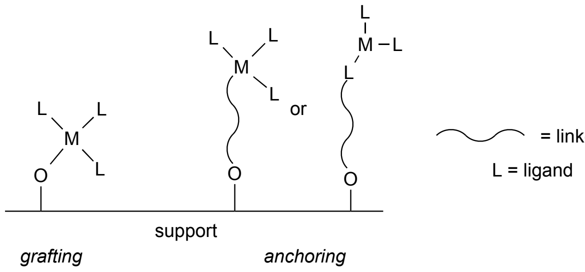


Figure 1. Schematic representation of grafted and anchored complexes.

The definition in Figure 1 discriminates, from a metallocentric point of view, systems in which one (or more) atoms of the surface participate to the coordination sphere of the complex (grafting) from those in which the metal is separated from the surface by the sequence of covalent bonds of the linker (anchoring). In the grafted complex, the nature of the surface/support directly influences the electronic situation, coordination number, and oxidation state of the metal, whereas anchored complexes are designed to avoid such interactions.

Grafted and anchored complexes involve different synthetic strategies. Grafting is achieved by removal of labile ligands from the catalyst precursor to give a complex with altered structure and reactivity, whereas anchoring requires either chemical modification of the ligand to be attached to the surface or the inclusion in the coordination sphere of a surface-bound linker as ancillary ligand. Grafting and anchoring represent two different approaches, where the former aims at simulating a heterogeneous catalyst in a controlled fashion, whereas the goal of the latter is to reproduce the behaviour of a homogeneous catalyst on a surface.

Of these two different approaches to covalent binding, the more widely explored method is anchoring, which is designed to prevent the interaction between the surface of the support and the metal catalyst and is only briefly mentioned here. Several examples of anchored species have been reported, such as metallocene $[ZrCl_2(Cp_2)]$[31] and bis(imino)pyridine iron(II) catalysts[32] for oligo/polymerization,[33] ruthenium carbene complexes anchored on silica for olefin metathesis,[34] Mn(salen) catalysts for enantioselective epoxidation,[35] and various chiral catalysts for the asymmetric hydrogenation of C=C and C=N double bonds.[36] The grafting approach, which is the main topic of this perspective, is described in the following sections.

Grafting on silica: The surface as ligand

Grafted complexes feature a direct bond between the metal and the surface. The potential of surface silanols of silica as ligands was recognised early by Ballard.[37] In particular, silica-based materials with high surface area have found enormous application thanks to the high thermal stability of the amorphous network and to the possibility of obtaining variable structures. In the 90's, the discovery of the families of mesoporous silicas like MCM[38] and SBA[39] introduced materials that are considered nowadays very attractive[40] because of their periodic and uniform structure, and tunable pore diameter (between 20-300 Å) with a narrow pore size distribution. The last feature is particularly useful for grafting studies, as the mesoporous structure prevents diffusion limitations and allows for intrapore chemistry,[41] but makes these materials less stable to thermal treatments.

Following the order of increasing complexity, the following sections focus on the properties of the silica surface as ligand, describe the electronic properties of the siloxo ligand, introduce molecular models of the silica surface, and discuss the effect of the presence of multiple silanol and siloxo groups.

In general, the metal ion covalently binds to silica surface via a deprotonated silanol to form a surface siloxo complex.[42] The siloxo ligand acts not only as σ- but also as a π-donor (see below). This is particularly favourable in combination with ions of early transition metals, which typically feature the d^0 electron configurations. In contrast, ions of late TMs have typically a d^n configuration ($n = 5–10$). The interaction between the lone pairs of the siloxo ligands and the partially filled d-orbitals can be either favourable or destabilizing depending on the electron count, geometry and ancillary ligands of the grafted complex.

To understand the electronic effects that control the final outcome and the differences between grafted complexes of early and late transition metals, the next paragraphs give a closer look at the electronic nature of the silica surface as ligand with the classical tools of coordination chemistry. To simplify the discussion and to support it with more data, we extend it to siloxo ligands in general, which can be conveniently used as soluble analogues of the silica surface.

Siloxo as ligand

Siloxo complexes of transition metals (both early and late) and their use in catalysis have been reviewed.[43] Silanolate ligands were developed as a replacement for cyclopentadienyl and can also be described as "pseudohalides with adjustable steric parameters".[44] Similarly to alkoxides, siloxo ligands can interact with metals with a σ-orbital and two p_π orbitals (Figure 2).[45] The strength of the σ- and π-donation is strictly related to the electrophilicity of the metal centre and increases with electron deficient metal ions. Hence, siloxo ligands are versatile and stabilise low-coordinated complexes.

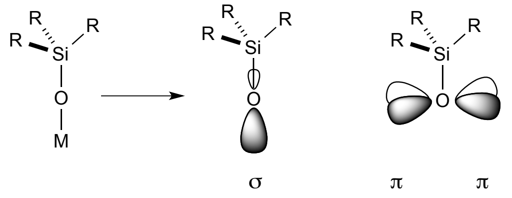
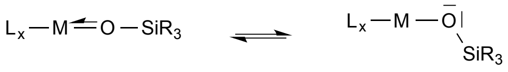


Figure 2. Schematic representation of σ and p_π orbitals of siloxo ligands.

Based on the IR stretching of the carbonyl ligand in the coordinatively unsaturated complex $[RuH(X)(CO)(P^tBuMe_2)_2]$, Caulton and Eisenstein have suggested that the overall (σ + π)-donor ability of the X ligand increases according to I < Cl < OPh < NHPh < OH < OCH_2CF_3 < $OSiPh_3$ < $OSiMe_2Ph$ < $OSiMe_3$.[46] They concluded that siloxo ligands have a higher composite donating ability than chloro, but the contribution of the π-donation remained elusive.

The extent of π-effects can be evaluated from structural data, as the π-donation causes a decrease of the M–O bond length and an increase of the M–O–Si angle. Scheme 1 shows the canonical forms in the presence of π-donation (left) or of σ-bonding exclusively (right). The structurally characterised siloxo complexes of transition metals feature widely variable M–O–Si angles between 120 and 160 °.[43a]



Scheme 1

The π-donation from the (sil)oxo ligands may play an important role in certain catalytic transformations, and in particular in alkene metathesis with supported Grubbs-type catalysts (see below).[47] The beneficial effect of pseudohalide ligands in connection with homogeneous ruthenium carbene catalysts for alkene metathesis has been recently discovered[48] and may have a similar origin as the effect of π-donating ancillary ligands (in particular oxo) in alkylidene catalysts for alkene metathesis with early transition metals.[49] Also, as briefly mentioned above, the π-donating ability of siloxo ligands is of extreme importance to stabilise grafted d^0 complexes of early transition metals. In the case of late transition metals, the π-donation is known to stabilise coordinatively unsaturated 16-electron d^6 complexes.[50]

Siloxo complexes as models and precursors

A number of soluble models of the silica surface have been used to understand the structure and properties of grafted complexes, but also as precursors of grafted species (Figure 3). Simple silanols such those reported in Figure 3 well represent the three different types of silanols occurring at the silica surface and have been used to prepare analogues of grafted complexes.[51]

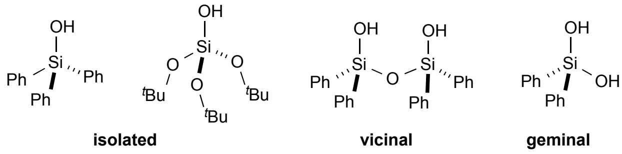
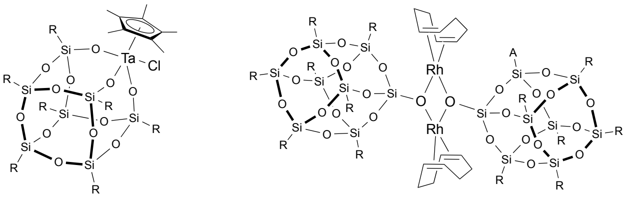


Figure 3. Soluble silanols as models of silica surface.

