Molecular design of heterogeneous catalysts: the case of olefin metathesis

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Within the context of sustainable technology, catalysis is a means to more efficient processes (lower energy demands, highly selective, waste-free), thereby providing a better use of raw materials. Industry relies heavily on heterogeneous catalysis to perform chemical transformations, but the development of these systems can be slowed down by the difficulty in understanding them, since they are often ill-defined and may contain several types of active sites (which can also be detrimental to selectivity). More recently, homogeneous catalysis has emerged, and it is probably because of a molecular understanding of chemical phenomena with well-defined systems that new processes have been rapidly set up. Our approach, called Surface Organometallic Chemistry (SOMC), has been to bring these two fields together: the result is a molecular approach to the design of heterogeneous catalysts. Within this short review, our strategy is delineated and the case of olefin metathesis is used to exemplify this approach. The design, the preparation and characterisation of a well-defined rhenacarbene are described. Based on a combined use of mass balance analysis, IR spectroscopy, advanced NMR techniques and EXAFS, it has been shown that $[Re(=CHtBu)(\equiv CtBu)(CH_2tBu)_2]$ reacts with a partially dehydroxylated silica at 700 °C to give a single surface complex: *syn*-$[(\equiv SiO)Re(=CHtBu)(\equiv CtBu)(CH_2tBu)(\equiv SiOSi\equiv)]$ (**1**). This surface complex **1** catalyses olefin metathesis at low temperatures and without co-catalyst. The structure and the activity of this type of catalyst are discussed and compared with other existing homogeneous and heterogeneous catalysis systems.

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Christophe Copéret received his degree of 'Ingénieur' in 1992 from Chimie Lyon, France (officially called CPE Lyon). A year before, he joined the PhD program of Purdue University, Indiana (USA) where he worked on the development of synthetic methodology through organometallic chemistry and catalysis under the direction of Prof. E.-i Negishi. In 1996, after obtaining his PhD degree, he joined the group of Prof. Sharpless at the Scripps Research Institute to work on selective oxidation reactions. He then accepted a full-time position at the CNRS (1998), where he is currently developing the surface organometallic chemistry of transition metals on metal oxides directed towards the generation of single-site heterogeneous catalysts.

Introduction

Catalysis deals with the acceleration and the control of reaction rate and, in turn, allows the understanding and the development of efficient chemical processes that are low-energy, highly selective chemical transformations giving no by-products. This field of chemistry has been traditionally fragmented into three distinctive areas: enzymatic, homogeneous and heterogeneous catalysis. In term of industrial developments, it is often better—when possible—to develop heterogeneous catalysts, because they can be more readily transposed to continuous processes and provide an easy way to separate the products from the catalytic phase. Yet in the past 40 years, homogeneous catalysis has undergone a rapid development and led to several high tonnage chemical processes.[1,2] One reason stems from the level of understanding of molecular chemistry, which can readily help to identify the key requirements for better catalytic systems (design of active sites through structure-activity relationship), hence their rapid development. In contrast, heterogeneous catalysts are often more ill-defined (unknown and numerous active sites), which can impede their selectivity and secondly hinder a rational improvement of such systems. Thus, with this in mind, the proposed strategy is to design the active sites of heterogeneous catalysts with a similar approach to that implemented in homogeneous catalysis in order to generate well-defined systems.

The first step is to start by analysing the desired chemical transformation, that is by looking at thermodynamic data and by postulating the chemical events (elementary steps) necessary to perform the desired reaction. Such an approach

defines, *ab initio*, the postulated intermediates and will therefore condition what type of active site (or its precursor) should be generated. The second step consists in constructing the active sites through a careful understanding of the interaction of molecular complexes with a surface. This approach, termed Surface Organometallic Chemistry (SOMC), is targeted at obtaining heterogeneous catalysts with well-defined active sites.[3–6] The third step entails the testing of these catalysts in order to gather data on their activities, selectivities and lifetimes, which will be used to decide upon a strategy to improve the catalytic system (new generation of catalysts in the development loop).

In the next section, each step of the process will be detailed and the following section will illustrate this approach through the development of catalysts for olefin metathesis.

General strategy to design and test a heterogeneous catalyst prepared *via* SOMC

Design of the targeted catalytic system

Chemical reactions rely on successive bond-breaking and bond-making processes, and over the years molecular chemistry has established most, if not all, the possible elementary steps. In homogeneous catalysis, the strategy is to prepare a well-defined stable intermediate, which often consists of a transition metal decorated with the proper ligands: one propagating ligand—the reactive bond (or in some cases just a vacant site)—and ancillary ligands, which will control the stability of the complex (life time) and confer the stereoelectronic properties of the reactive centre (control the activity and the selectivity). In surface organometallic chemistry, the surface will also play a role and must be therefore considered as a ligand (Scheme 1). Depending on the reaction and its corresponding

catalytic cycle, it will be necessary to propose an adequate system based on the fundamental rules of organometallic chemistry. For instance, homogeneous catalysis has taught us that olefin polymerisation catalysts will require electrophilic metal-alkyl complexes,[7] while olefin metathesis necessitates metal-alkylidene systems (*vide infra*). Conversely, oxidation catalysts will probably include oxo, peroxo, or alkylperoxy ligands[8] while hydrido complexes can be useful in alkane chemistry.[9–11]

Consequently, the design of a heterogeneous catalyst will be based on using the concepts and the level of understanding of molecular chemistry (identification of potential intermediates) and transferring them to the chemistry of surfaces in order to generate well-defined active sites dispersed on a support.

Preparation and characterisation of the catalyst *via* SOMC.[6]

After identifying the targeted metal and the desired coordination sphere, it is necessary to devise a strategy to implement them.

Firstly, it is essential to understand the surface structure of the support and how it will interact with a metal complex. Therefore, the solid has to be understood *via* the measurement of its surface area and morphology (non-porous, porous, mesoporous), but also by understanding its surface structure. The surface of oxide supports (M_xO_y) are typically composed of various types of (M–OH) and (M–O–M) units, which should be identified and quantified *via* spectroscopic or chemical methods (number of Lewis and Brønsted acidic sites).

