DOI: 10.1002/adsc.200600443

Strategies to Immobilize Well-Defined Olefin Metathesis Catalysts: Supported Homogeneous Catalysis *vs.* Surface Organometallic Chemistry

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Received: August 28, 2006

Abstract: This review is mainly devoted to a description of the strategies that have been implemented to develop well-defined olefin metathesis catalysts immobilized on solid supports. Two main approaches have been investigated involving supported homogenous catalysts or heterogeneous catalysts prepared by surface organometallic chemistry. Advantages, limitations and possible developments of these systems are discussed.

Keywords: heterogeneous catalysts; immobilization; olefin metathesis; supported homogeneous catalysts; surface organometallic chemistry

1 Introduction

Olefin metathesis was discovered more than forty years ago in heterogeneous catalysis and disclosed as "olefin disproportionation", and it has been used industrially in the production of basic chemicals ever since.[1,2] For these processes, the catalysts are typically group 6–7 oxides supported on large surface area oxide supports (silica, alumina, magnesia), which are robust and which can be regenerated by simple calcination. However, these systems usually work at relatively high temperatures (>150 °C), with the exception of Re_2O_7/Al_2O_3, and are typically not compatible with functional groups unless co-catalysts are used (metathesis of olefinic esters).

Therefore, it has only been recently that olefin "metathesis", as named later by Calderon,[3] has become a key reaction in organic synthesis and material science with the emergence of a series of well-defined homogeneous catalysts which work at low temperatures (25–80 °C) and are compatible with a wider variety of functional groups. These catalysts are divided in two main subclasses: 1) the d^0 early transition metal catalysts based on group 6 and 7 transition metals (Scheme 1a),[4–9] which are referred to as the Schrock-type complexes, and 2) the Ru complexes, i.e., the Grubbs-type complexes[10,11] as well as related systems[12–15] (Scheme 1b).

Well-defined homogeneous catalysts present the advantage of working at rather low temperatures, giving good selectivities (not including stereoselectivity) and providing ways to implement structure-reactivity relationships, which are necessary for a rational development of the best catalytic system for a given reaction.

However, some of the main drawbacks of homogeneous catalysts are, likely, their decomposition *via* bimolecular pathways and the necessity to use complex processes to separate the reactants/products from the catalysts. Overall, this can lead to metal contamination of the products, particularly not acceptable for pharmaceutical or even polymer industry, and also hinders the recycling or the regeneration of homogeneous catalysts.

In contrast, heterogeneous catalysts can easily be separated from reactants/products and thereby used in continuous flow processes. Yet, the nature of their

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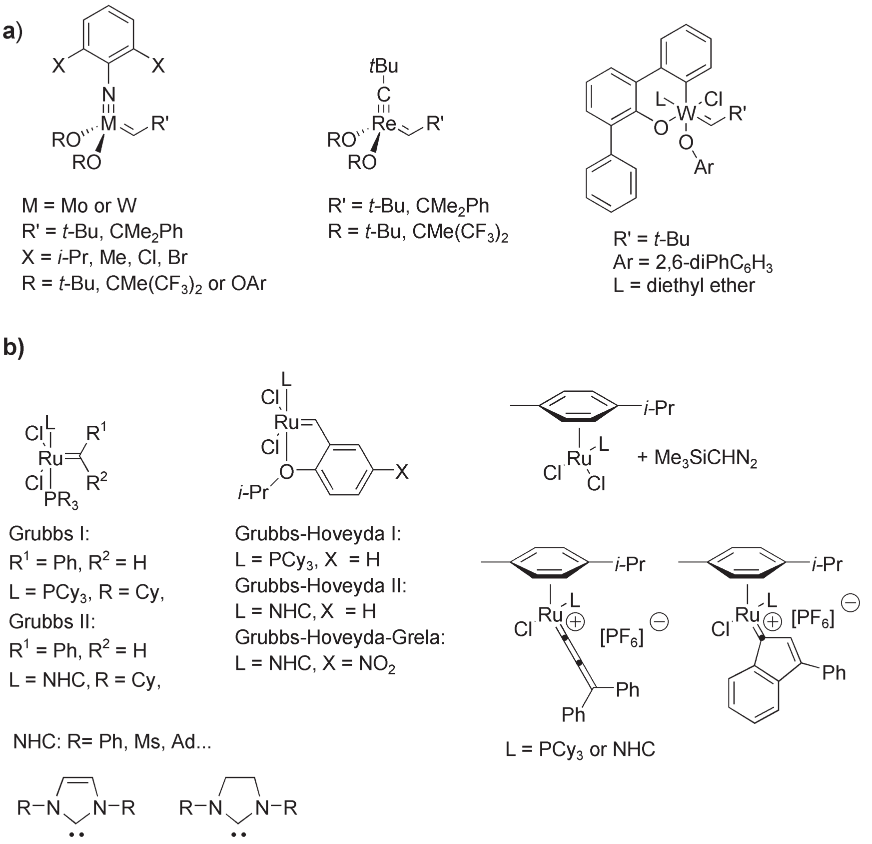
active sites is often difficult to assess, and therefore they are more difficult to improve. In fact, after more than forty years of research, there are still no heterogeneous catalysts which can achieve efficiently the metathesis of functionalized olefins: the maximum productive turnovers are limited to several hundreds and, in these cases, it is necessary to use activators (such as R_4Sn for Re_2O_7/Al_2O_3), which make the catalytic system difficult to regenerate (poisoning of the Re by tin or even volatilization of tin).

Thus, in order to combine the advantages of homogeneous and heterogeneous catalysis, two main strategies have been proposed to construct well-defined heterogeneous catalysts (Scheme 2).

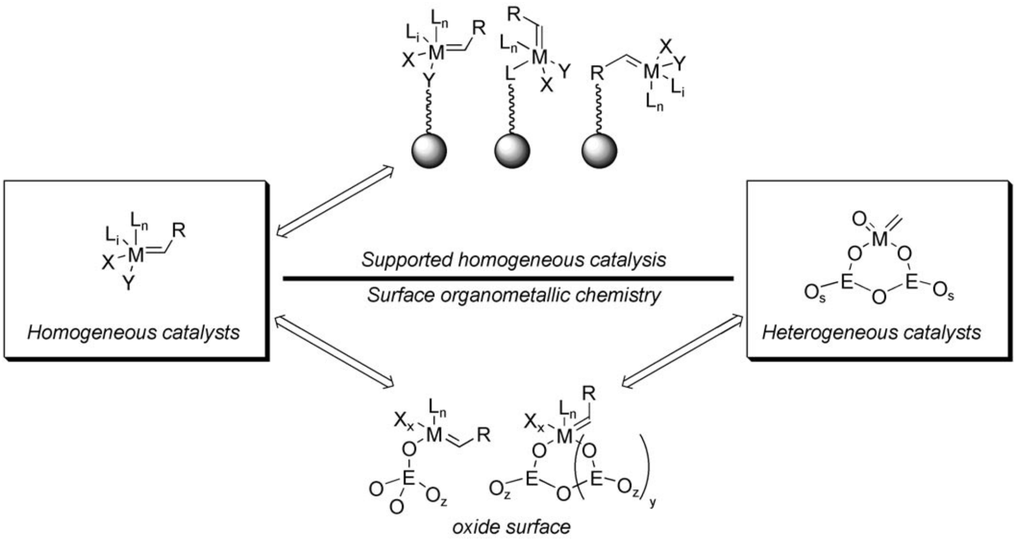
Firstly, immobilization of a homogeneous catalyst can be carried out by substituting one of its ligands by a similar one attached *via* a linker and usually a covalent bond to a support/carrier (oxide, polymer, dendrimer). This approach is referred to as supported homogeneous catalysis (Section 2).[16]