Beside these simple molecules, polyhedral oligosilsequioxanes (POSS) are versatile compounds that accurately mimic the features of a surface.[52] A variety of models are now available, which can be adapted to simulate different surface silanols and podality. Scheme 2 shows a binuclear monopodal POSS Rh(I) complex[53] and a tripodal POSS Ta(IV) complex[54] that mimic silica-supported species.



Scheme 2

A common approach to prepare soluble siloxo ligands is metathesis with a silanolate salt, whereas other synthetic methods exploit the reactions of silanols with metal precursors bearing protolysable ligands (alkyl, amido, halides, and alkoxides)[55] and are analogous to those used for the preparation of silica-grafted complexes discussed below. As an extension to these strategies, we have recently reported the first example of a reaction of the dihydride pincer complex $[IrH_2(POCOP)]$ (POCOP is 1,3-bis((di-*tert*-butylphosphino)oxy)benzene) with polysesquioxanes to give the corresponding siloxo complexes and dihydrogen.[56] Interestingly, no reaction was observed between $[IrH_2(POCOP)]$ and Et_3SiOH, which we tentatively explain with the lower acidity of the hydroxo group with respect to POSS. The reaction of hydrides with silanols to give soluble siloxo complexes has already been reported in relation to main group hydrides of zinc,[57] gallium,[58] aluminum,[59] and tin,[60] but was unprecedented for transition metal hydrides.

Coordination number and podality

Before discussing specific examples of grafted complexes, it is convenient to introduce a feature that is essential to understand subtle effects that add complexity to the coordination of a TM ion onto a surface in general. The surface bonding of the grafted complex can be classified on the basis of its podality, that is, the number of surface oxygen atoms bound to the metal. Metal ions presenting a single Si–O–M interaction are monopodal, whereas two or three interactions give bipodal or tripodal species, respectively (Figure 4). Additionally to siloxo, also nondeprotonated silanols or oxo-bridges can interact with the metal (dashed in Figures 4 and 5).

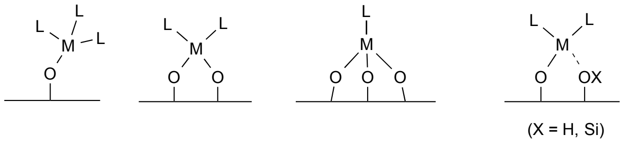
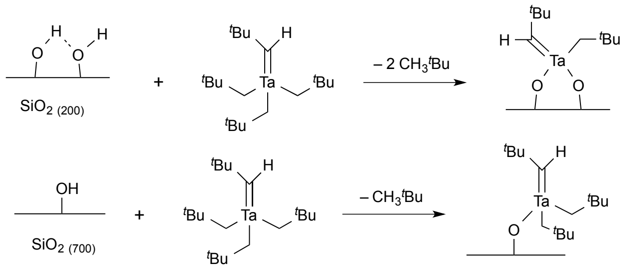


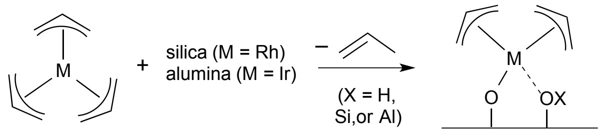
Figure 4. Podality of grafted complexes and secondary M···O(X)Si interaction.

The podality depends on the concentration of the surface silanols of the support, as well as on the curvature of the surface. An organometallic precursor can give different supported species in relation to the concentration of surface silanols. Scheme 3 shows an example in which the pretreatment of the silica (at either 200 or 700 °C) influences the number of silanols per surface unit and, hence, the podality of the resulting grafted species.[42]



Scheme 3

Additionally, also the nature of the metal complex itself plays a role in determining the number of metal–surface interactions. Secondary interactions with nondeprotonated surface silanols may complete the coordination sphere of the metal,[42] as illustrated by the bis(allyl) complexes [Rh(η^3-C_3H_5)$_3$] on silica[61] and [Ir(η^3-C_3H_5)$_3$] on alumina[62] (Scheme 4).



Scheme 4

The rhodium complex was initially formulated as a five-coordinate species, but molecular modelling and IR spectroscopic studies of the reaction between [Rh(η^3-C_3H_5)$_3$] and the surface of silica, alumina, titania, and magnesia,[63] as well as calculations,[64] led to the proposal of three possible coordination environments, generating the three different species *a* - *c* shown in Figure 5.

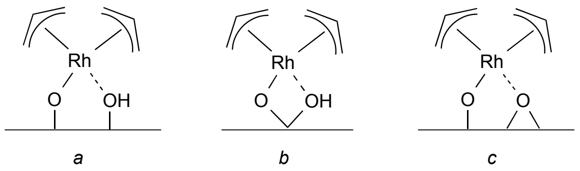
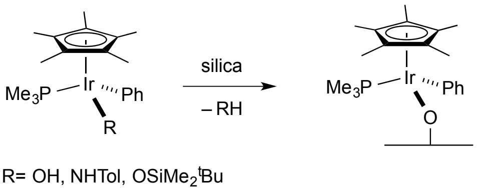


Figure 5. Possible coordination environments of silica-grafted [Rh(η^3-C_3H_5)$_3$].

The relative amount of the three different structures, and especially *a* and *c*, depends on the extent of dehydroxylation of the silica surface and on the concentration of the supported species. In the case of the iridium analogue (supported on alumina), ^{13}C NMR spectroscopy indicated the presence of two equivalent allyl ligands in the grafted complex.[62] On the basis of the spectroscopic data, the authors were not able to exclude the occurrence of an additional Ir–O interaction with a non deprotonated silanol (or oxo bridge) to give a coordinatively saturated complex.

A possible way to obtain a well-defined coordination geometry, albeit at the cost of reactivity, is to graft a coordinatively saturated complex. In the early 90's, Bergman showed that the hydroxo complex [Ir(OH)(Ph)(Cp*)(PMe_3)] reacts with the surface silanols of silica to give the first example of grafted iridium complex (Scheme 5).[65]

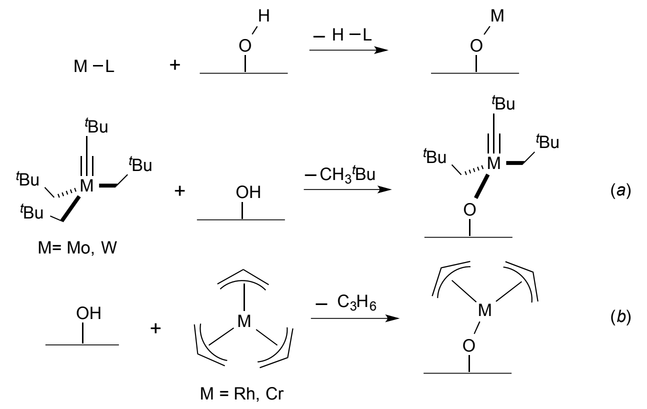


Scheme 5

The reaction of the amido or silanolato analogues with silica released the corresponding protonated fragments (amine and silanol), which proved the formation of a covalent bond between the metal center and the support and ruled out the formation of physisorbed species. The formulation of the complex was confirmed by ^{13}C NMR spectroscopy. This silica-grafted half-sandwich complex fulfils a number of requirements, as it gives a single, easily characterizable species on the surface with a well-defined six-coordinate geometry. Also, the resulting complex does not rearrange into geometric isomers and the protonolysis products are easily removed under mild conditions. For this complex, however, we are not aware of any application in catalysis.