Secondly, the interaction of a molecular complex with a surface needs to be investigated to understand the factors that influence the coordination sphere of the surface complex in order to generate a well-defined system. Therefore, it is necessary to have a "palette" of characterisation tools to probe the
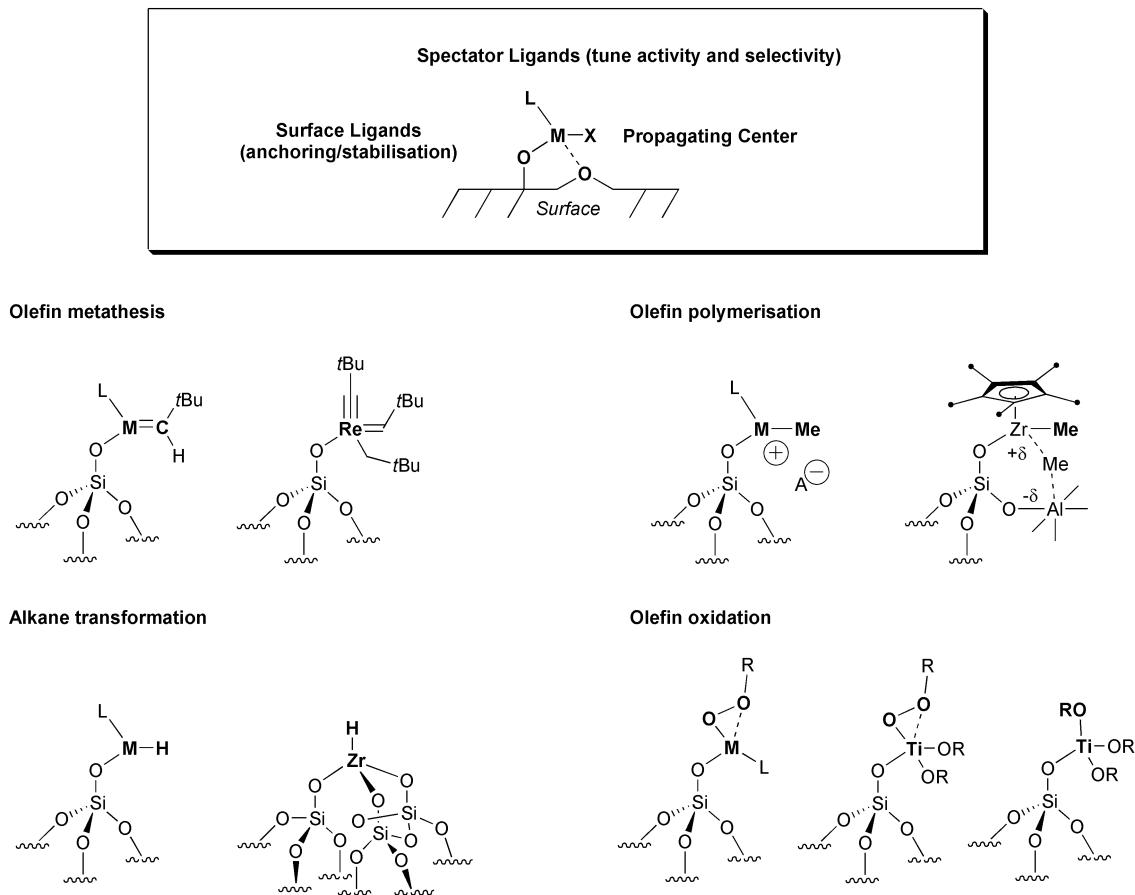
Scheme 1 Molecular approach to the construction of active sites of heterogeneous catalysts.

structure of the surface complex,[12] its exact coordination sphere and the surroundings of the active centre (Scheme 2). These tools can include (1) chemical reactivity studies (including the grafting step) in combination with *in situ* IR spectroscopy to obtain information on the grafting stage and the reactivity of the surface complex towards further treatments, (2) solid state NMR spectroscopy to determine the nature of the ligands around the metal centre (and their dynamics), (3) EXAFS to further investigate the coordination sphere of the metal centre (distances and average coordination numbers), (4) ESR, UV and XANES to probe the oxidation state, the electronic state and the geometry of the surface metal complex. These techniques, together with the use of molecular models,[13–16] molecular modelling and surface science techniques (BET, XPS, …) will provide a molecular understanding of the reaction of an organometallic precursor with a surface and help to establish the molecular structure of the surface complex.
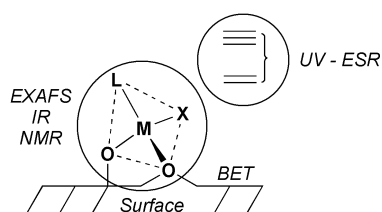
Scheme 2 General strategy to investigate the coordination sphere of a surface complex.

Catalyst testing and improvement of catalytic systems

After ascertaining the structural identity of the surface complex, its reactivity towards the targeted substrate is then investigated. It is typically performed by looking at the reaction conversion and selectivity in batch reactors at various temperatures. However, the use of continuous flow reactors is often highly desirable (especially in gas–solid reactions) to obtain better kinetic data (activation energies, selectivity through contact time studies, identification of primary products, deactivation kinetics, …). Catalytic testing in combination with an understanding of the fate of the catalyst through its characterisation at various stages of the catalytic test are very important to assess structure-activity relationships, which will allow a strategy for improvement/development of the catalysts to be proposed. Based on this approach, a new generation of catalysts can be proposed. This is how the loop of improvement proceeds, as in homogeneous catalysis, the ultimate goal being a viable chemical process (Scheme 3).
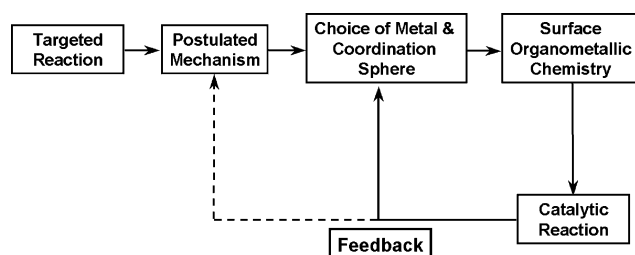

Scheme 3 Strategy of development of heterogeneous catalysts *via* Surface Organometallic Chemistry.