Secondly, the organometallic complex is attached directly to the oxide support [E_xO_y, silica ($E=Si$, $x=1$, $y=2$), alumina ($E=Al$, $x=2$, $y=3$)…] *via* either a covalent/ionic bond or a Lewis acid–Lewis base interaction. In these systems, the surface has the role of a ligand and is directly involved in the coordination sphere of the metal, which also contains other ancillary ligands in order to influence the stability, the activity and the selectivity like in homogeneous catalysis. This approach requires a detailed understanding of the structure of the surface complex like in homogeneous catalysis and is called surface organometallic chemistry (Section 3).[16–18]

The main difference between the two approaches is the tendency to loose the molecular character of the complex when switching from supported homogeneous catalyst to catalysts prepared *via* "surface organometallic chemistry". In the former case, most of the synthetic effort is to preserve as much as possible the molecular structure after grafting. In the latter case, the surface of the oxide plays the role of a "rigid" ligand, and the mobility of the complex is eliminated as the number of covalent bonds with the support increases (y), a limit case being when there is only one covalent bond between the surface and the metal: it is an "hybrid situation" with a very short distance between the metal and the surface.



Scheme 1. Examples of homogeneous catalysts based on **a**) d^0 group 6 and 7 transition metal complexes and **b**) Ru complexes.



Scheme 2. E: heteroelement in the oxide (Al, B, Si...), O_s: surface oxygen atoms, x: the number of X-type ligand, n/i: the number of L-type ligands, $(y+1)$ = the number of covalent bond between the oxide support and the metal center, and $(z-2)$: the number of oxygen attached to E.

2 Immobilized Olefin Metathesis Catalysts *via* the Supported Homogeneous Catalysis Approach

2.1 Immobilized Schrock-Type Catalysts

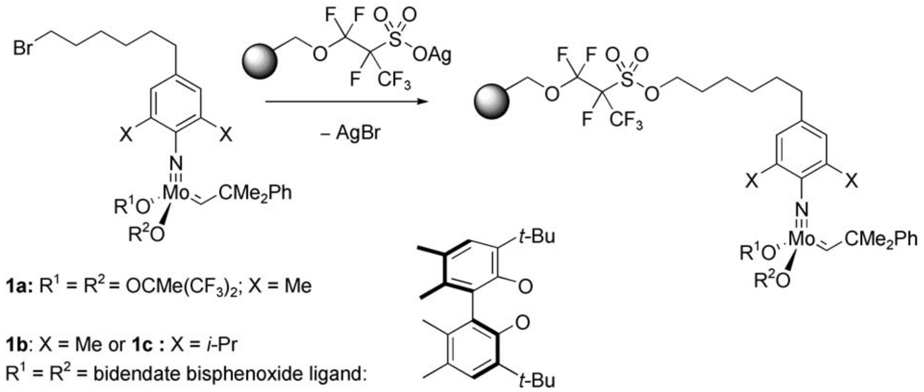
The coordination sphere of the metal in the Schrock-type catalysts is usually composed of 1) the alkylidene ligand, 2) an imido ligand, or 3) two alkoxide ligands. Of the three possible approaches to immobilize the Schrock-type catalysts, only two strategies have been implemented so far: *via* the imido ligand (Section 2.1.1) and *via* the alkoxide ligands (Section 2.1.2).

2.1.1 Immobilization through the Imido Ligand

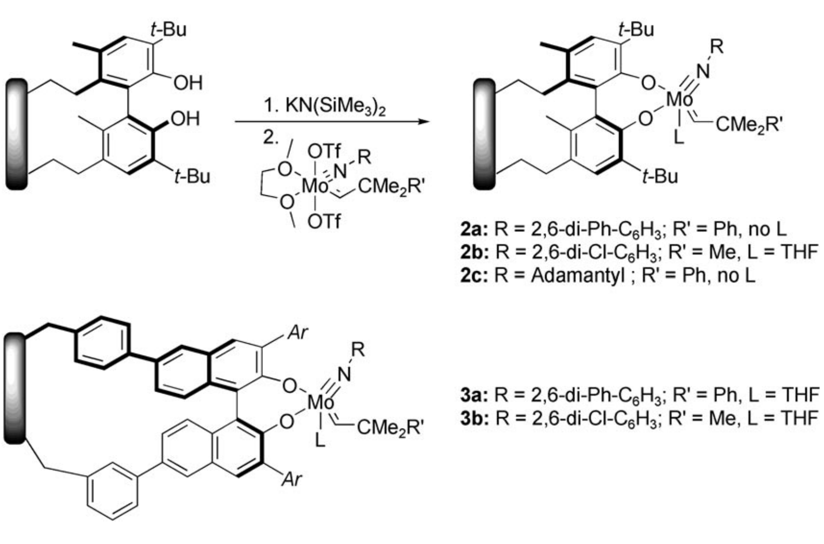
The immobilization is carried out by reacting Schrock catalysts having a bromohexyl substituent in the *para* position of the arylimido ligand with a silver perfluorosulfonated group attached to a polymer (Scheme 3).[19] This catalyst (**1**) displays similar activities in ring-closing metathesis reactions (RCM). Moreover, through this route, it is also possible to prepare the corresponding asymmetric olefin metathesis catalysts, which display similar activities and enantioselectivities (usually lower) as their homogeneous equivalents. This shows that the coordination sphere at Mo is not too affected by the immobilization.

2.1.2 Immobilization through the Alkoxide Ligand

A polymer-supported Mo imidoalkylidene bisphenoxide asymmetric complex **2a** has been prepared by reaction of the potassium salt of a bisphenol-containing polymer with [Mo(=CMe$_2$Ph)(=NR)(OTf)$_2$(DME)] (Scheme 4). Asymmetric ring-closing metathesis (ARCM) and the tandem asymmetric ring-opening metathesis–cross-metathesis (AROM/RCM) with this catalyst give products in good yields and high enantiomeric excesses.[20] The activities and selectivities are



Scheme 3.



Scheme 4.

either close or a little lower than these obtained for the corresponding homogeneous catalytic system. Moreover, while the selectivities are constant with each cycle, the activity decreases, and Mo leaching is also detected. Noteworthy, using this approach, by changing the imido group (**2b**, **c**) or the chiral bisphenoxides (**3a**, **b**), it is possible to improve activities and selectivities, but they never reach those obtained for the corresponding homogeneous catalysts.[21]

Improving the synthesis and the performance of such types of catalysts has been sought by carrying out most synthetic steps prior to polymer formation. For instance, using norbornenyl-substituted bisphenol allows the polymer synthesis to be carried out at the last step (Scheme 5), either prior to attaching Mo (**4**),[22] or as Mo is already attached to the phenoxide (**5**).[21] In the former case, good activities and enantioselectivities are obtained (still lower than their homogeneous equivalent), and lower Mo contamination is obtained. In the latter case, it was necessary to carry out the polymerization in the presence of co-monomers in order to obtain a catalyst with good performances (problem of diffusion of the reactants in a highly cross-linked polymer).