General grafting strategies

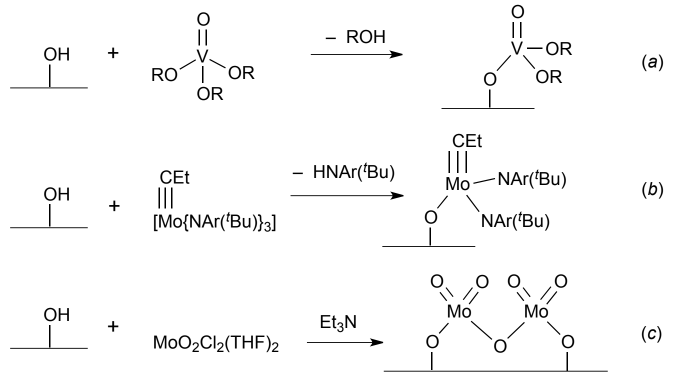
As a general principle, any complex (either of an early or of a late TM) containing a protolizable ligand can react with surface silanols to give a covalent surface-metal bond and release the protonated ligand (Scheme 6). Soluble precursors containing such ligands can be used as precursors to generate surface organometallic complexes. Among all, ligands such as alkyl, alkoxide, and amide have been used most. Representative examples of synthetic approaches are reported below.



Scheme 6

Alkyl complexes of tantalum,[66] tungsten, molybdenum, rhenium,[34a, 67] ruthenium,[68] nickel,[69] and platinum[70] have been used as precursors to graft organometallic species (Scheme 6*a*). Similarly, *allyl complexes* have been investigated as suitable precursors for grafting. For instance, $[M(\eta^3\text{-}C_3H_5)_3]$ (M: Rh, Cr) react with silica upon elimination of propene giving the grafted fragment $[M(OSi\equiv)(\eta^3\text{-}C_3H_5)_2]$ (Scheme 6*b*).[61, 71]

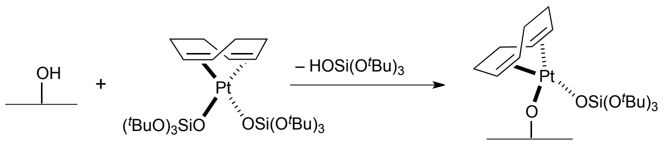
Metal alkoxides such as $[VO(OR)_3]$ readily react with silanols to generate a supported complex and liberating the corresponding alcohol as shown in Scheme 7*a*.[72]



Scheme 7

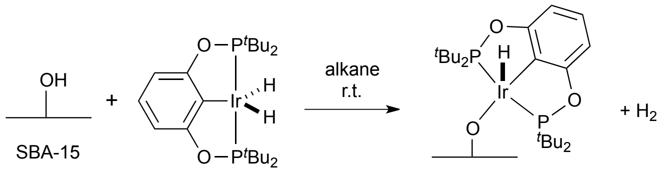
Acetylacetonato[73] and *hydroxo*[65, 74,75] complexes have been used, too. Metal *amides* (or *silylamides*) react with surface sites liberating the amine as the protonated product (Scheme 7*b*).[76] *Chloro* complexes eliminate HCl directly or in the presence of an amine to activate the silanols (Scheme 7*c*).[72b, 77]

Siloxo complexes have been extensively used by Tilley[78] as organometallic precursors for grafting on silica. For instance, $[Pt(OSi(O^tBu)_3)_2(COD)]$[78c] reacts with SBA-15 releasing the corresponding silanol (Scheme 8). Besides being important precursors to silica-grafted complexes, siloxo complexes play a major role as soluble models for such species, as will be discussed below.



Scheme 8

Hydride complexes. We have recently reported the use of hydride ligands as grafting functionality.[79] The dihydride pincer complex $[IrH_2(POCOP)]$ (POCOP is 1,3-bis((di-*tert*-butylphosphino)oxy)benzene) reacts with SBA-15 to give the corresponding surface siloxo monohydride complex and dihydrogen (Scheme 9). The formation of dihydrogen as protonolysis product during the synthesis of $[IrH(OSi\equiv)(POCOP)]$ was proven by trapping with an excess of the reagent itself $[IrH_2(POCOP)]$, which gave the tetrahydride $[IrH_4(POCOP)]$.



Scheme 9

Interestingly, the ruthenium(II) hydroxo hydride complex $[RuH(OH)(dmpe)_2]$ (dmpe = 1,2-bis(dimethylphosphino)-ethane) reacts with silica in THF suspension to give water (and not H_2) and the grafted hydride $[RuH(OSi\equiv)(dmpe)_2]$.[75] To the best of our knowledge, the use of a metal hydride to graft the metal onto the silica surface is unprecedented for transition metals and has been reported only for tin hydride species.[60, 80] Goldman and Brookhart reported that $[IrH_2(POCOP)]$ apparently undergoes adsorption on alumina, but did not determine the nature of the resulting species.[81,†]

Grafted late TM catalysts

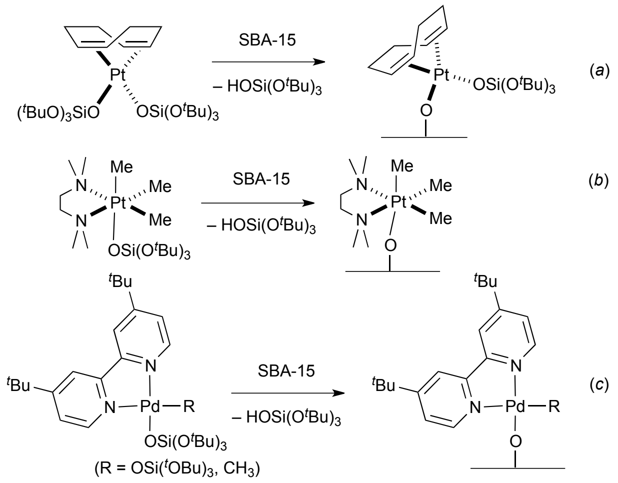
The fact that the grafting strategies are substantially the same both for early and for late TM complexes should not distract from the profound differences between the chemical behaviour of the resulting surface species. Indeed, whereas early TM ions (typically in the d^0 configuration) generally tend to form stable site-isolated grafted species, their analogues on the right of the period table tend to reduction and aggregation.[42, 82] This tendency is either deliberately used to generate oxide-supported nanoparticles[55, 83] or intervenes under catalysis conditions. Illustrative examples, classified according to their application in catalysis, are given below.

Hydrogenation. One of the first examples of late transition metal complexes grafted on silica surface was prepared by Schwartz by grafting $[Rh(\eta^3\text{-}C_3H_5)_3]$ onto silica (Scheme 4).[61a] It was proposed that its reaction with hydrogen gives a dihydride rhodium complex (see below)[61b] that catalyses the hydrogenation of alkenes[61b] and arenes,[84,85] The grafted rhodium allyl complex was also reported to catalyse D/H exchange in CH_4, which implies the activation of the C–H bond of methane.[86] Gates[87] and Basset[88] showed later on that the grafted allyl complex decomposed under hydrogenation conditions to give rhodium(0) nanoparticles.