Preparation of well-defined heterogeneous catalysts for olefin metathesis *via* SOMC

### Background, strategy and design

The olefin metathesis reaction was incidentally discovered using heterogeneous catalysts while studying the reactivity of propene–alkane mixtures over $Mo(CO)_6$ supported on alumina.[17] Under these conditions, propene was transformed into a mixture of ethylene and butenes, a disproportionation reaction later named olefin metathesis. The current industrial catalysts typically used are MoO_3 or WO_3 supported on silica or alumina, which require high reaction temperatures (Scheme 4).[18] Despite the discovery by BP a few years later of a catalyst, Re_2O_7/Al_2O_3, that works at much lower temperatures (typically 35 °C),[19–21] it is still not used today in a large scale production process.[22] It is noteworthy that this latter system can also be used to transform functionalised olefins when activated by organotin agents.[23–25] Despite years of research, the exact nature of the active sites or the initiation steps in these types of heterogeneous catalysts are still unknown.[20,21] This had, in fact, led to important discussions in the seventies to decide what was the most likely reaction mechanism to explain olefin metathesis. Today, it is widely accepted that metallocarbenes (and metallacyclobutanes) are the key intermediates [eqn. (1)], as proposed by Herisson and Chauvin of the IFP in 1971.[26]
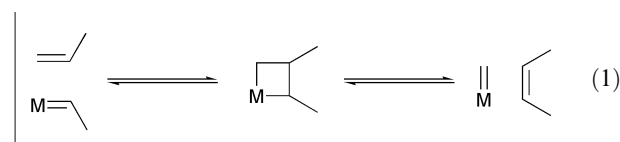
This proposition directed the search for stable metallocarbene complexes, which could be used in homogeneous catalysis.[27,28] After about 30 years of investigation, two main classes of well-defined homogeneous catalysts have emerged: the d^0 early transition metals (groups 6 and 7)[29–35] and the d^4 Ru systems (Scheme 4).[36–39] The latter system has changed the field of olefin metathesis by providing easily handled catalysts compatible with most functional groups used in organic synthesis. Noteworthy are the requirements for basic ligands to obtain a good activity, which is exactly the contrary to what has been found for d^0 systems, which are all based on generating highly electrophilic systems.[30] For well-defined homogeneous catalysts, the initiation step has been established (cross-metathesis), and their stability allows TON of more than $\frac{1}{2}$ million to be reached in some cases.[40] Moreover, while the de-activation pathways have been understood to a good extent,[41] they have not yet been solved and regeneration is a problem.

In contrast, heterogeneous catalysts are not as well understood at the molecular level, but they are readily regenerated under calcination and constitute the main systems used by the chemical industry. Re_2O_7/Al_2O_3 is still a promising system, but the low concentration of active sites of unknown nature has slowed down the search for improved catalysts. Several
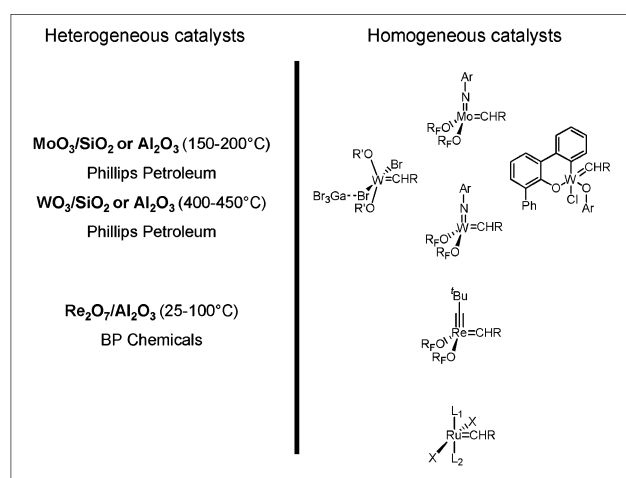
Scheme 4 State of the art in heterogeneous and homogeneous catalysis applied to olefin metathesis.

homogeneous models have been prepared (Scheme 5) and showed very good activity, but are equally difficult to understand (initiation-deactivation).[42]

One question arises: is it therefore possible to generate a well-defined rhenacarbene at the surface of a support? This is a question that falls into the area of surface organometallic chemistry.[4,43–45]
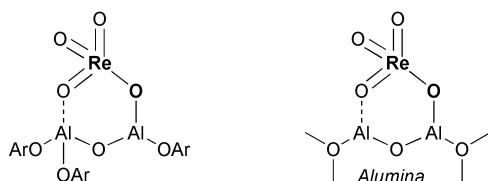
Scheme 5 Homogeneous model and its heterogeneous catalyst equivalent.

Choice of support

In order to have a better understanding of the system, the first step is to select a support. The first criterion is to work with a support that does not generate parallel reactions (neutral) and the second one is to have a reasonable knowledge of its surface structure in order to understand its reactivity with an organometallic complex. Silica is a good candidate, since it is available as regular 50 nm spheres, free of metal and carbon traces and with a high surface area (200 m^2 g^{-1}). It is a neutral support having a surface covered with siloxane bridges (of various sizes) and silanols (of various types: isolated, vicinal and gem), of which the concentrations can be controlled by thermal pre-treatment.[46–48] Silanols are orders of magnitude more reactive than siloxane bridges, and will be used to graft the metal via a (Si–O–M) bond. If a thermal treatment at high temperatures (above 600–700 °C) under vacuum is applied, the surface is mainly composed of isolated silanols (0.7 ± 10% OH nm^{-2}) besides siloxane bridges, while at lower temperatures the concentration in silanols is higher (1.4 ± 10% OH nm^{-2} at 500 °C and 3.5 ± 10% OH nm^{-2} at 200 °C) and favours the presence of vicinal and gem silanols. The use of higher temperatures will lower the concentration of surface silanols, but also favours the formation of strained siloxane bridges, which can become reactive. Based on these observations, it is possible to generate selectively mono-grafted complexes by using a silica treated at 500 °C and higher (typically 700 °C), while the use of dehydroxylation temperatures in the 200–300 °C range provides an access to bis-grafted complexes (Scheme 6).[49–51]

Choice of molecular precursor

The goal is to generate a rhenacarbene on the surface of silica, and one possible route is to use a molecular complex containing both a carbene ligand and a reactive bond, a metal-alkyl for example, which will react with the surface silanols and thus generate a covalent bond between the support and the metal centre. [Re(≡CtBu)(=CHtBu)(CH$_2$$t$Bu)$_2$],[52,53] a well-defined molecular complex, has been reported and fulfills the aforementioned requirements. Its reactivity with silica and the methodology applied for the characterisation of the corresponding surface complex will be detailed hereafter.