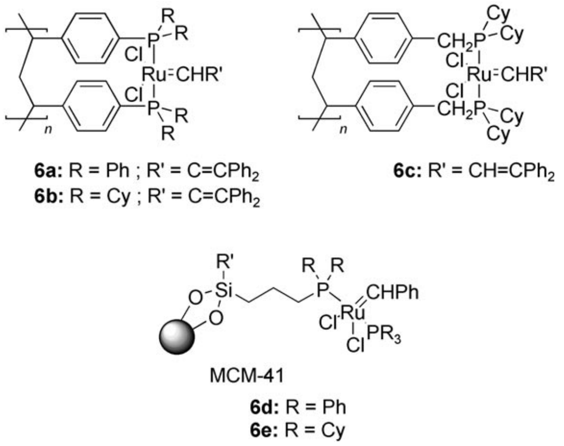
2.2 Immobilized Grubbs-Type Catalysts

The Ru coordination sphere of the Grubbs-type catalysts is usually composed of 1) an alkylidene, 2) two chloride, and 3) two neutral ligands, which are either two phosphine (Grubbs I), one phosphine and one NHC ligand, where NHC stands for N-heterocyclic carbene ligands (Grubbs II), or one ether combined with either a phosphine or an NHC ligand (Grubbs–Hoveyda). Therefore, three strategies have been implemented to immobilize the Grubbs-type catalysts *via* substituting the neutral ligands (Section 2.2.1), exchanging of the chloride ligands (Section 2.2.2.) or anchoring the alkylidene ligand (Section 2.2.3). A fourth strategy has been to encapsulate the homogeneous catalyst inside a polymer matrix (Section 2.2.4).

2.2.1 Immobilization through the Phosphine or NHC Ligand

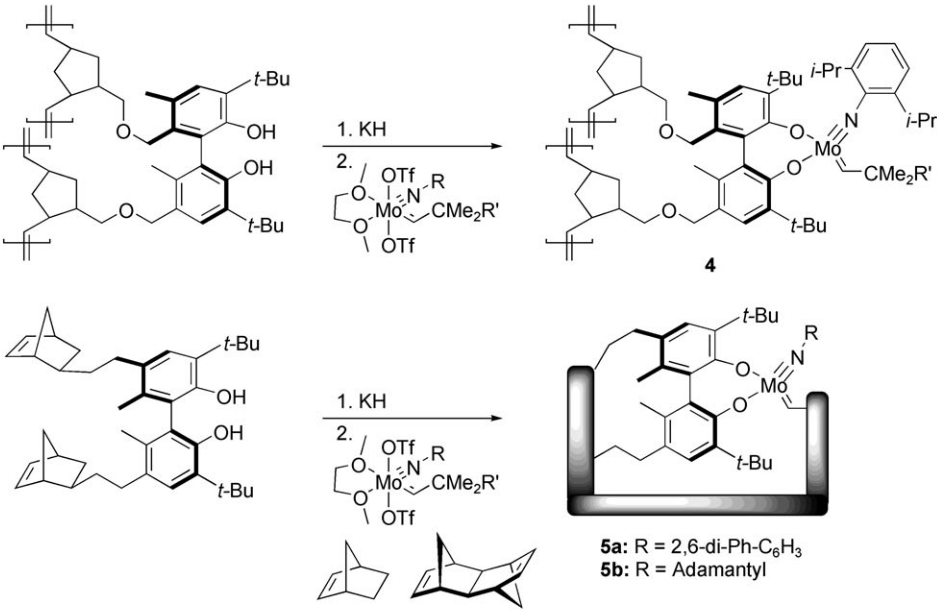
2.2.1.1 The Grubbs I Catalyst

The first attempt to immobilize the Grubbs I catalyst was carried out by exchanging its phosphine ligands (Scheme 6) with phosphines incorporated on a polystyrene-divinylbenzene polymer (PS-DVB) (**6a–c**):[23]



6a: R = Ph ; R' = C=CPh$_2$
6b: R = Cy ; R' = C=CPh$_2$
6c: R' = CH=CPh$_2$
6d: R = Ph
6e: R = Cy

Scheme 6.



5a: R = 2,6-di-Ph-C$_6$H$_3$
5b: R = Adamantyl

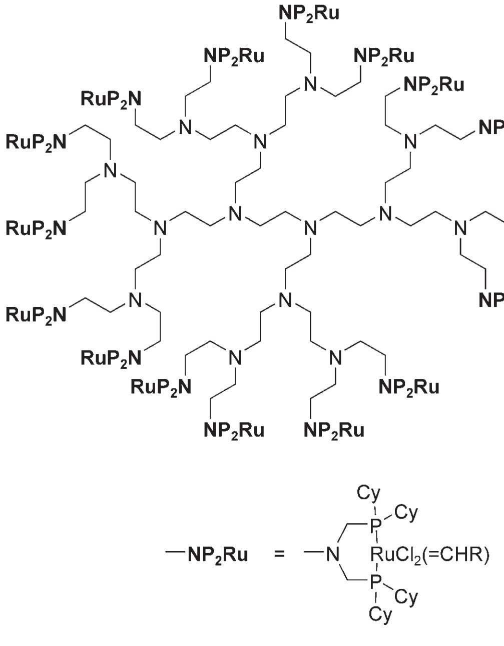
Scheme 5.

as observed in homogeneous systems, the activity of the supported catalyst system depends on the nature of the phosphine ligand,[24–26] the more electron rich the better (**6c** > **6b** > **6a**), however the performances are very far below those of their homogeneous equivalents (150 times less active). A similar approach has been carried out by using MCM-41 supported phosphine ligands (**6d**, **e**).[27] In this case, the performances are improved, probably because of the larger pores, which do not limit the diffusion of reactants (one problem encountered with polymers), but they are still lower than those of the corresponding homogeneous catalysts. Note that, in these cases, olefin metathesis requires the dissociation of one phosphine, and therefore it is likely that the Ru species has to "leach" from the support in order to obtain metathesis activity, but the high local density of phosphine ligands probably helps to recapture the coordinatively unsaturated Ru active species. Hence, while these types of catalysts can probably be useful in solid-phase synthesis as, for example, in combinatorial chemistry, they are probably not compatible with flow reactor technology (leaching).

Finally, Gatard et al. have prepared a Grubbs I-type supported catalyst **7** by replacing both PCy_3 ligands by a bidendate phosphine attached to a dendrimer, and it has been used to prepare the dendritic star-polymer by the subsequent ROMP of norbornene (Scheme 7).[28–30]

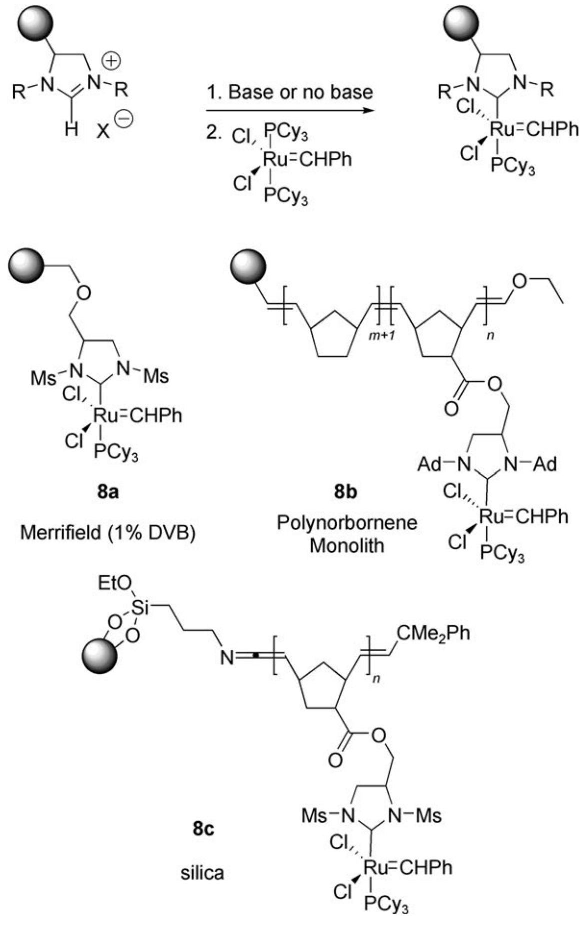
2.2.1.2 The Grubbs II Catalyst

Grubbs II catalysts contain one NHC ligand,[31–34] which provides several advantages: 1) it increases the interaction of the olefin with Ru compared to phosphines and thereby it usually increases the rate of olefin metathesis,[35,36] and 2) it forms a strong M–L bond, hence it does not lead to dissociation in contrast to phosphine ligands.[37] The latter property makes it an interesting ligand to anchor permanently a catalyst to a support, and therefore several strategies have been used to link the Grubbs II catalysts *via* the NHC ligand.