Later on, Iwasawa reported the preparation of molecular-imprinted rhodium complexes grafted on silica. A model ligand with the desired shape (phosphinite or amine, for instance) was coordinated to the metal, layers of the silica matrix were overlaid, and then the template ligand was eliminated. The imprinting procedure effectively enhanced the hydrogenation performances in olefins and α-methylstyrene hydrogenation.[89]

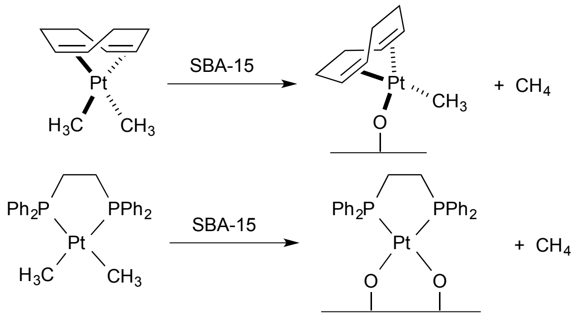
More recently, Baker has described the grafting of the iridium analogue $[Ir(\eta^3\text{-}C_3H_5)_3]$ on partially dehydroxylated alumina and has concluded that the resulting species are marginally more stable than their rhodium(III) analogues.[62] However, bulky basic ligands such as P^iPr_3 were found to stabilise monomeric hydride complexes that catalytically hydrogenate 2-butene (see below).[90]

Recent progress has shown that chelating ligands can be exploited to control the tendency to aggregation of late TM ions. Thus, Tilley has reported that ancillary ligands such as COD and TMEDA stabilise isolated Pt(II) and Pt(IV) complexes on SBA-15 (Scheme 10*a,b*). However, the fate of the grafted complexes during alkene hydrogenation was not conclusively ascertained.[78c] It should be noted that silica grafted COD complexes of platinum form nanoparticles in the 2-3.3 nm range by reduction with H_2 at 300 °C.[83b]



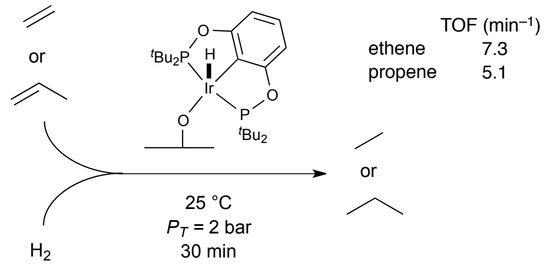
Scheme 10

Also palladium siloxo complexes bearing bipyridyl ligands were used to prepare grafted species that selectively catalyse the semi-hydrogenation of 1-phenyl-1-propyne (Scheme 10*c*).[78d] A number of observations suggested that the grafted complexes may decompose under catalytic conditions to give either Pd clusters or Pd(0) sites. Gaemers showed that the effect of chelating ligands persists even upon calcination at 500 °C. Under such conditions, silica-grafted COD and 1,2-bis(di-phenylphosphino)ethane (dppe) complexes of Pt(II) (Scheme 11) give highly dispersed small-size nanoparticles that are particularly active in the hydrogenation of toluene.[70] It was not established whether the catalytically active site is an isolated surface complex or a metal(0) aggregate.



Scheme 11

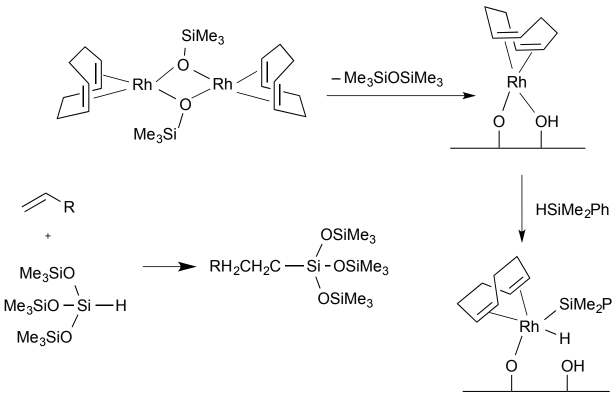
We have recently reported that the SBA-15-grafted hydride [IrH (OSi ≡) (POCOP)] catalyses the hydrogenation of ethene and propene at room temperature and 1 atm (Scheme 12).[79]



Scheme 12

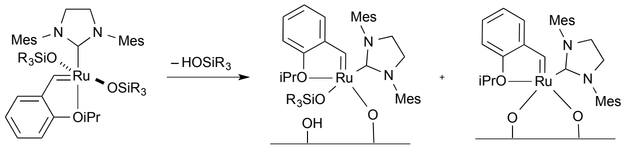
The hydrogenation reaction has no induction period and is faster at 70 °C (TOF/min^{-1} at 25 °C (70 °C) after 30 min for ethene and propene are 7.3 (28.7) and 5.1 (24.7), respectively). The catalyst is recovered intact after catalysis (as indicated by solid-state ^{31}P NMR spectroscopy) and can be reused without significant loss of activity. As will be discussed in more detail below, this is, to the best of our knowledge, the first example of a silica-grafted hydride complex of a late transition metal that resists decomposition and aggregation to metal nanoparticles under hydrogenation conditions.

Hydrosilylation Another reaction class that involves the intermediacy of a hydride complex is hydrosilylation. In this case, however, the reagent is a silane and not dihydrogen, which is an important detail as will be discussed below. Marciniec and coworkers have recently prepared silica-grafted rhodium catalysts from siloxo precursors and used them for the hydrosilylation of alkenes (Scheme 13),[91] for which they suggested the involvement of an undetected rhodium-hydride intermediate (see below).



Scheme 13

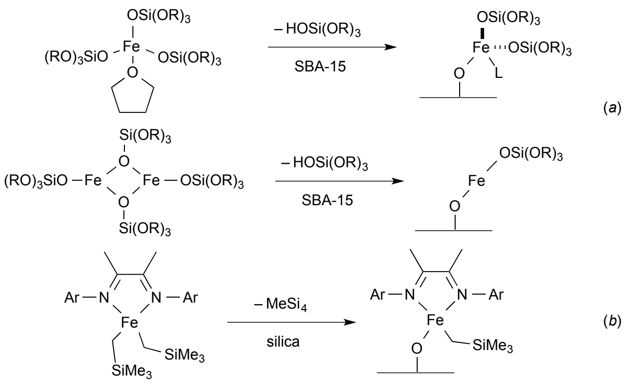
Olefin metathesis. Siloxo derivatives of Grubbs' ruthenium metathesis catalyst were prepared and supported on silica (Scheme 14). The resulting material is active in the ROMP of 1,5-cyclooctadiene and in the homometathesis of 4-chloro-styrene.[47] The ^{13}C solid-state NMR spectra indicated that two different grafted species with either one or two Ru–O bonds were formed by substitution of one or both siloxo ligands of the molecular precursor. It should be noted that siloxo ligands (including surface silanolates) can be considered as *pseudo* halides (see above) and their presence in the coordination sphere of the ruthenium catalyst plays thus a pivotal role.[48]



Scheme 14

Olefin polymerization. A nickel(II)-diimine dialkyl derivative was grafted onto silica to give a well defined complex [Ni(OSi≡)(CH_2SiMe_3)(α-diimine)], which was activated with gaseous BF_3 to give a species that polymerised ethene in the gas-phase.[69] Other silica supported α-diimine acetylacetonato Ni(II) complexes catalyse the gas-phase polymerisation of ethene, but the nature of the interaction between the complex and the surface was not investigated.[92]