### Preparation and characterisation (Surface Organometallic Chemistry)

Firstly, in situ IR spectroscopy experiments show that there is a chemical grafting of the complex since the surface silanols are consumed during the sublimation step. Secondly, mass balance analysis shows that about 1.06 ± 0.13 equiv. of CH$_3$$t$Bu
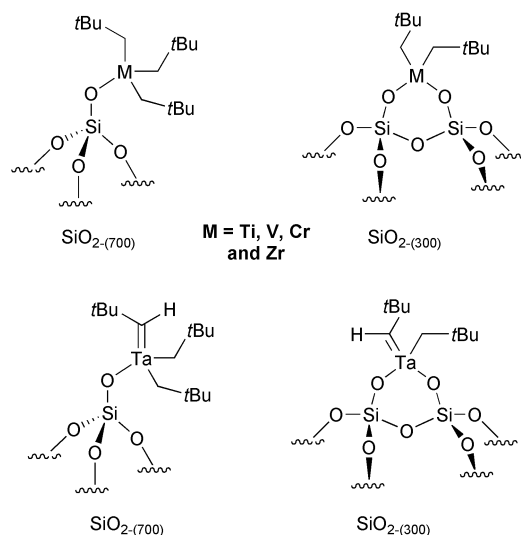

Scheme 6 Effect of the temperature of partial dehydroxylation of silica (SiO$_{2-(T)}$; T = temperature of dehydroxylation) on the resulting surface complex structure: the tuneable hapticity of silica.

evolved during grafting and that the corresponding solid contains 15.5 ± 0.8 carbons per grafted Re. Furthermore, 3.9–4.7%$_{wt}$ of Re is typically grafted on silica partially dehydroxylated at 700 °C, which corresponds to the consumption of 0.21–0.26 mmol g^{-1} of silanol groups (0.63–0.78 OH nm^{-2}) and thus to the amount of silanols accessible for bulky complexes on a silica partially dehydroxylated at 700 °C (vide supra).[54] Therefore, the data are consistent with the loss of approximately one equivalent of neopentane during the grafting, leaving on average three "neopentyl-like" ligands around the metal centre (Scheme 7).

Further investigation of the structure was undertaken through the use of 1D and 2D solid state NMR spectroscopy.[54–56] While the ^{1}H solid state NMR spectrum of **1** displays signals at 11.0, 3.0, 2.6, 1.5, 1.3 and 1.1 ppm (Scheme 8), which are assigned to the carbene proton (=CH), the two diastereotopic protons (CH$_a$H$_b$) and the methyl groups of the three different tBu groups, the ^{13}C CP/MAS spectrum of the natural abundance sample gives little information. On
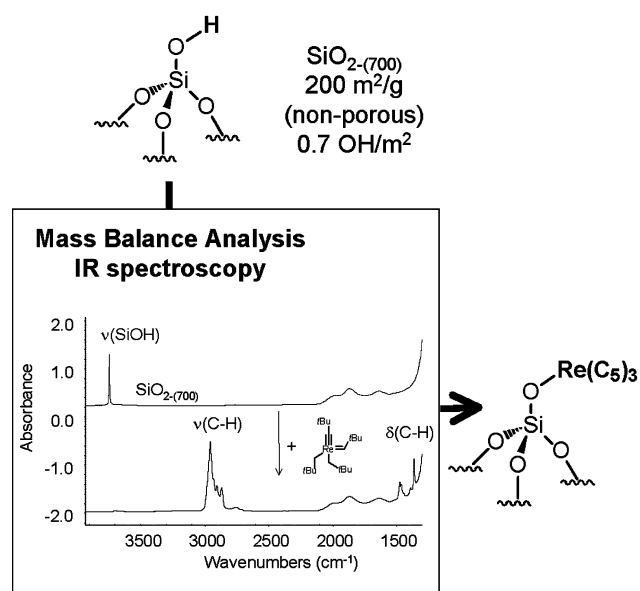
Scheme 7 Initial proposed structure from mass balance analysis (elemental analysis and gas evolution during grafting) and IR spectroscopic data.
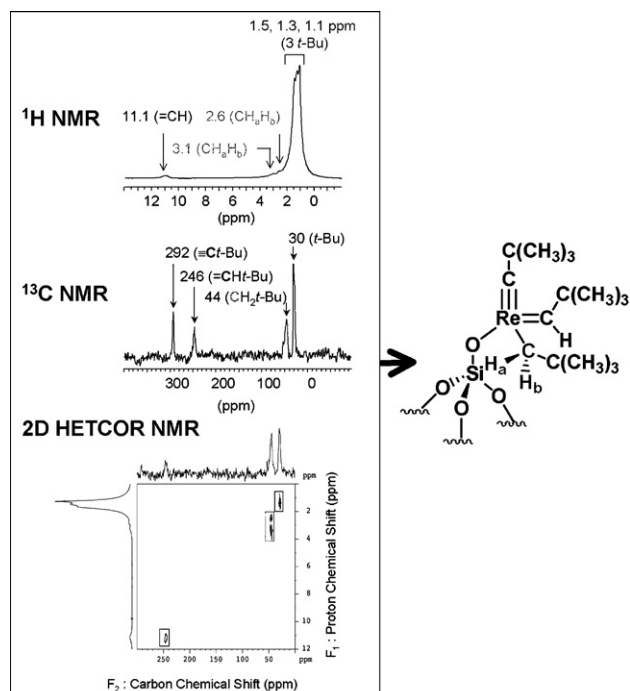
Scheme 8 1D and 2D HETCOR solid state NMR spectroscopy, a tool to determine structures on surfaces.

the other hand, applying H-decoupled ^{13}C solid state NMR on a 10% ^{13}C-enriched sample provided evidence for the presence of three types of hydrocarbyl ligands around Re: a neopentyl (46 ppm, CH_2tBu), a neopentylidene (246 ppm, $=CHt$Bu), and a neopentylidyne (292 ppm, $\equiv Ct$Bu).[54] Moreover, 2D HETCOR (heteronuclear correlation) solid state NMR using magic angle spinning (MAS) clearly allowed these assignments to be confirmed.[56] Firstly, by using short contact times during the pulse sequence, it is possible to selectively detect the protons directly linked to a carbon. For example, the two signals at 2.6 and 3.0 ppm attributed to the two diastereotopic protons are indeed borne by the same carbon, while that at 11 ppm in the H dimension correlates with that at 246 ppm in the C dimension, confirming their assignments to the carbenic fragment. Using longer contact times (> 1 ms), it is possible to observe extra correlation peaks, which arise from longer range dipolar through-space interactions, and which allow the full ^{13}C NMR spectrum of **1** (including all quarternary carbons) to be reconstituted. Combining the information given by 1D and 2D solid state NMR spectroscopy provides a relatively complete NMR data set for the surface compound, which is fully consistent and indicates that the reaction of $[Re(\equiv Ct$Bu$)(=CHt$Bu$)(CH_2t$Bu$)_2]$ with $SiO_{2-(700)}$ leads to the formation of $[(\equiv SiO)-Re(\equiv CtBu)(=CHtBu)(CH_2tBu)]$, **1**, as the sole surface species.