Scheme 7. The dendrimer-supported Grubbs-type catalyst 7.

First, because imidazolium salts are usual precursors to generate NHC carbene, several strategies have described the immobilization of these functionalities and their conversion to immobilized Grubbs II catalysts (Scheme 8):



Scheme 8.

1) A Merrifield resin (PS-DVB 1%) can be derivatized in order to obtain imidazolium pending ligands, which can be converted into **8a**.[38]

2) Functionalization of the surface of a monolithic material by ring-opening metathesis polymerization (ROMP) of norbornene in the presence of an imidazolium-containing polynorbornene provides a material with pending imidazolium salt, which is readily converted into **8b**.[39]

3) A polynorbornene polymer having pending imidazolium ligands and one triethoxy end-group can be grafted on the surface of a silica material (**8c**).[40]

Other approaches include (Scheme 9):

4) Functionalization of the surface of a monolithic material by ROMP of norbon-5-ene-2-carboxylic chloride, and reaction of the acyl chloride end-groups with a modified Grubbs II catalyst having a pending OH group on the side chain of the NHC ligand (**9a**).[41]

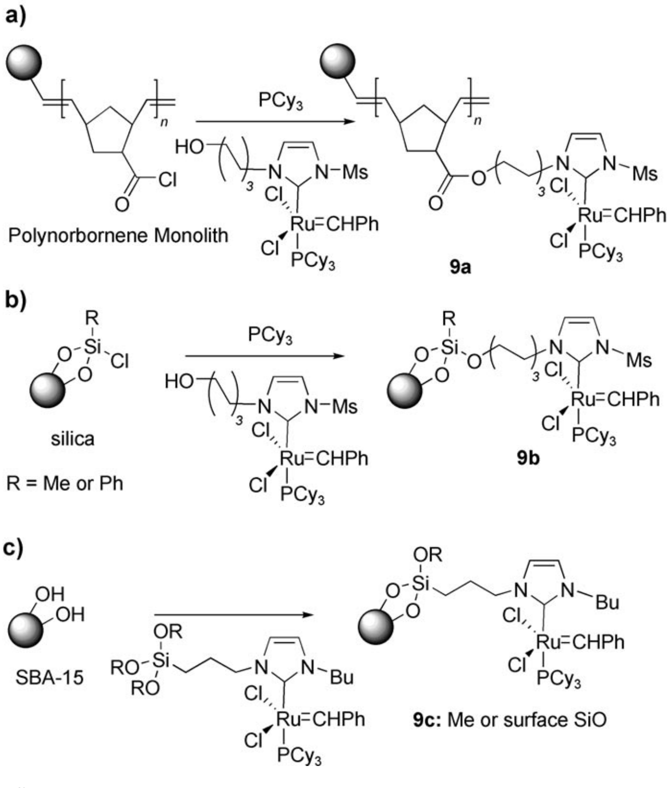
5) Reaction of a modified Grubbs II catalyst having a pending OH group on the side chain of the NHC ligand with the surface of a silica previously modified with trichlorophenylsilanes (**9b**).[42]

6) Reaction of a modified Grubbs II catalyst having a pending trimethoxy group on the side chain of the NHC ligand with the surface of a SBA-15 (**9c**).[43]

These catalysts have been mainly used in RCM and related reactions. In all cases, good catalytic performances are obtained, the catalysts can be recycled, and the Ru-contamination is lowered. Yet, it is not clear whether or not the catalyst performances have been improved compared to the homogeneous analogues, even if site isolation should have limited decomposition.

2.2.2 Immobilization by Exchanging Chloride Ligands

Grubbs et al. have shown that chlorides can be replaced by carboxylates by reacting their silver salt with $[Cl_2Ru(=CHR)(PR_3)_2]$.[26] This methodology has been used to immobilize Ru olefin metathesis catalysts on supports (Scheme 10). Merrifield resins functionalized with hydroxyethyl groups are first reacted with perfluoroglutaric anhydride, and the carboxylic acid thus formed is converted into the corresponding silver salt, which upon reaction with $[Cl_2Ru(=CHPh)(PCy_3)_2]$ provides an immobilized Grubbs I catalyst (**10a**).[44] In a similar way, using the hydroxymethyl-functionalized Merrifield resins, the immobilized Grubbs II catalyst can be prepared (**10b**).[45] A Grubbs II catalyst can also be supported on monoliths (**10c**) or silica (**10d**).[46] Immobilized Grubbs–Hoveyda or Grubbs–Hoveyda–Grela catalysts can also be prepared on monoliths based on PS-DVB polymers (**10e–g**).[45,47–49]



Scheme 9.

These catalysts display good performances in RCM. Noteworthy, Ru leaching is very low, and product contamination by Ru is extremely low, i.e., < 100 ppb/g. Additionally, this property makes them suitable to be used in a continuous flow reactor, where high TON can be achieved (up to several thousands), but deactivation remains a problem, and their performances are still somewhat lower than those of their homogeneous analogues.