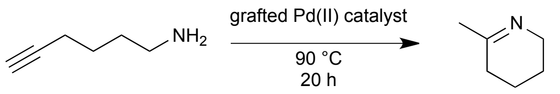
Benzylic oxidation and epoxidation. Surface complexes of iron(III) and iron(II) were prepared by reacting SBA-15 with [Fe(OSi(O^{t}Bu)$_3$)$_3$(THF)] and [(Fe(OSi(O^{t}Bu)$_3$)$_2$)$_2$], respectively (Scheme 15*a*). After calcination, both precursors gave isolated Fe(III) species (as indicated by UV-vis and EPR measurements) that are active in the oxidation of aliphatic and aromatic C–H bonds with H_2O_2.[78a, 78f] A selective alkene epoxidation catalyst was obtained with the iron(II) complex [Fe(OSi≡)-(CH_2SiMe_3)(diimine)] grafted on $SiO_{2(700)}$ (Scheme 15*b*), which was characterised by EXAFS.[93]



Scheme 15

Recently, ruthenium bipyridine or terpyridine complexes were grafted by exchange of an alkyl ligand with surface silanols. These complexes were reported to be active and stable catalysts for the oxidation of benzyl alcohols with *tert*-butyl hydroperoxide.[68] The bipyridyl complex [Co(OSi(O^{t}Bu)$_3$)$_2$(4,4'-di-^{t}Bu-bipy)] was grafted onto SBA-15 and the resulting material, which was characterised as a pseudo-tetrahedral cobalt(II) complex, catalysed the liquid-phase oxidation of alkyl aromatics with *tert*-butylhydroperoxide.[78b] Ethylbenzene was converted to acetophenone with up to 83% chemoselectivity.

Hydroamination. Several palladium(II) complexes were grafted onto silica to give a mixture of surface species that catalysed the cyclisation of aminoalkynes (Scheme 16).[74] The most active catalyst was obtained from [Pd$(NO_3)(CH_3)$-$(PMe_3)_2$], and the grafted complexes are more stable than their soluble precursors, are only slightly air-sensitive, and can be recycled with only moderate loss of activity.[74]



Scheme 16

Pathways to aggregation

As discussed in the former section, grafted complexes can evolve according to different pathways during catalysis. They can either maintain their molecular nature as discreet species or decompose to elemental metal. In the latter case, as mentioned above, particles of different sizes can be formed, which influences the catalytic performance of the supported metal. Therefore, the grafting of a metal complex can be deliberately used with two different goals, which are either the formation of a catalytically active centre with a well-defined coordination environment or the targeted formation of clusters or nanoparticles of a given size by controlled decomposition of the surface grafted species.

The evolution of the grafted complex depends on the conditions under which the catalytic reaction is run. As discussed above, these can be oxidizing (benzylic oxidation), neutral (olefin metathesis), or reducing (hydrogenation). This classification is not very momentous for early TMs, but is pivotal for late TMs, which have a much higher tendency to exist in lower oxidation states.

A common feature of grafted complexes of early TMs is that they contain a metal in a high oxidation state and typically have the d^0 electron configuration. Such highly oxidized metals ions are hard and interact strongly with the oxide surface, which is also chemically hard. Hence, these metals have a low tendency to undergo reduction and aggregation.

As the hardness of a metal ion increases with its oxidation state,[94] late TMs do not behave much differently than early ones under oxidizing conditions. However, the situation is completely different under reducing conditions, e.g. in the presence of hydrogen (which triggers the formation of hydride complexes), π-accepting ligands such as carbon monoxide, isonitriles, alkenes, and allyls, or of soft ligands like phosphines. When such ligands are present, grafted complexes of late TMs tend to undergo reduction and eventually to aggregate to metal nanoparticles, as illustrated by the examples discussed below. As H_2, CO, and alkenes are among the most common reagents in catalysis, this tendency has vast repercussions. Indeed, in a catalytic reaction with an atomically dispersed transition metal catalyst, such molecules act both as reagents and as ligands, thus affecting the chemical behaviour of the metal centre.

Reductive elimination is the main reaction responsible for the aggregation of a late TM on an oxide surface. It is generally appreciated that late TMs have a much larger tendency to reductive elimination than their congeners on the left side of the periodic table. As discussed in the next sections, reductive elimination can intervene in different contexts. Silica-grafted hydrides of late TMs are particularly prone to the reductive elimination of silanol, which is not surprising in view of the considerable bond dissociation energy (BDE) of the H–OSi bond (119.3 kcal/mol),[95] which contributes significantly to the thermodynamic drive of the reaction.

The reason why π-accepting (or soft) ligands trigger reductive elimination mainly descends from the fact that such ligands stabilise TM complexes in a low oxidation state, but the HSAB approach offers a complementary viewpoint. In the case of a late TM grafted on an oxide support, there is a mismatch between the hard oxygen atoms on the surface and the soft metal ion, which destabilises the grafted complexes and drives aggregation.

The soft character of a late TM increases upon lowering its oxidation state and by coordinating soft (e.g. hydride, phosphine) and/or π-accepting ligands (CO, alkenes). Thus, when a late TM complex on an oxide surface contains hydride, alkene, or phosphine ligands, its oxophilicity further decreases, and the mismatch between the hard nature of the surface and the soft character of the metal ion increases.

The next sections discuss these two possibilities (reductive elimination / aggregation induced by hydride formation or by π-accepting (or soft) ligands). Before this, hydride grafted complexes of early transition metals are briefly discussed to highlight their different chemical behaviour.

Grafted hydride complexes: Late vs. early TMs

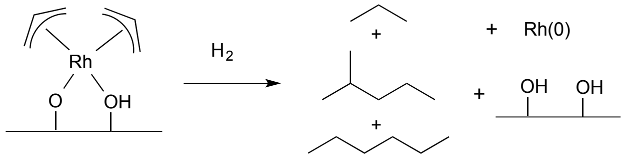
In 1977,[96] Yermakov and Zhakarov reported that supporting $[Zr(C_3H_5)_4]$ on silica, followed by hydrogenolysis, gives stable surface zirconium hydrides. Later on, this material (and a related titanium derivative) has been confirmed to contain isolated Zr(IV) hydrides bonded to surface silanolates, and was used to catalyse the hydrogenation of alkenes[97] and benzene under mild conditions.[98] Basset has thoroughly investigated silica grafted hydride complexes of Ta, Cr, and W and their use in alkane homologation (“alkane metathesis”).[99] Loosely related systems are Marks' actinide bis(cyclopentadienyl) complexes supported on alumina that catalyse alkene hydrogenation, but the nature of the interaction between the metal and the surface in these species has not been conclusively ascertained.[100]

In terms of coordination chemistry, the fact that hydride complexes of early TMs (or chemically analogous species such as the actinides) are stable on an oxide surface indicates that the d^0 metal ions maintain their hard character even in the presence of a soft ligand such as hydride. This is not obvious, because the HSAB character of a ligand influences that of the metal it binds to according to the principle of symbiosis.[101] Apparently, although hydride ligands reduce the hardness of d^0 complexes, this effect is not large enough to trigger the decomposition of the M–H species and the formation of metal nanoparticles.

In contrast, late TMs have a larger tendency to reductive elimination, which explains why silica grafted hydride complexes of late TMs are generally unstable. The thermodynamic drive given by the formation of a strong H–OSi bond reinforces this well-documented general tendency. Representative examples thereof, as well as the rare exceptions, are discussed in the following.