As in solution chemistry, one would like to have more information on the coordination sphere of the metal, which is typically obtained by using X-ray crystallography. Silica is amorphous, but EXAFS can nonetheless allow the coordina-

tion sphere of surface complexes to be probed and identifies the first neighbours of the heavy element and their distances. EXAFS data from the Re–surface complex (Scheme 9) agree with what has been proposed from the NMR data, that is two carbons at relatively short distances (not resolved at 1.79 Å), corresponding to the ($=CHt$Bu) and ($\equiv Ct$Bu) ligands, another carbon and an oxygen atom at larger distances (not resolved at 2.01 Å), corresponding to the (CH_2tBu) and ($\equiv Si O$) ligands. However, EXAFS data point to the presence of an extra ligand, an oxygen at 2.42 Å, probably arising from a dative bond from a siloxane bridge to the rhenium centre. Furthermore, in solution chemistry, it has been shown that measuring J(C–H) coupling constants can provide further insight into the way perhydrocarbyl ligands interact with the metal since they are directly correlated with the hybridisation of the carbon atoms.[57] Scalar information are difficult to obtain in solid state NMR since dipolar interactions overshadow scalar information, nonetheless it is possible to extract this through J-resolved 2D NMR spectroscopy.[58] Therefore, the corresponding spectrum presents the following features (Scheme 9): a quadruplet [q, $J_{C-H} = 126$ Hz, 29 ppm, CH_3 (tBu)], a triplet (t, $J_{C-H} = 126$ Hz, 46 ppm, CH_2tBu), a doublet (d, $J_{C-H} = 110$ Hz, 246 ppm, CHtBu) and a singlet (s, 292 ppm, CtBu). While all the splitting patterns and most of the J_{C-H} values correspond to what is expected for each type of coupling system, the J_{C-H} value of the doublet is quite low for an sp^2 carbon, indicating that this C–H bond is probably elongated and that the (Re–C–H) bond angle is distorted from the typical 120° value.[59,60] In fact, the J_{C-H} value has been correlated to the bond angle and in this case would correspond to a bond angle on the order of 85° (Scheme 9). Such a type of interaction points towards a *syn* configuration of the carbene ligands (low coupling constant)[53,61,62] and the presence of an extra ligand (pentacoordinated complex).[63]

In conclusion, by assembling all the data, it is possible to have a molecular view of surface complex as in homogeneous catalysis.

Comparison with molecular organometallic chemistry: the use of molecular models

Another important tool to obtain further insight into surface organometallic chemistry is the use of soluble molecular models of silica, like alkyl silanols or polyoligomeric silsesquisioxanes (POSS).[13–16] Upon reaction of the molecular complex with either [Ph$_3$SiO–H] or [Si$_{POSS}$O–H] in benzene solution (Scheme 10) the corresponding monosiloxy complexes [Ph$_3$SiO–Re($\equiv Ct$Bu$)(=CHt$Bu$)(CH_2t$Bu$)$] and [Si$_{POSS}$O–Re($\equiv Ct$Bu$)(=CHt$Bu$)(CH_2t$Bu$)$] are formed, like those observed for the silica surface.[54,56] Both of these products are, however, obtained as a 10-to-1 mixture of the *syn* and the *anti* rotamers, contrary to the surface complex, which is obtained stereoselectively as the *syn* rotamer according to the NMR data. Note that the chemical shift data for the *syn* rotamers of the molecular complex exactly match those obtained for the surface complex, while the *anti* rotamers have quite different chemical shifts.[53] Rotational isomers (rotamers) are common in the organometallic chemistry of alkylidene complexes. Some alkylidene organometallic syntheses yield only one rotamer
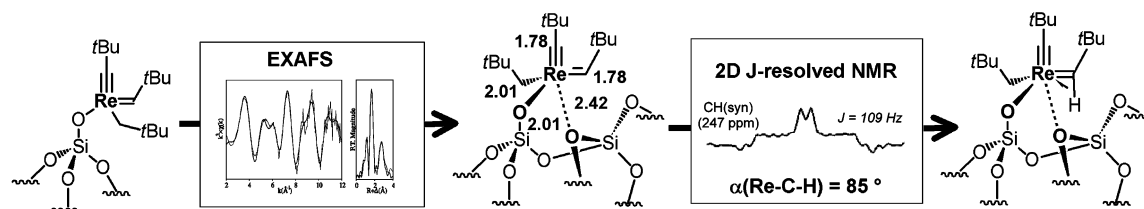
Scheme 9 Refinement of the structure through the combined use of EXAFS and 2D J-resolved solid state NMR spectroscopy.
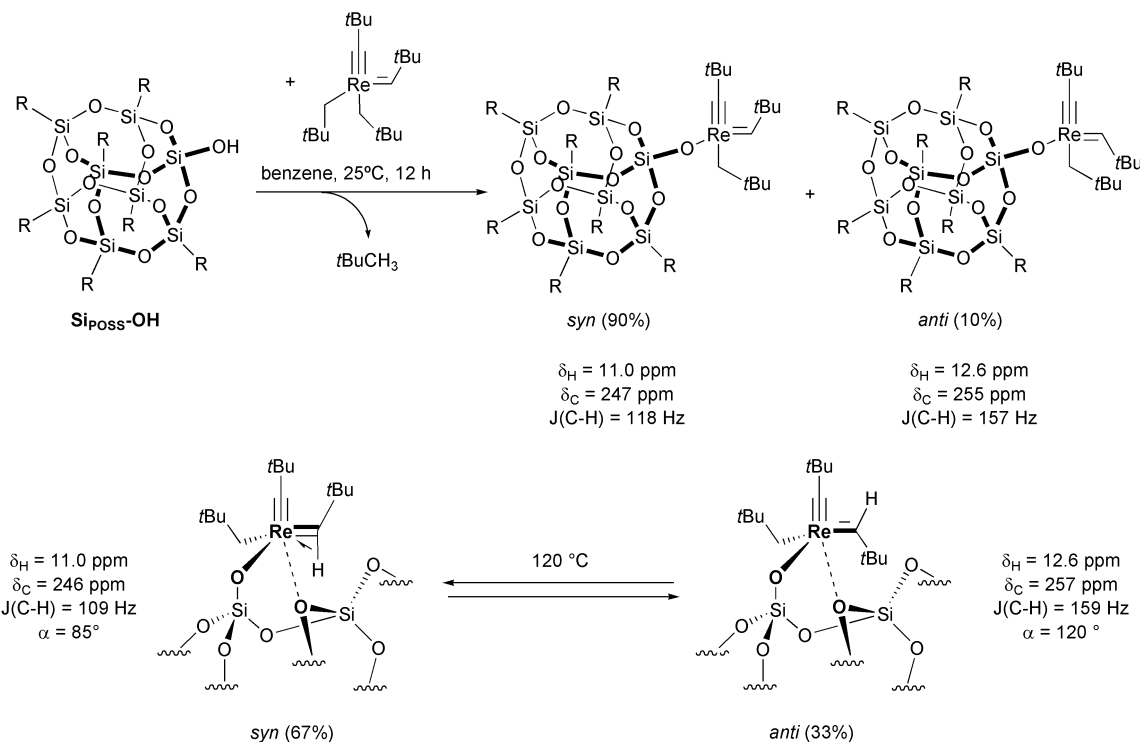
Scheme 10 Comparison between molecular and surface complex equivalents.