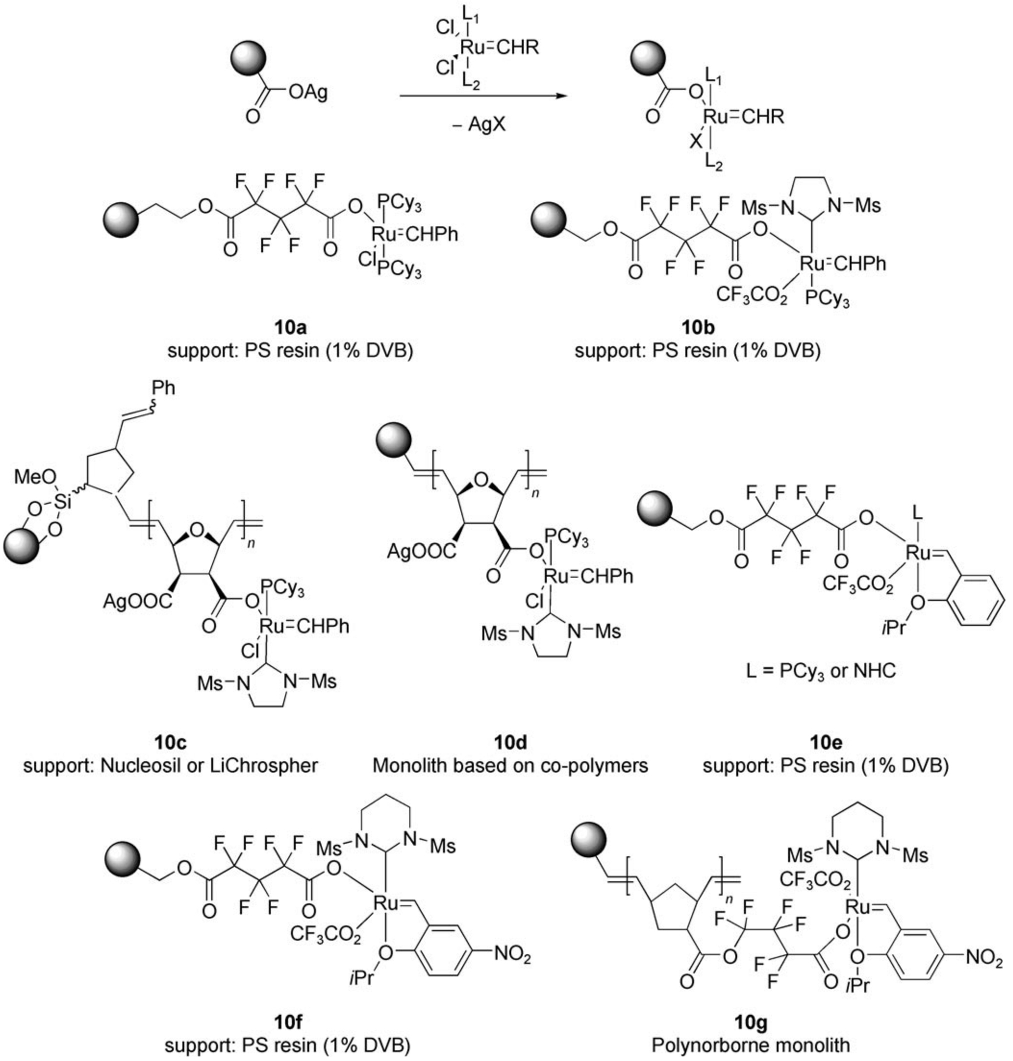
2.2.3 Immobilization *via* the Alkylidene Ligand

2.2.3.1 The Grubbs I and II Catalysts

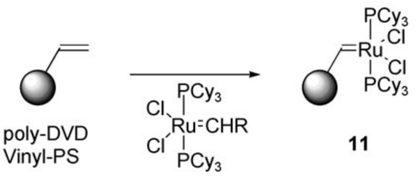
Immobilizing the catalyst precursor is also possible through its carbene ligand (Scheme 11). This can be achieved by reaction of Grubbs I[50–53] or Grubbs II[54,55] catalysts with a macroporous polystyrene or poly-DVB resin having pendant vinyl groups. In these heterogeneous catalysts, the active species is in fact a homogeneous catalyst, and it is not clear how much of Ru is then re-incorporated as the initial carbene (boomerang concept), because of a significant loss of activity after each cycle. However, the contamination of the final product by Ru is decreased using these catalysts. Additionally, these systems can be used to prepared polymer beads with high loading of functionalities,[56] stationary phase of liquid chromatography,[57–59]] or star-polymers based on simple first-generation dendrimers[60,61] through ROMP.

2.2.3.2 The Hoveyda–Grubbs Catalyst

The Hoveyda–Grubbs catalysts have the particularity of containing a benzylidene ligand, in which the *ortho* position of the phenyl group bears an ether group, which binds to the metal.[11,62–68] These catalysts are usually more robust (less air sensitive and can be purified by chromatography) and are more efficient with



Scheme 10.



Scheme 11.

several substrates. One possible reason for the specific properties of this catalyst is due to the strong affinity of Ru for the initial ligated alkylidene ligand. Therefore, the resting state of the catalyst is the catalyst precursor, which releases (slowly) the active species, but is also able to recapture it (boomerang concept). Because of these specific properties, much effort has been directed at immobilizing these types of complexes through the alkylidene ligands.

The main approach has been to anchor the benzylidene by a substituent of the phenyl ring attached to (Scheme 12):

1) a polyethyleneglycol (PEG) (**12a**),[69,70]

2) a dendrimer (**12b**),[71]

3) a polystyrene support *via* a butyldiethylsilyl linker (**12c**),[72]

4) silica *via* several types of organic linkers by Hoveyda (**12d**)[73,74], Blechert (**12e**)[75] and Moreau (**12f**),[76]

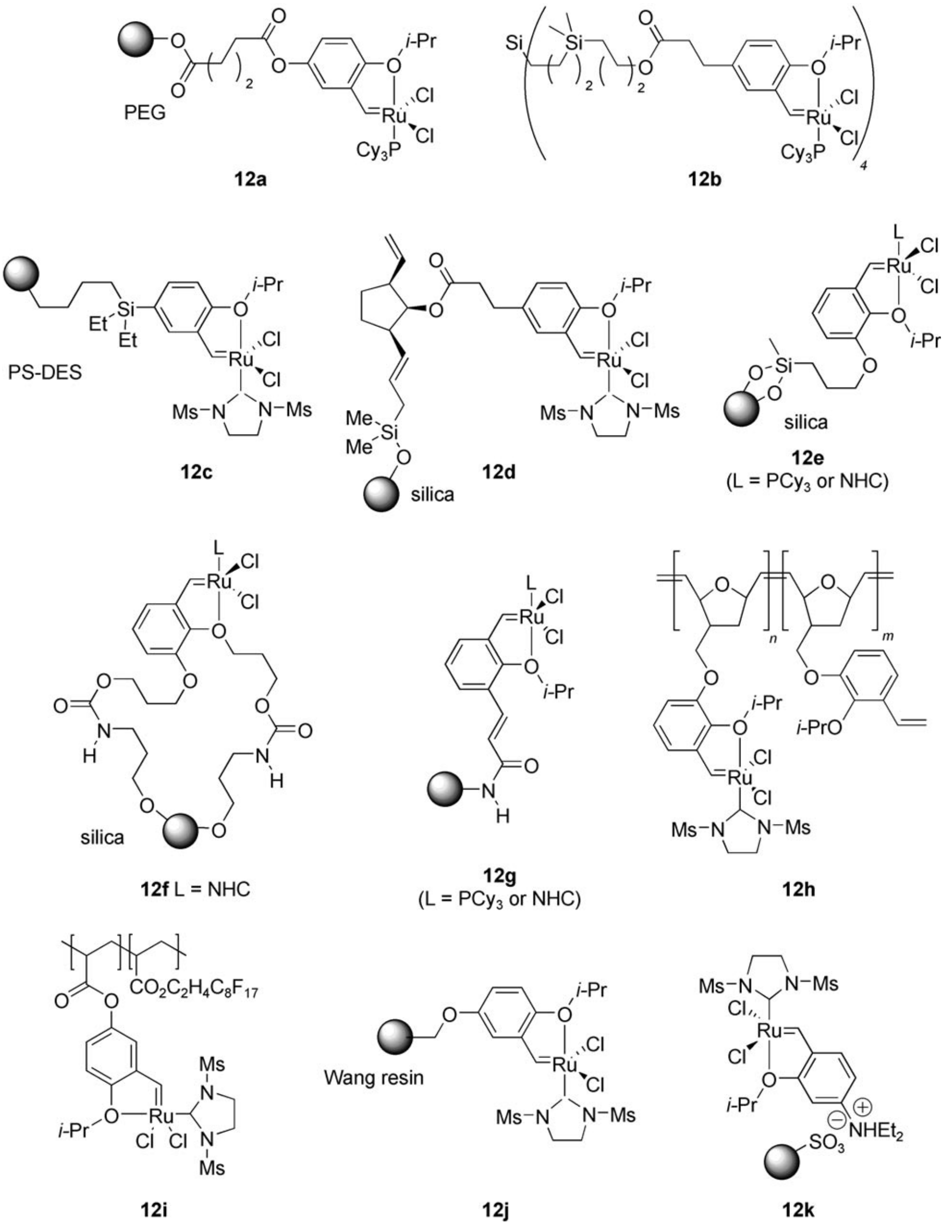
5) silica with polymer linkers (**12g**),[77]