On the same lines used for grafted zirconium complexes, Schwarz reported in 1980 that the grafted siloxo bis(allyl) species $[Rh(OSi\equiv)(\eta^3\text{-}C_3H_5)]$ (see Scheme 4 above) undergoes hydrogenolysis to give a mixture of terminal and bridging hydride complexes that catalyse the hydrogenation of alkenes[61a] and arenes.[84] The reactivity of the silica-grafted rhodium(III) hydrides with HCl, H_2, alkenes, and PMe_3 was reminiscent of that of their soluble analogues[61b] and has prompted a vast number of investigations.[102]

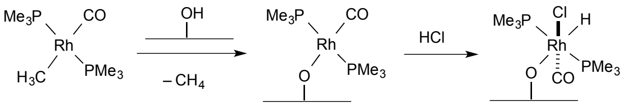
Although the silica grafted hydrides of rhodium(III) remained extremely elusive, these pioneering studies sparkled a lively debate on their nature. Thus, in 1983, Gates and coworkers reported that $[Rh(OSi\equiv)(C_3H_5)]$ is readily reduced by H_2 at 25 °C to give lower valent rhodium species, including aggregates of rhodium metal, with concomitant reformation of silanol groups (Scheme 17). An induction period in the catalytic hydrogenation of toluene to methylcyclohexane, which was followed by a rapid rise in the conversion, was attributed to the formation of Rh(0) under hydrogenation conditions.[87] In agreement with Gates' suggestion, Basset found that most of the allyl ligands of $[Rh(OSi{\equiv})(C_3H_5)]$ are eliminated as propane and hexanes upon reaction with H_2 according to the stoichiometry in Scheme 17.[88, 103]



Scheme 17

Baker has recently reported a somewhat similar behaviour for $[Ir(C_3H_5)_3]$ supported on partially dehydroxylated γ-alumina, whose catalytic activity in the dehydrogenation of cyclohexane to benzene in a flow reactor at 180-200 °C has been tentatively explained with the formation of iridium(0) nanoparticles.[62] Interestingly, he suggested that the addition of iridium complexes bearing chelating ligands to highly acidic surface might also be useful in circumventing the formation of iridium metal, a strategy that we have successfully applied (Scheme 9) and will be discussed in more detail below.

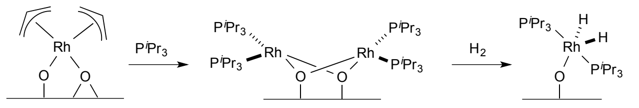
Even simple, monodentate ligands stabilise surface hydrides of late TMs, though. Again, Schwartz's work[61b] with the PMe_3 adducts of $[Rh(OSi{\equiv})(\eta^3\text{-}C_3H_5)]$ has been inspiring to later chemists. Indeed, phosphines as ancillary ligands help control the coordination sphere of the metal, increase the stability of the hydride species, and introduce additional spectroscopic handles. Thus, the phosphine hydride rhodium(I) complex $[Rh(OSi{\equiv})(CO)(PMe_3)_2]$ oxidatively adds HCl to give the corresponding silica grafted rhodium(III) chlorohydride complex (Scheme 18).[104]



Scheme 18

The oxidative addition of H_2 to $[Rh(OSi{\equiv})(CO)(PMe_3)_2]$ has not been reported, but a dihydride complex was prepared by exposing $[Rh(OSi{\equiv})(\eta^3\text{-}C_3H_5)_2]$ to PMe_3, then H_2 without removing the excess PMe_3. The resulting 18-electron cationic complex *cis*-$[RhH_2(PMe_3)_4]^+$ is attached to the silica surface by ion pairing and was extracted into a nitromethane solution of $NaBPh_4$ or $^nBu_4NCl$.[105] It should be noted that this is not a grafted complex, as the silica surface acts as a counterion and not as a ligand.

In contrast, after treatment with the bulky phosphine $P(^iPr_3)_3$, $[Rh(OSi{\equiv})(\eta^3\text{-}C_3H_5)_2]$ oxidatively adds H_2 to give a monomeric dihydride complex of rhodium(III), which was tentatively formulated as the coordinatively unsaturated $[RhH_2(OSi{\equiv})(P^iPr_3)_2]$ (Scheme 19) (although the coordination of an additional siloxane oxygen was not ruled out).[90] At difference with the degrafted 18-electron dihydride *cis*-$[RhH_2(PMe_3)_4]^+$ mentioned above, which is inactive in alkene hydrogenation, $[RhH_2(OSi{\equiv})(P^iPr_3)_2]$ hydrogenates *cis*-2-butene to butane in the presence of dihydrogen, but no details of the stability and reusability of this catalyst were given.



Scheme 19

We have recently shown that this approach, which takes advantage of bulky ancillary ligands to stabilise coordinatively unsaturated, silica-grafted hydride complexes, can be further developed by using robustly bound polydentate ligands. Indeed, the pincer complex $[IrH_2(POCOP)]$ gives the stable surface hydride complex $[IrH(OSi{\equiv})(POCOP)]$ with a well-defined 16-electron environment (Scheme 9).[79] The complex binds to surface by means of an Ir–OSi bond, is formed as a single species, is indefinitely stable under inert atmosphere, and has a well-defined, 16-electron coordination, as indicated by solid-state ^1H, ^{31}P, and ^{13}C NMR spectroscopy, and does not decompose during the hydrogenation of ethene and propene. The coordinatively unsaturated nature of $[IrH(OSi{\equiv})(POCOP)]$ is supported by its reactions with carbon monoxide and ethene (see below).

It should be noted that, in the absence of such polydentate ligands that ideally also bear a spectroscopic handle, the characterisation of surface hydride complexes remains a daunting task. A rare example of such a "naked" surface hydride has been recently prepared by hydrogenolysis of [Ru(cod)(cot)] grafted on silane-functionalised silica. The spectroscopic data of the resulting material, in particular the 1H NMR signal at δ – 8.3, are in agreement with the presence of a coordinatively unsaturated, mononuclear hydride silyl siloxo complex of ruthenium(II) (Figure 6).[106] The EXAFS data support this formulation as a grafted complex and rule out aggregation of the metal.

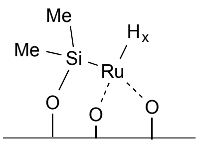
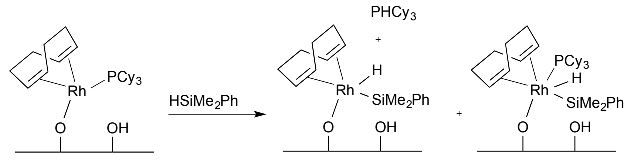


Figure 6

In other cases, the formation of surface hydrides of late transition metals was inferred on the basis of indirect evidence from the catalytic behaviour of the grafted complexes. Thus, Marciniec has suggested that a silica-grafted rhodium-phosphine catalyst for hydrosilylation reacts with silanes forming two different hydride complexes (in analogy to the system shown in Scheme 13).[107] However, no spectroscopic evidence was given to support this hypothesis (Scheme 20).



Scheme 20

Ligand-induced reductive elimination

In the former section, we have seen that surface hydride complexes of late TMs tend to be unstable and decompose to metal(0), which eventually aggregates to nanoparticles. It is reasonable to assume that the reaction that contributes most conspicuously to this development is reductive elimination. In this section, we will discuss representative examples of reduction to metal(0) that are triggered by π-acceptors (CO) or soft (PMe_3) ligands, which stabilise low-valent TM complexes. This mechanistic pathway is only accessible to metal ions that undergo reductive elimination, typically rhodium, iridium, palladium, and platinum. A suitable illustration of this general phenomenon is given – once more – by the silica grafted allyl complexes of rhodium(III), which reacts with carbon monoxide or phosphines to give the complexes shown in Figure 7.