(usually the *syn* one), which can be generally converted into a mixture of the *syn* and the *anti* rotamers either thermally or photochemically. Upon heating the surface complex *syn*-**1** at 120 °C under Ar for 30 min, new sets of NMR signals in the ^{1}H and ^{13}C NMR spectra appear, which correspond to those of the *anti* rotamers of the molecular complex. These assignments were further confirmed by 2D HETCOR and *J*-resolved solid state NMR spectroscopies. The *syn/anti* ratio is approximately 2.0 ± 0.5, which corresponds to a $\Delta G°$ of about 2 ± 1 kJ mol^{-1} at 120 °C. This ratio does not evolve upon cooling to room temperature. Similarly, upon exposure of the *syn* complex to daylight for a couple of days, a *syn-anti* isomerisation is also observed (*syn/anti* = 1.5). As in solution chemistry, carbene on surfaces can be present as *syn* and *anti* rotamers. Yet, upon grafting, the *syn* isomer is the sole isomer obtained, which shows that the grafting step is stereospecific.

Understanding of the grafting mechanism.[56]

Based on these data, the grafting was further investigated in order to understand the origin of the stereospecificity of grafting. First, grafting of [Re($\equiv$CtBu)(=CHtBu)(CH$_2t$Bu)$_2$], specifically ^{13}C-enriched at the neopentyl and neopentylidene carbons, onto SiO$_{2\text{-}(700)}$ provided a sample that displayed no carbynic resonance in both the CP/MAS and direct excitation ^{13}C solid state NMR spectra. The absence of scrambling of the ^{13}C-label into the carbynic position shows that the neopentylidyne is a spectator ligand during grafting.[64] Therefore, the silanols must react either with the neopentylidene and/or the neopentyls, which can readily be probed by using deuterated silica (prepared *via* exchange of the surface silanols with D$_2$O). The grafting onto deuterated SiO$_{2\text{-}(700)}$ yielded undeuterated and monodeuterated neopentane, whose isotopic composition was consistent with a grafting mechanism that took place *via* direct electrophilic cleavage ($61 \pm 10\%$) and a two-step mechanism ($39 \pm 10\%$) involving addition followed by α-H abstraction (Scheme 11). Since the molecular precursor contains two alkyl ligands for one alkylidene ligand, the reactivity towards silanols of the alkyl and alkylidene moieties are in fact similar. In solution chemistry, the reaction of

[Re($\equiv$CtBu)(=CHtBu)(CH$_2t$Bu)$_2$] with Brønsted acids (HX, X = Cl, OC$_6$F$_5$, BF$_4$, OTf, …) gives the products resulting exclusively from protonation onto the alkylidene moiety, [Re($\equiv$CtBu)(CH$_2t$Bu)$_3$X],[53] which can be isolated in fairly good yields (60–80%), and their transformation into the corresponding alkylidene complexes only takes place upon the addition of donor ligands such as pyridine. By comparison, its reaction with silica directly gives [($\equiv$SiO)–Re($\equiv$CtBu)(=CH-tBu)(CH$_2t$Bu)($\equiv$SiOSi$\equiv$)] (**1**), which shows that the surface plays a role. The presence of a siloxane bridge (donor ligand) in **1** as observed by EXAFS suggests that the surface induces the spontaneous extrusion of the neopentyl ligand in [($\equiv$SiO)–Re($\equiv$CtBu)(CH$_2t$Bu)$_3$] to form **1**.

Catalytic reactivity

Preliminary catalyst testing. After preparing and characterising a well-defined rhenacarbene on silica, the next step has been to evaluate its reactivity towards olefins. This is typically carried out by contacting propene onto the catalyst in a batch reactor at 25 °C. Using 0.2% of catalyst, the thermodynamic equilibrium (30% conv.) is reached within 50–60 min, with an initial rate on the order of 0.25 mol mol^{-1} s^{-1}.[54,65] Note that the molecular precursor is not active in olefin metathesis, which shows the dramatic effect of the siloxy substituent, probably *via* an increase of electrophilicity of the metal centre.[3] A 3:1 *E*:*Z* ratio of butene stereoisomers (thermodynamic mixture) is obtained at the end of the reaction, while it is slightly lower (2.5:1) at the very beginning of the reaction, which probably indicates the intrinsic selectivity of the catalyst (Scheme 12). Such a selectivity—in favour of the *E* olefin—is expected at zero conversion for the metathesis of terminal olefins like propene since the stereochemical outcome of the reaction is usually related to the relative stability of the metallacyclobutane intermediate, that is by minimizing [1,2] interactions. Therefore, formation of *E*-2-butene through an intermediate having two substituents in equatorial arrangements is favoured over *Z*-2-butene, which involves an intermediate having the substituents in both equatorial and axial arrangements.[66] Beside the self-metathesis products of propene, 0.7 equiv of
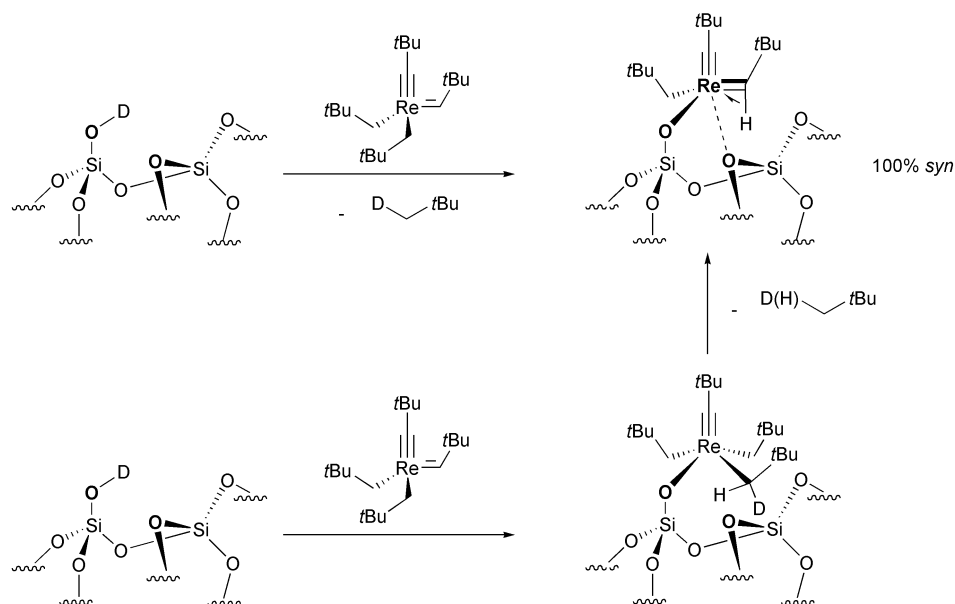
**Scheme 11** Reaction of [Re(≡C*t*Bu)(=CH*t*Bu)(CH₂*t*Bu)₂] with the silica surface: mechanisms of grafting.