6) polymers based on polynorbornene (**12h**)[78] or copolymer of acrylate perfluoroester and acryloyl chloride (**12i**),[79]

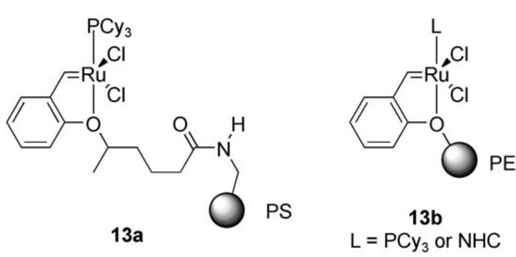
7) a Wang resin (**12j**)[80]

8) *via* ionic interaction with a polymer (**12k**).[81]

The other approach has been to anchor the benzylidene by the alkyl substituent of the ether group either to PS[82] or to PEG (Scheme 13).[83]



Scheme 12.

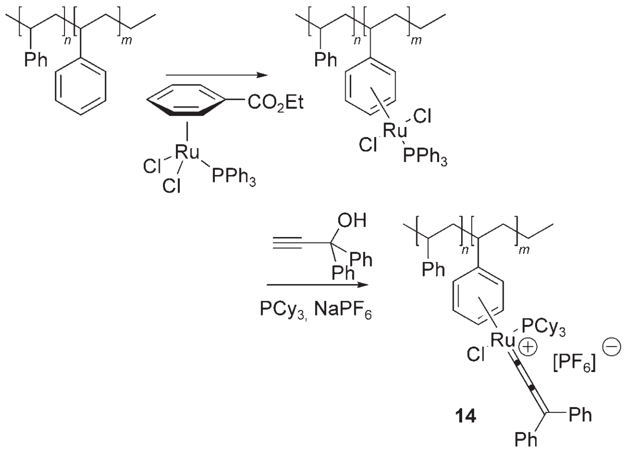


Scheme 13.

In contrast to the Grubbs I and II catalysts immobilized through the alkylidene ligand, in the case of the Grubbs–Hoveyda catalyst, Ru leaching is quite low (in most cases below 100 ppm), and the catalyst can be easily recycled without a significant loss of activity. Note that here again the active species is probably homogeneous, and this has been clearly shown by cross-over experiments: in fact, the propagating species can be transported from one bead to another (2%).[74] Yet, it is possible that a large fraction is recaptured through formation of the more stable alkylidene ligand. From all available literature data, it is clear that the supported system have never out-performed the homogeneous systems (TON ranges from 100–2000 in RCM, and after 5–7 recycling using 1–5 mol%, most systems show a sharp drop in activity), but it helps to decrease the amount of Ru in organic samples, one of the best systems being **12i** (up to 20 cycles at 0.5–1 mol% with a marginal loss of activity).[79] Several of these systems are quite easy to synthesize, and, considering their performances, are good candidates for their use in combinatorial chemistry.

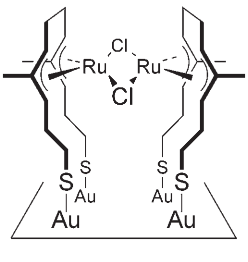
2.3 Other Immobilized Ru Olefin Metathesis Catalysts

Another class of Ru-based olefin metathesis catalysts is composed of Ru bound to an arene ligand, and therefore the pendant phenyls of polystyrene have been used as a way to support the Ru catalyst precursor (Scheme 14).[84]



Scheme 14.

Another approach has consisted in generating well-defined Ru complexes on the surface of gold colloids by using thiol as an anchoring agent (Scheme 15).[85] Noteworthy, this system display better activity in the ROMP of norbornene (16,000 h^{-1}) than the corresponding homogeneous catalyst (3000 h^{-1}), and the activity is even improved when flat gold surfaces are used (80,000 h^{-1}).



Scheme 15.

2.4 Immobilization by Micro-Encapsulation

Micro-encapsulation by incorporating the Grubbs II catalyst in a polymer film can also be used as a method to generate a recoverable olefin metathesis catalyst and to minimize the contamination of the product by Ru (< 500 ppm).[86]

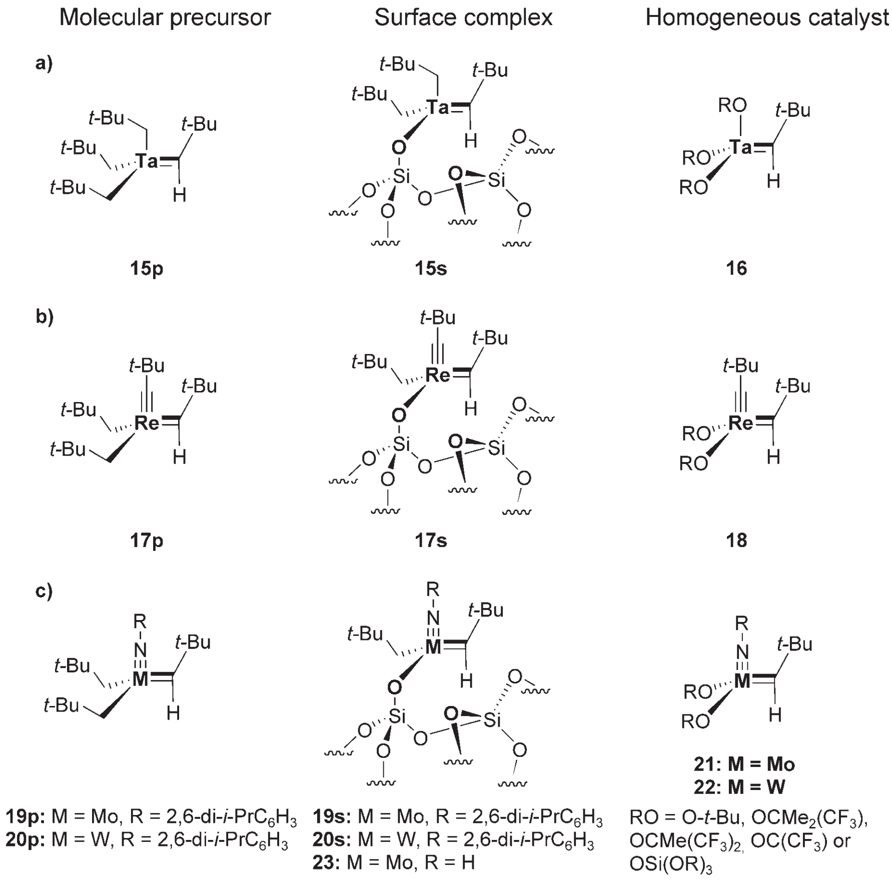
3 Immobilized Olefin Metathesis Catalysts *via* Surface Organometallic Chemistry