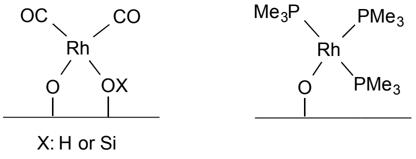
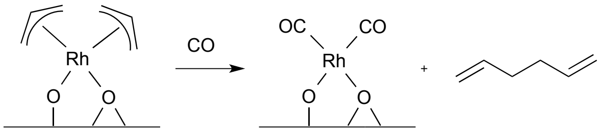


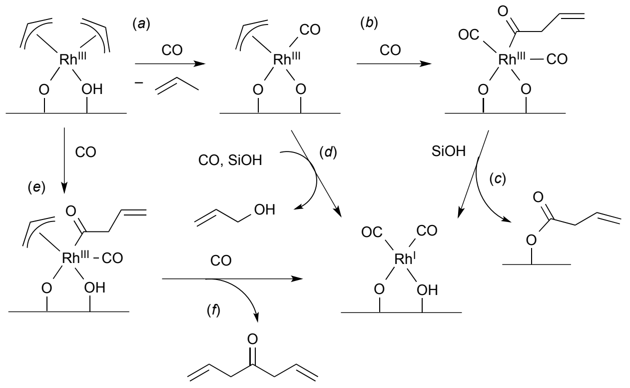
Figure 7

On silica surface with low proton content, that is, on silica$_{(400)}$ at high rhodium loading, the grafted bis(allyl) complex exists mainly as $[Rh(OSi\equiv)(\eta^3\text{-}C_3H_5)_2(SiOSi\equiv)]$. Upon reaction with CO, this grafted species reductively eliminates 1,5-hexadiene and forms monomeric $[Rh(OSi\equiv)(CO)_2(SiOSi\equiv)]$, which then spontaneously dimerises to $[Rh(OSi\equiv)(CO)_2]_2$ (Scheme 21).[117]



Scheme 21

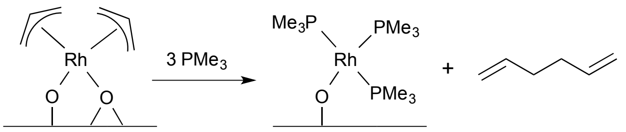
With higher surface hydroxyl content (that is, on silica$_{(200)}$ or at low loading on silica$_{(400)}$), propene was the main product upon exposure to carbon monoxide, and traces of allyl alcohol and 1,6-heptadien-4-one were observed. The reaction pathways shown in Scheme 22 rationalise these results.



Scheme 22

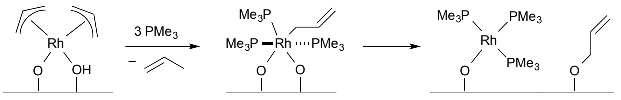
In the main pathway (*a*) of the reaction with CO, the protonation of an allyl ligand by silanol eliminates propene, which was the main gaseous product. The resulting grafted complex $[Rh^{III}(OSi\equiv)_2(\eta^3\text{-}C_3H_5)(CO)]$ undergoes CO insertion into the σ-allyl (*b*) to give an acyl complex. Reductive elimination from this species (*c*) generates surface esters, which were detected by IR spectroscopy. Allyl alcohol is formed from the monocarbonyl complex of Rh(III) by the combined reductive elimination/silanol condensation step *d*, whereas 1,6-heptadien-4-one is formed by CO insertion into the bis(ally) complex (*e*) followed by reductive elimination (*f*).[108]

Similarly, the reaction course of $[Rh(OSi\equiv)(XOSi\equiv)(\eta^3\text{-}C_3H_5)]$ with PMe_3 depends on the degree of dehydroxylation of the silica surface.[109] Upon exposure of a sample of the complex grafted on silica that had been dehydoxylated at ≥ 400 °C to PMe_3 (0.1 torr), 1,5-hexadiene and propene were released into the gas phase, and $[Rh(OSi\equiv)(PMe_3)_3]$ was formed. 1,5-Hexadiene is formed by reductive elimination of both allyl ligands from the grafted complex (Scheme 23).



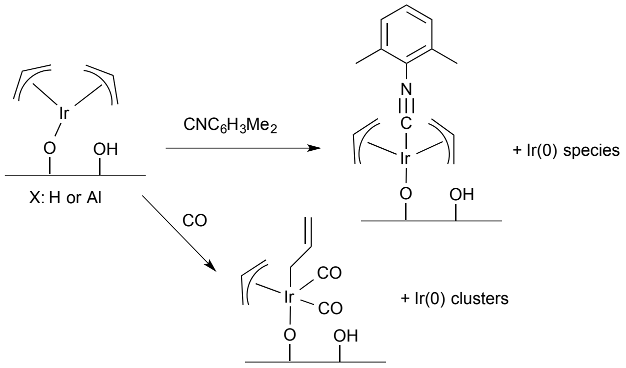
Scheme 23

The elimination of propene by protonation of an allyl ligand becomes the only reaction observed when the silica has a higher content of surface hydroxyls. In this case, the metal product was formulated as the Rh(III) σ-allyl bis(siloxo) complex $[Rh(OSi\equiv)_2(\sigma\text{-}C_3H_5)(PMe_3)_3]$, which tends to undergo reductive elimination of allyl and siloxo to give $[Rh(OSi\equiv)(PMe_3)_3]$ and a surface silyl allyl ether (Scheme 24).[109b] When exposed to H_2, $[Rh(OSi\equiv)_2(\sigma\text{-}C_3H_5)(PMe_3)_3]$ gives $[Rh(OSi\equiv)(PMe_3)_3]$ and a propene/propane mixture, which suggests heterolytic H_2 splitting.



Scheme 24

The coordination chemistry of the alumina-grafted bis(allyl) iridium complex, which has been investigated more recently, is similar.[62] The main difference with rhodium is that $[Ir(\eta^3\text{-}C_3H_5)_3]$ does not react with silica, but readily does with the more Brønsted acidic sites on alumina. The bis(allyl) grafted species reacts both with isocyanide and with carbon monoxide (Scheme 25).



Scheme 25

Exposure of the alumina grafted complex to a stoichiometric amount of 2,6-dimethylphenyl isocyanide gave the corresponding six-coordinated adduct and a secondary compound that was formulated as an iridium(0) species. The authors suggested that the formation of iridium(0) compounds on the alumina surface is due to the presence of environments that are much more reactive than the analogous sites of silica.[62]

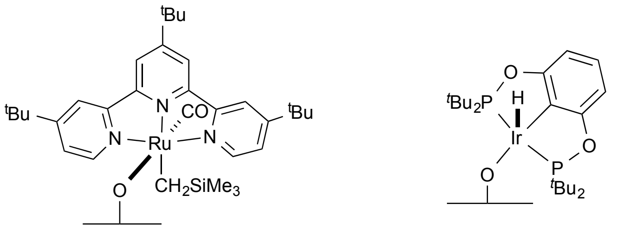
Differently from the reaction with isonitriles, exposure to carbon monoxide for five minutes gave a product containing one σ-allyl, one η^3-allyl, and two CO ligands, as indicated by ^{13}C NMR and IR spectroscopy. Under these conditions, only a small amount of the starting material was converted to the carbonyl complex. For an exposure longer than five minutes, the colour of the alumina turned from tan to blue-green. IR and ^{13}C NMR spectroscopy confirmed the presence of a second carbonylated species, and the data of the carbonyl frequencies were consistent with the formation of iridium(0) clusters. The ratio between the iridium(III) and iridium(0) carbonyl species did not change over time and even for exposure times to CO of more than one week. Also, such prolonged exposure did not cause the formation of other secondary products due, for instance, to the insertion of a CO molecule into the metal-allyl bond.