neopentyl-containing products are also detected, namely 3,3-dimethylbutene and 4,4-dimethyl-2-pentene as a 3:1 mixture. They correspond to cross-metathesis products and therefore identify the initiation step (Scheme 13). The relative ratio in cross-metathesis products is also explained by the relative stabilities of the metallacyclobutane intermediates, for which [1,2] interactions are avoided and [1,3] interactions are minimised.[66] Note that, in contrast, the initiation step is still not fully understood for classical heterogeneous catalysts such as Re₂O₇/Al₂O₃.

Similarly, *Z*-3-heptene is converted efficiently into an 1:1 mixture of 3-hexenes and 4-octenes with an initial rate of 0.7 mol (mol Re)⁻¹ s⁻¹.[65] The initial ratios for 3-hexenes and

4-octenes are 3:4 and 6:10. They are constant up to 45% conversion and then reach 7:1 (thermodynamic equilibrium) as conversion proceeds. In the case of internal olefins, the partial retention of configuration depends on the minimisation of [1,3] interactions in the metallacyclobutane intermediates (Scheme 14).[66] Furthermore, these constant *E*:*Z* ratios show that 3-hexenes and 4-octenes are primary products.
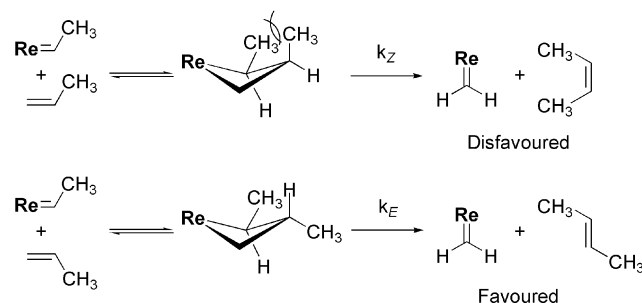
Scheme 12 Initial stereoselectivity in propene metathesis (minimisation of [1,2] interactions).
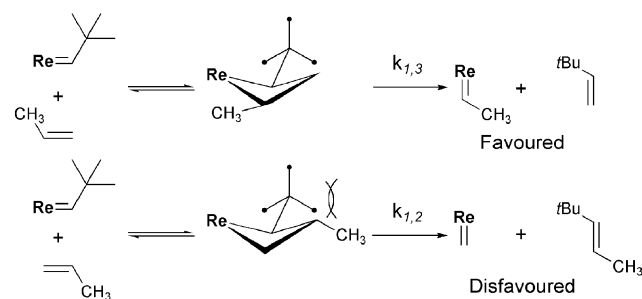
Scheme 13 Initiation step with a well-defined metallocarbene.
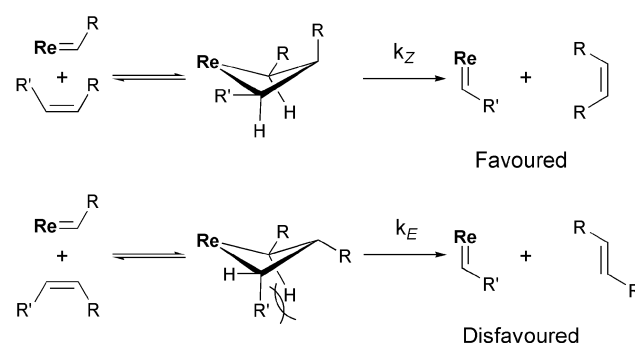
Scheme 14 Initial stereoselectivity for the metathesis of *Z*-olefins (minimisation of [1,3] interactions).

The metathesis of bulky olefins is also possible with this system. For example, isobutene is converted into 2-3-dimethyl-2-butene and propene–isobutene mixtures lead to 2-methyl-2-pentene, besides the self-metathesis product of propene. Finally, the reactivity of **1** towards functionalised olefins is also noteworthy, and currently up to 900 TON can be reached in the metathesis of methyl oleate.

Comparison with other systems. First of all, by using SOMC, well-defined group 5 and 6 metallocarbenes and carbynes have also been prepared and fully characterised using the same rigorous methodology (Scheme 15).[55,67,68] The activities (initial rates in mol mol⁻¹ s⁻¹) in propene metathesis under identical experimental conditions (Table 1) are as follows: Mo (0.53) ∼ Mo = NH (0.47) > Re (0.25) ∼ W (0.23) ≫ Ta (inactive). Moreover, in the case of the metathesis of methyl oleate, the following order of stability towards the ester functional group has been observed: Re ∼ W > Mo.[69] Both of these

M = Mo and W
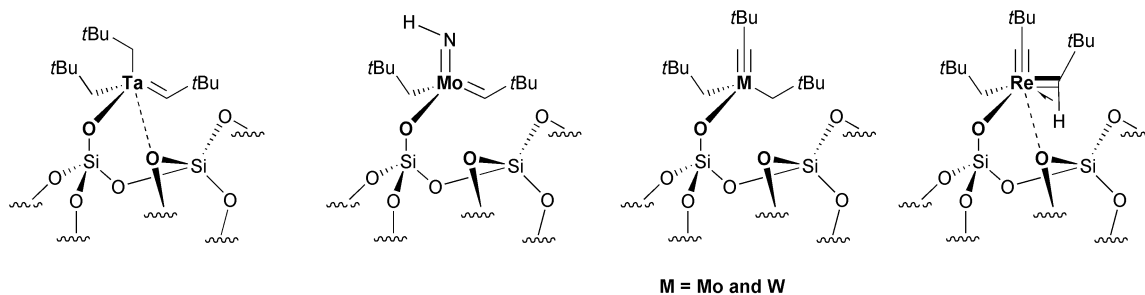
Scheme 15 First generation of olefin metathesis catalysts prepared *via* SOMC.

results parallel quite well what has been observed for related homogeneous systems.