3.1 Grafting Hydrocarbyl Complexes

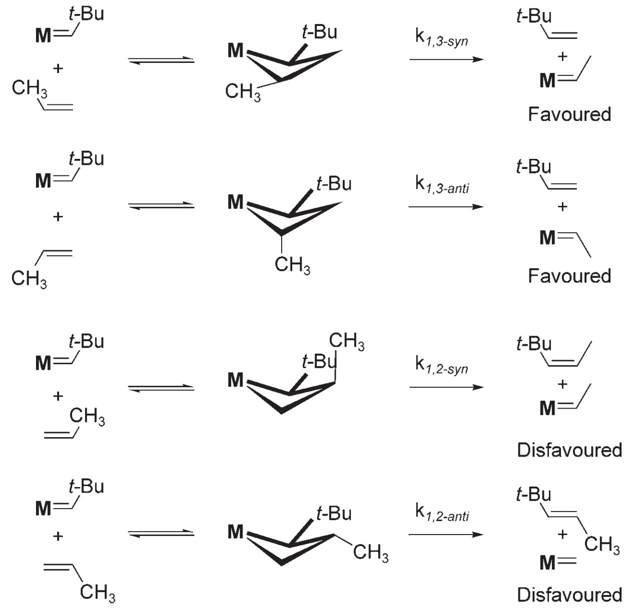
The first well-defined silica-supported alkylidene complex was based on Ta: **15s** [(≡SiO)Ta(=CH-*t*-Bu)(CH_2-*t*-Bu)$_2$], obtained by grafting [Ta(=CH-*t*-Bu)(CH_2-*t*-Bu)$_3$] (**15p**) on silica partially dehydroxylated at 700 °C, $SiO_{2-(700)}$, a support which contains *ca.* 0.26 mmol of OH/g (Scheme 16a). However, it was only marginally active in olefin metathesis as its homogeneous equivalents (**16**).[87] In contrast, the well-defined silica supported Re alkylidene complex **17s** has shown unprecedented activities in olefin metathesis (Scheme 16b),[88–92] which exceeds those obtained for both heterogeneous and homogeneous Re-based catalysts (**18**).[93,94]

Beside being characterized at a molecular level as the *syn*-isomer by a combination of spectroscopic methods[95] and DFT calculations,[96,97] its catalytic behavior is also typical of a well-defined catalyst: the initiation step corresponds to the cross-metathesis of the olefin and the neopentylidene ligand. In the case of propene, a 3:1 ratio of *t*-BuCH=CH_2 and *t*-BuCH=$CHCH_3$ is obtained, which is in agreement with the following model (Scheme 17): the favored reaction pathway corresponds to that in which interactions between the alkyl substituents of the metallacyclobutane are minimized, that is, pathway involving [1,3]-interactions > pathway involving [1,2]-interactions.[98]

Moreover, this catalyst can achieve up to 900 TON in the metathesis of oleate esters in the absence of activators.[91] This is in sharp contrast to Re_2O_7/Al_2O_3, which requires the use of an activator (R_4Sn) to reach *ca.* 150 TON. The observed high reactivity of **17s** probably comes from the optimized ligand set (*vide infra*)[96] and the presence of isolated species, which prevent deactivation *via* dimerization pathway (*vide infra*). Investigation of the origin of the unexpected high performances of **17s** by DFT calculations has shown that olefin metathesis, even for a d^0 metal, is in fact a four-step process involving (Scheme 18): coordination of the olefin, [2+2] cycloaddition and the corresponding reverse steps {[2+2] cycloreversion and de-coordination of the olefin}, each step being optimized differently. The energy barrier for coordination/de-coordination is lowered by having a strong σ-donor ligand (alkyl > alkoxy or siloxy) *trans* to the incoming olefin, and the energy barriers for cycloreversion is mainly controlled by the stability of the metal-



Scheme 16.

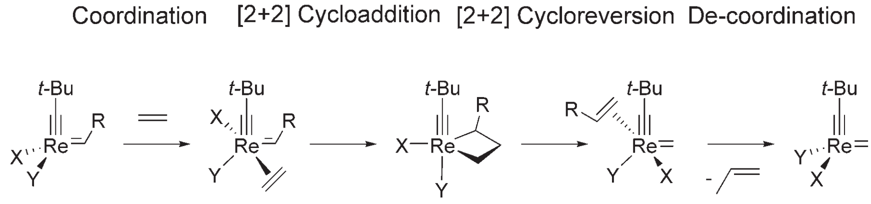


Scheme 17.

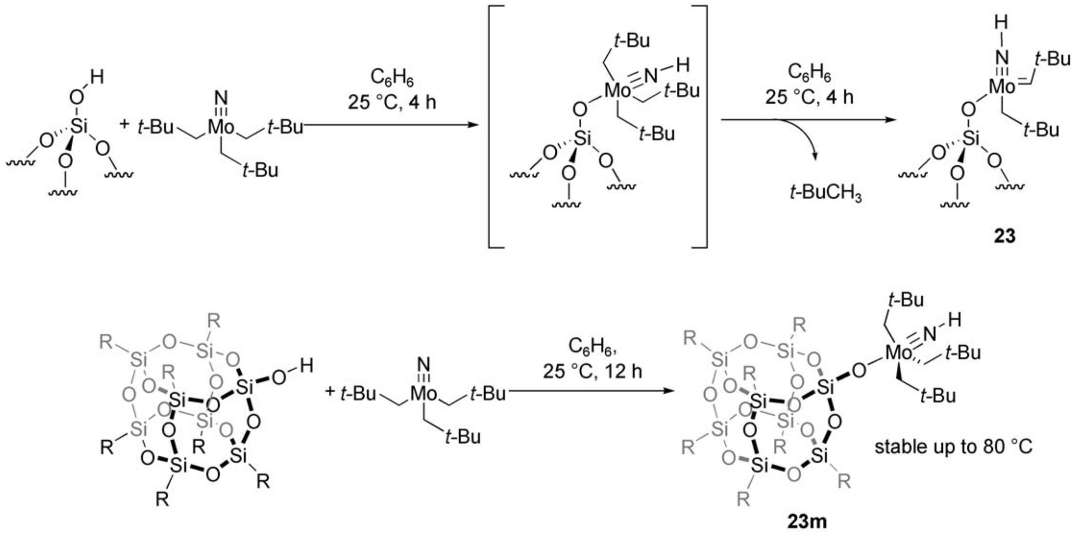
lacycle so that having alkyl ligands destabilizes this intermediate and lowers the energy barrier for cycloreversion. Therefore, unsymmetrical catalysts such as **17s** are better optimized for each step and constitute better candidates as highly efficient olefin metathesis catalysts as was only recently recognized.[99]

Thus, the recent development of an efficient synthesis of **19p** (M = Mo)[100] and **20p** (M = W)[101] has lead to the preparation of the silica-supported equivalents of **17s**: **19s** and **20s**. Both are formed as *syn* isomers (Scheme 16c)[102–104] and display reactivities far greater than those of **19p/20p** and somewhat better that those of the well-known corresponding bisalkoxide homogeneous derivatives (**21** and **22**, for M = Mo and W, respectively).[8,105] Moreover, it has been shown that the molecular and surface monosiloxy Mo complexes have similar initial rates, but that the supported complex displays a much better stability in agreement with the effect of site isolation, which probably prevents dimerization pathways.[101,106]

Access to well-defined imido Mo alkylidene complexes was also realized by reaction of the nitrido ligand in [Mo(≡N)(CH$_2$-*t*-Bu)$_3$] with the surface silanol of silica (Scheme 19).[107,108] The trisalkyl intermediate cannot be isolated and gives directly **23** [(≡SiO)Mo(≡NH)(=CH-*t*-Bu)(CH$_2$-*t*-Bu)] by elimination of one 2,2-dimethylpropane molecule. The surface complex **23**, a homologue of **19**, is also a highly active olefin metathesis catalyst. Noteworthy, the reaction of [Mo(≡N)(CH$_2$-*t*-Bu)$_3$] with molecular sila-



Scheme 18.