These selected examples substantiate that either soft or π-accepting ligands induce reductive elimination. They also show that this general process can stop at the level of relatively well-defined grafted complexes or go all the way to cluster or nanoparticle formation. Our recent results with the grafted pincer complex $[IrH(OSi\equiv)(POCOP)]$ (POCOP = 1,3-bis((di-*tert*-butylphosphino)oxy)benzene)[79] suggest possible ways to control this process, as discussed in the next section.

Grafting, quo vadis?

The aggregation processes discussed above for iridium can be dissected – at least ideally – into different stages, both of which are favoured by soft and/or π-accepting ligands that stabilise lower oxidation states. In the first step, iridium(III) undergoes reductive elimination to an Ir(I) complex. The second step of aggregation is the decomposition of the grafted complex to elementary metal, which implies the formation of metal–metal bonds. A multidentate ligand can inhibit the latter process if it does not dissociates from the metal and is bulky enough to prevent the formation of M–M bond.

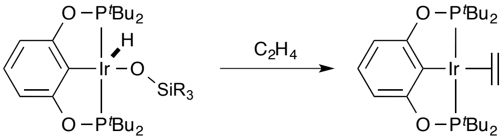
Although it has been recognized that chelating ligand may prove valuable to circumvent the formation of metal nanoparticles on highly acidic surfaces,[62] the examples discussed above show that little success has been obtained yet. However, ligands of higher denticity than bidentate have been barely used to stabilise complexes of late TMs grafted on silica. We are aware of only two examples with tridentate ligands, the terpyridyl complex $[Ru(OSi\equiv)(CH_2SiMe_3)(CO)(NNN)]$[68, 110] and our pincer hydride $[IrH(OSi\equiv)(POCOP)]$ (Scheme 26).[79]



Scheme 26

The preliminary tests in the catalytic hydrogenation of ethene and propene mentioned above (Scheme 9) indicate that, at difference with complexes containing mono- or bidentate ligands, $[IrH(OSi\equiv)(POCOP)]$ is stable under hydrogenation conditions and does not undergo aggregation. Indeed, the catalyst shows no induction period, maintains its colour during and after the hydrogenation reaction, is recovered intact after the catalytic hydrogenation of propene, and shows the same catalytic activity when reused up to 3 times.[79] Therefore, even if we cannot rule out that degrafting may occur during catalysis, the reaction must be reversible.

We suggest that the bulky multidentate pincer ligand stabilises the 16-electron configuration of $[IrH(OSi\equiv)$-(POCOP)] and protects the iridium centre from strong interactions with the silica surface and with other iridium ions. Furthermore, the POCOP ligand probably also plays a further role by affecting the stability of product of reductive elimination. We have recently found that [IrH (OSi ≡) (POCOP)] – and a soluble polysesquioxane (POSS) analogue thereof – reductively eliminates SiO–H in the presence of ethene (Scheme 27) or carbon monoxide to give the corresponding iridium(I) complexes, whereas higher alkenes (propene, 3,3-dimethylbut-1-ene, and 1-dodecene) did not react.[56]



Scheme 27

Accordingly, ethene has been reported to act as a "trapping ligand" for iridium(III) anilido hydride complexes such as [IrH(CO)(NHC$_6$F$_5$)(POCOP)] (11),[111] as it favours the formation of the corresponding iridium(I) ethene complexes, but we are not aware of analogous reactions with higher alkenes. Indeed, the X-ray structures of the alkene complexes [Ir(C$_2$H$_4$)-(POCOP)] and [Ir(C$_3$H$_6$)(POCOP)] suggest that the propene derivative is more sterically congested that its ethene analogue, which suggests that a stable iridium(I) complex must be formed for silanol elimination to occur. We are studying the reactivity of [IrH (OSi ≡) (POCOP)] with H$_2$ and alkenes to get insight into the mechanism of the hydrogenation reaction.

Overall, tridentate ligands may be regarded as privileged ligands for silica grafted species. Indeed, they form robust complexes, fulfilling the first requirement to prevent aggregation, and tend to fix the metal ion in a well-defined coordination environment. Also, high-sensitivity NMR-active nuclei (in particular ^{31}P) can be easily incorporated, which enormously simplifies the characterisation of the grafted complexes and yields a wealth of structural information.

In the specific case of pincer ligands, it should be noted that many of their complexes are polyhydrides, which makes them good candidates for grafting. Also, pincer complexes find application in important catalytic reactions such as CO$_2$ reduction,[112] alcohol dehydrogenation,[113] deuteration,[114] ammonia and N–H bond activation,[115] and hydrogenation reactions.[116] The development of silica grafted pincer catalysts may open new perspectives at the interface between homogeneous and heterogeneous catalysis.

Conclusion and outlook

The tendency of complexes of late transition metals grafted on an oxide surface (in particular silica) to undergo aggregation under reducing conditions and/or in the presence of soft or π-accepting ligands can be understood on the basis of basic coordination chemistry concepts. The role of reductive elimination in the stepwise process that leads from isolated surface complexes to the formation of metal nanoparticles is still awaiting systematic investigation, though. This process is particularly relevant for late TM complexes under hydrogenation conditions because the reductive elimination of silanol, which has a large thermodynamic driving force, results in degrafting of the complex.

Strategies to overcome the tendency to aggregation encompass the use of strongly bound multidentate ligands that stabilise mononuclear molecular species and inhibit the formation of metal–metal bonds. Grafted complexes of late TMs containing multidentate ligands with P donors are ideally suited for such studies. Like their prototype [IrH (OSi ≡) (POCOP)], they can be expected to form single species with a well-defined configuration with podality independent from the degree of dehydroxylation of silica.

When appropriately bulky, such ligands stabilise coordinatively unsaturated, 16-electron complexes that are intrinsically reactive, yet stable. They also offer numerous NMR spectroscopic handles (^{1}H, ^{31}P, and ^{13}C). Therefore, the use of rigid, bulky, multidentate phosphorus ligands offers unprecedented possibilities in terms of control of the chemical behaviour of the metal on the surface and of unprecedented ease of characterization.

Finally, as the soluble analogues of such future grafted complexes are well-studied catalysts for a number of important transformations, the development of such systems would bring chemists and engineers a step forward toward closing the gap between heterogeneous and homogeneous catalysts.

Acknowledgements

We thank Professor Jeroen A. van Bokhoven for inspiring the original project and Professor Christophe Copéret for the numerous useful discussions.

Notes and references

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† Furthermore, the pincer iridium(I) complex [Ir(C$_2$H$_4$)(POCOP)] (POCOP is 1,3,5-tris(di*tert*-butylphosphinooxy)benzene) has been anchored onto silica and alumina by cleavage of the O–P bond in the *para* position of the benzene backbone of POCOP.[117]

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Site isolated complexes of late transition metals grafted on silica: Challenges and chances for synthesis and catalysis

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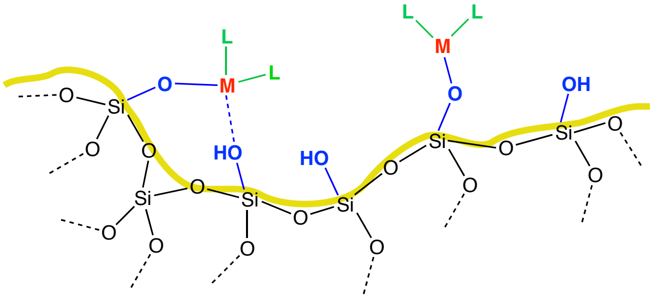

Grafting, quo vadis? The reasons for the aggregation of late transition metal complexes on oxide supports under reducing conditions and/or in the presence of π-accepting ligands are discussed, and strategies are suggested to prevent it.