Secondly, this catalyst, **1**, is as active and more robust than Re-based homogeneous systems. For example, $[Si_{POSS}O–Re(\equiv CtBu)(=CHtBu)(CH_2tBu)]$ decomposes rapidly in the presence of olefins while $[\{R_{F6}O\}_2Re(=CHtBu)(\equiv CtBu)]$ reaches a TON of 25 in the metathesis of methyl oleate.[70] On the other hand, it is still far from the current best homogeneous systems such as $[\{RO\}_2Mo(=CHtBu)(=NAr)]$, which reaches initial rates of 2–8 mol mol^{-1} s^{-1} and TON on the order of 10 000 (terminal and internal olefins)[71,72] or $[Cl_2Ru(=CHR)(PCy_3)L]$, with TON exceeding $\frac{1}{2}$ million for various substrates (diallylmalonate, octene and methyl oleate), depending on the substituent on the heterocyclic carbene ligand L.[40]

Finally, classical heterogeneous catalysts are comparatively less active, even when using high temperature conditions (Table 1). Moreover, highly branched or functionalised olefins are still a problem and, for example, the metathesis of methyl oleate is typically in the 25–160 TON range, after activation by tin reagents, depending on the support.[25] In the case of the surface complex **1**, cross-metathesis is clearly the initiation step and therefore its behaviour is identical to that of well-defined homogeneous catalysts. It is, therefore, easier to understand this system than classical heterogeneous catalysts such as the Re_2O_7/Al_2O_3 system, in which less than 2% of the Re is active.[73,74] A new generation of catalysts has appeared, such as methyl trioxorhenium supported on silica–alumina, which are compatible with a variety of functional groups, but again the nature of the active sites is still ill-defined.[75–77] Note also that well-defined silica-supported systems, such as $[\equiv SiO–ReO_3]$, are nearly inactive.[78–81] As shown with **1**, for which the carbene is already set, silica is not a problem *per se* in terms

of activity in olefin metathesis, however, the formation of the necessary carbene intermediate from oxo ligands is probably the most difficult step for $[\equiv SiO–ReO_3]$ (Scheme 16). In contrast, Re oxo species on alumina are readily converted into carbene intermediates, but the initiation process has yet to be clarified.[18,82–84] It is fair to say that catalysts prepared *via* surface organometallic chemistry provide a molecular insight into heterogeneous catalysts, which is a new way to think about these systems. Further developments in olefin metathesis catalysed by heterogeneous catalysts are currently in progress.
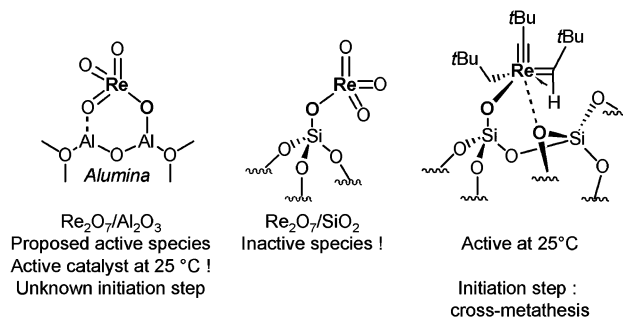
Scheme 16 Comparison of Re-based heterogeneous catalysts.

Future and outlook

In conclusion, these types of heterogeneous catalysts display a level of molecular understanding and activities unprecedented in the field of heterogeneous catalysis. The active site is well-defined, the initiation step understood and the activity quite high (initial rates and TON). Preliminary results are encouraging and emphasise a further need to understand such types of systems. Several questions already arise: what is the fate of the catalysts? Does it deactivate and how? Can we understand its pathway of deactivation and prevent it? Is it possible to regenerate such types of catalysts? Through these studies, it should be possible to transfer the knowledge accumulated on this "model" system to more complex systems used in industry and to potentially give answers to unsolved problems, which have typically been difficult to address due to the complexity of classical heterogeneous catalysts (low number and numerous types of active sites). We are currently developing methodologies to test these catalysts under industrially relevant conditions and also to probe the structure of the catalysts under working conditions.[85] This obviously calls for the development of better spectroscopic tools (*in situ* techniques), the large scale production of these catalysts and a better understanding of the reactivity of catalysts through the combined use of experimental evidence and molecular modelling. The gap between homogeneous catalysis and heterogeneous catalysis is closing, but there are still many open questions, which should be solved in the near future.

Table 1 Initial rates for the metathesis of propene with various heterogeneous catalysts

Catalyst	TOF^a	R^b
$[\equiv SiO–Ta(=CHtBu)(CH_2tBu)_2]$	Inactive[25]	10^3
$[\equiv SiO–Mo(\equiv CtBu)(CH_2tBu)_2]$	0.53[25]	500
$[\equiv SiO–Mo(=NH)(=CHtBu)(CH_2tBu)]$	0.47[25]	870
$[\equiv SiO–W(\equiv CtBu)(CH_2tBu)_2]$	0.23[25]	1700
$[\equiv SiO–Re(\equiv CtBu)(=CHtBu)(CH_2tBu)]$	0.25[25]	500
MoO_3/SiO_2	0.004[400]	–^{c}
WO_3/SiO_2	–[400] ^{c}	–^{c}
Re_2O_7/SiO_2	<0.002[150]	–^{c}
$[Re(CO)_3OH]_4/SiO_2$	7,4.10$^{-4[150]}$	–^{c}
MoO_3/Al_2O_3	0.05–0.5[200]	–^{c}
WO_3/Al_2O_3	0.1–1.0[300]	–^{c}
Re_2O_7/Al_2O_3	0.05–0.1[35]	–^{c}

^{a} Initial or steady state rates in mol mol^{-1} s^{-1} at the temperature indicated in parentheses. ^{b} Substrate-to-catalyst ratio, for which the reaction reaches at least the thermodynamic equilibrium. ^{c} Not readily calculated from the published data.

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