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Review

Well-defined silica supported metallocarbenes: Formation and reactivity

Nuria Rendón, Frédéric Blanc, Christophe Copéret*

Université de Lyon, Institut de Chimie de Lyon, C2P2 UMR 5265 CNRS, Université Lyon 1 – ESCPE, Lyon 43 Bd du 11 Novembre 1918, 60616 Villeurbanne Cedex, France

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ABSTRACT

This overview describes how well-defined silica supported metallacarbenes are prepared, what is their mechanism of formation, what is their reactivity towards alkanes and alkenes, and these data are compared with the current knowledge of modern organometallic chemistry.

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1. Introduction

Metallocarbenes belong to an important class of ligands in organometallic chemistry. They are divided in two sub-classes depending on the substitution at the C_{sp2} carbon doubly bonded to the metal: (1) Fischer type carbenes, which usually contain a heteroatom in the α-position and are electrophilic; (2) Schrock type carbenes or alkylidenes, which contain H and/or alkyl substituent and are nucleophilic (Scheme 1).

While the former display interesting stoichiometric reactivities, which have been exploited in organic synthesis [1,2], the latter display both stoichiometric and catalytic reactivities (they are key intermediates in alkene metathesis) and will be discussed in more details thereafter both in term of structure and reactivity [3]. First, these Schrock type carbene ligands have often a distorted geometry at the carbon directly linked to the metal centre: wide M—C—C bond angle, acute M—C—H bond angle and an elongated C—H bond, which is due to the presence of an α-H agostic interaction (Scheme 2a). This typically gives rise to lower ν(C—H) and J_{C-H} values in IR and NMR spectroscopies, respectively [3–6]. In the case of d^0 early transition metal complexes, carbenes react with σ-bonds, such as the O—H bond of alcohols [7], or even the C—H bond of unactivated alkanes (Scheme 2b) [8].

These reactions take place through σ-bond metathesis; the corresponding reverse reaction (α-H abstraction) is often encountered in the formation of alkylidene ligands. Moreover, metallocarbenes can also react with π-bond systems (Scheme 2c). The reaction with alkenes gives metallacyclobutanes via a [2+2]-cycloaddition and the reverse reaction (cycloreversion) yields either the original carbene plus the alkene or two new ones. This overall transalkylidenation (π-bond metathesis) is catalytic and is the basis of the Chauvin mechanism in alkene metathesis [9–11]. In contrast, the corresponding reaction with aldehydes or ketones is irreversible

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* Corresponding author.

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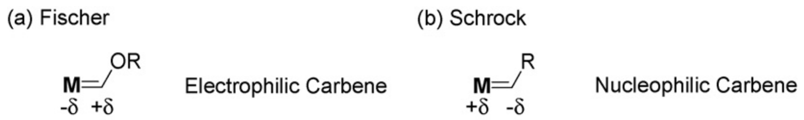
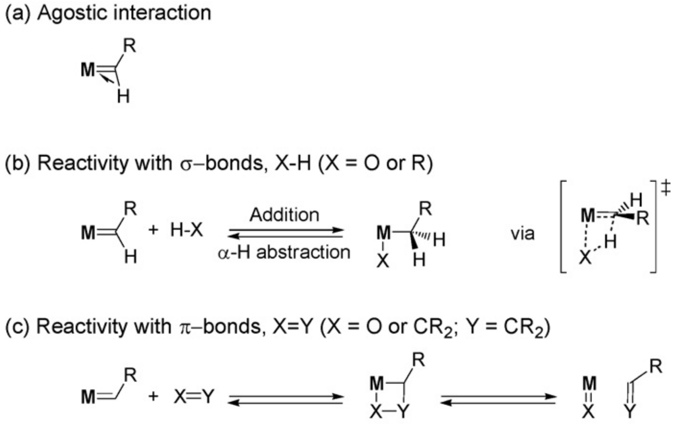


Scheme 1.



Scheme 2.

and yields alkenes, and is therefore related to the Wittig reaction, hence its name “pseudo-Wittig reaction”.