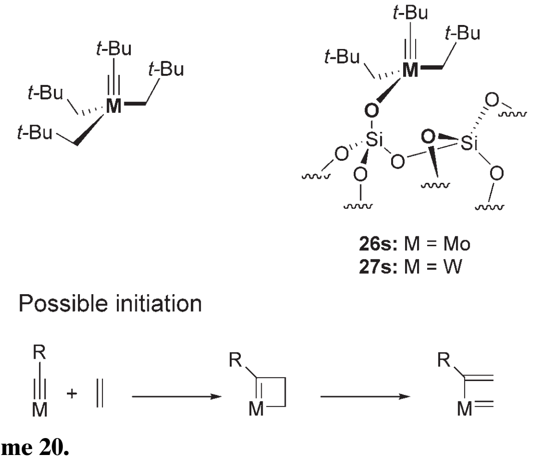


Scheme 19.

nols gives very stable trisalkylimidosiloxy complexes, which need to be heated at > 80 °C to loose 2,2-dimethylpropane to provide a highly unstable olefin metathesis catalyst.[108] Moreover, note that protonation of the nitrido ligand is not observed upon reaction of $[\mathrm{Mo}(\equiv\mathrm{N})(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})_3]$ with surface siloxy ligands.[109]

Besides alkylidene surface complexes (*vide supra*), well-defined Mo (**26s**)[108,110] and W (**27s**)[111–116] alkylidyne surface complexes, whether supported on silica or alumina, can also be used as catalyst precursors for olefin metathesis (Scheme 20). They display activities and selectivities, which are similar to those obtained for well-defined alkylidene complexes. While the initiation mechanism is not known, it possibly involves the [2+2] cycloaddition of the olefin onto the alkylidyne ligand.

Finally, some of these systems {e.g., $[(\equiv\mathrm{SiO})\mathrm{Re}(\equiv\mathrm{C}\text{-}t\text{-}\mathrm{Bu})(=\mathrm{CH}\text{-}t\text{-}\mathrm{Bu})(\mathrm{CH_2}\text{-}t\text{-}\mathrm{Bu})]$} can also be used as catalyst precursors not only in alkyne[89] but also in alkane metathesis {e.g., $[(\equiv\mathrm{SiO})\mathrm{Ta}(=\mathrm{CH}\text{-}t\text{-}\mathrm{Bu})(\mathrm{CH_2}\text{-}t\text{-}\mathrm{Bu})_2]$ or $[(\equiv\mathrm{SiO})\mathrm{Mo}(\equiv\mathrm{NAr})(=\mathrm{CH}\text{-}t\text{-}\mathrm{Bu})(\mathrm{CH_2}\text{-}t\text{-}\mathrm{Bu})]$},[117–119] a reaction, which also involves olefin metathesis as a key carbon-carbon bond formation step.[120]



Scheme 20.

3.2 Grafting of Other Types of Molecular Precursors

One of the first approach to generate well-defined alkylidene complexes has been to react well-defined alkylidyne complexes with silica-supported species.[111–113] While the supported systems catalyze olefin metathesis, it is still not clear if well-defined alkylidene complexes have been generated in these cases. In fact, recent results show that trisamidoalkylidyne Mo complexes $[\mathrm{Mo}(\equiv\mathrm{CEt})(\mathrm{N}\text{-}t\text{-}\mathrm{BuPh})_3]$ have been grafted on silica,[121] and gives the corresponding surface-bound alkylidyne complex, $[(\equiv\mathrm{SiO})\mathrm{Mo}(\equiv\mathrm{CEt})(\mathrm{N}\text{-}t\text{-}\mathrm{BuPh})_2]$, which is a highly active catalyst in alkyne metathesis.

Generating olefin metathesis catalysts by directly grafting the Schrock catalysts [$(RO)_2Mo(\equiv NAr)(=CH\text{-}t\text{-}Bu)$] on silica supports has been attempted. Nonetheless, the structures of the surface species have not been characterized, and it is not certain that grafting has occurred.[122,123] More work is probably necessary to develop these systems.

3.3 Activation of Molecular Organometallic Complexes by Surface Lewis Acid Sites

Herrmann et al. have shown that methyl trioxorhenium ($MeReO_3$) is activated by Lewis acids (e.g., Me_xAlCl_{3-x}) to generate a highly active homogeneous olefin metathesis catalyst.[124] Similarly, when $MeReO_3$ is contacted with oxide supports, which contain Lewis acid sites, it also generates highly active catalysts such as [$MeReO_3/SiO_2\text{-}Al_2O_3$],[124,125] [$MeReO_3/Al_2O_3$],[126] [$MeReO_3$/Y zeolite],[127] and [$MeReO_3/Nb_2O_5$].[128] While Re is fixed strongly (and irreversibly) to the Lewis site of the oxide supports,[125] the nature of the active site is unknown and is still under debate.[128]

4 Conclusion

Olefin metathesis catalysts immobilized through "supported homogeneous catalysis" can be used to efficiently transform functionalized organic molecules in good yields, especially *via* RCM and related reactions, including ARCM, to provide compounds with lower metal contents (Mo or Ru) than when using the corresponding homogeneous catalysts. In the case of ARCM, the enantioselectivies obtained are a little lower in all cases showing that the metal coordination is slightly modified in the immobilization process. Overall, this strategy is very suitable for parallel synthesis and can be used to develop libraries of organic compounds. Moreover, this strategy has also been successfully used to prepare polymer beads with high loading of functionalities, monoliths to develop well-defined heterogeneous catalysts or well-defined star-polymers *via* ROMP, starting from immobilized catalysts on dendrimers. Note, however, that in most cases the catalyst performances are either lower or much lower than those of their homogeneous equivalents (lower yields and selectivities), and more work is probably necessary to understand, at a molecular level, the origin of this difference. In contrast, the level of understanding of immobilized catalysts, prepared by surface organometallic chemistry, has already provided the following insights: 1) site isolation on a surface increases the life time of catalysts by avoiding dimerization pathways, 2) the siloxy ligand of silica, which is directly in the coordination sphere of the metal, activates the metal center and increases its reactivity in olefin metathesis [polarization of the $(+\delta)M{=}C(-\delta)$ bond] much like the fluoroalkoxy ligand introduced by Schrock et al. and 3) the coordination sphere around the metal is better optimized as evidenced by the better performances of these systems (rate, TON) compared to most of their homogeneous analogues, and recent calculations suggest that the non-symmetric natures of these supported catalysts (siloxy-alkyl in place of bisalkoxy) are a key to their reactivity (each ligand optimizes differently each step of olefin metathesis).[85] The molecular understanding of these catalysts has just emerged, and the scope of these systems in organic synthesis has yet to be investigated in detail. Another important aspect of this research is to find more simple routes to these systems.

Compared to homogeneous catalysts, both strategies have already provided some advantages and some molecular insights, and further developments along these lines are expected to provide more efficient, more robust, more tolerant and re-generable olefin metathesis catalysts.

Acknowledgements

We would like to thank our collaborators, who have been involved in these projects, as well as BASF AG, the French Ministry of Research and Education, the CNRS and the ESCPE Lyon for financial supports.

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