In this review, we will outline (1) how well-defined alkylidene surface complexes are formed on silica surfaces and (2) the reactivity of these systems, especially focusing on the difference and similarity of molecular and surface chemistry.

2. Discussion

2.1. Generality on silica

The bulk of silica is constituted of tetrahedral $\mathrm{SiO_4}$ units (Scheme 3), and its surface is amorphous and can be described as a complex assembly of cyclic structures of various sizes (typically between 6 and 12 member ring) using $\mathrm{SiO_4}$ as building block [12,13]. The surface $\mathrm{SiO_4}$ units can contain hydroxyl functionality, leading to different types of silanols:geminal, vicinal and isolated. The specific surface area is typically comprised between 50 and 400 $\mathrm{m^2/g}$, but higher surface areas are found in the case of mesoporous silica. Up to 700 °C, partial dehydroxylation under vacuum does not change the specific surface area of non-porous silica, while the OH concentration varies with the temperature treatment. At higher temperatures, there is a loss of specific surface area combined with the formation of highly reactive siloxane bridges, *e.g.* four member ring siloxane bridge. The dehydroxylation process takes place first by desorption of physisorbed water, followed by condensation of vicinal OH groups above 150–200 °C. Partial dehydroxylation leads to the formation of isolated hydroxyl groups. At 200–300 °C, this treatment yields very hydroxyl rich silica surfaces (0.86 mmol/g), which are mainly composed of vicinal OH, while a treatment at 700 °C ($\mathrm{SiO_{2-(700)}}$) allows the statistical distribution of isolated OH groups at an average distance of *ca.* 13 Å, which corresponds to 0.26 mmol OH/g.

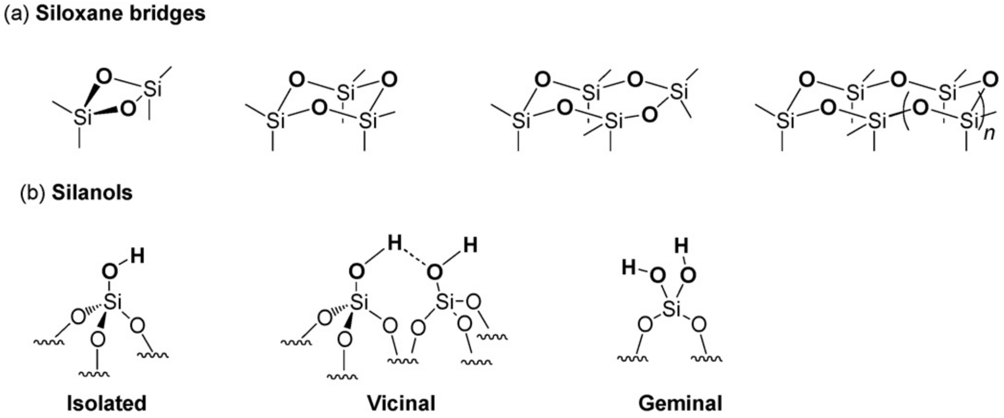
2.2. Formation of well-defined silica supported metallocarbene complexes

Most silica supported metallocarbene complexes have been obtained by grafting on silica, and more specifically $\mathrm{SiO_{2-(700)}}$. They are typically tetra-coordinated and have a d^0 configuration: $[\mathrm{Ta}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH_2}t\mathrm{Bu})_3]$, $[(\mathrm{R^1N}\equiv)\mathrm{Mo}(=\mathrm{CHR^2})(\mathrm{CH_2R^3})_2]$, $[(\mathrm{R^1N}\equiv)\mathrm{Mo}(=\mathrm{CHR^2})(\mathrm{NR_2})_2]$, $[(\mathrm{R^1N}\equiv)\mathrm{Mo}(=\mathrm{CHR^2})(\mathrm{OR})_2]$ and $[(t\mathrm{BuC}\equiv)\mathrm{Re}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH_2}t\mathrm{Bu})_2]$. They can be described with the following general formula $[(\mathrm{E})\mathrm{M}(=\mathrm{CHR^2})(\mathrm{X})_2]$, where E = X, $\mathrm{NR^1}$ or C*t*Bu, $\mathrm{R^2} = t\mathrm{Bu}$ or $\mathrm{CMe_2Ph}$. These complexes can graft on the surface OH group of silica through different possible competitive ways (Scheme 4):

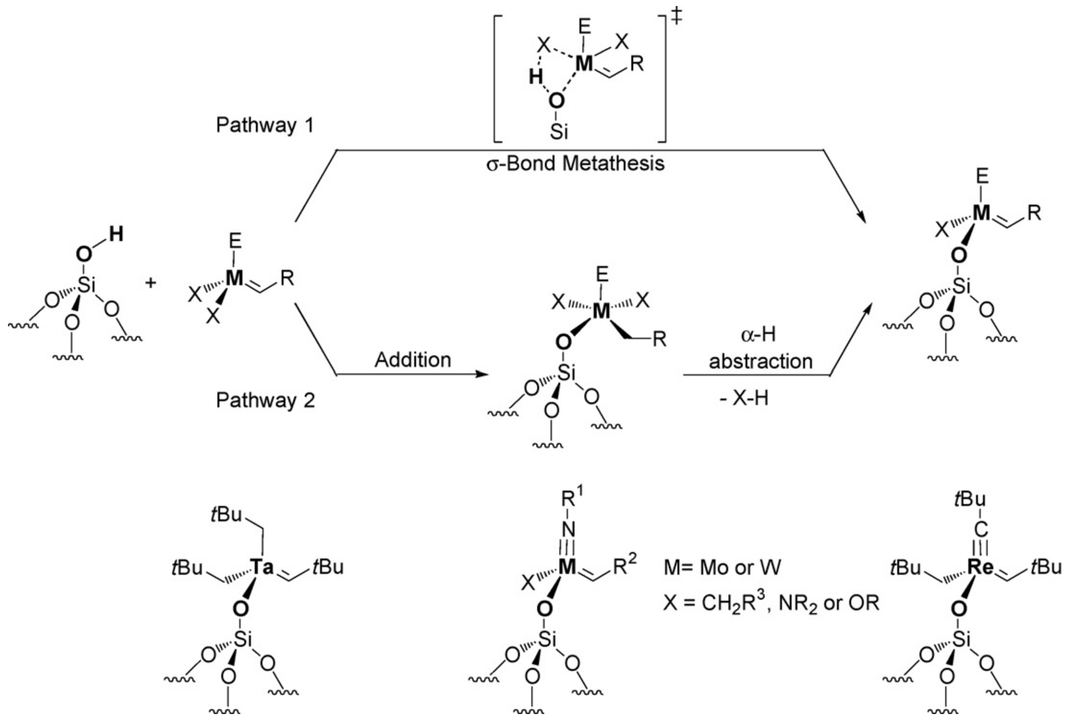
- *Pathway 1:* a direct electrophilic cleavage of one M—X bond by the surface O—H group via σ-bond metathesis, yielding XH and the corresponding surface alkylidene complex $[(\equiv\mathrm{SiO})(\mathrm{E})\mathrm{M}(=\mathrm{CHR^2})(\mathrm{X})]$, where one X ligand has been replaced by a siloxy.
- *Pathway 2:* an addition of the O—H group onto the alkylidene (M=CHR), giving $[(\equiv\mathrm{SiO})(\mathrm{E})\mathrm{M}(\mathrm{CH_2R^2})(\mathrm{X})_2]$, which can decompose via an α-H abstraction process to yield $[(\equiv\mathrm{SiO})(\mathrm{E})\mathrm{M}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{X})]$ along with XH.

Note that there has been no evidence for the reaction of the E ligand with surface O—H group for E=$\mathrm{NR^1}$ (imido) or C*t*Bu (alkylidyne).

Depending on the grafted complex, grafting has been shown to occur in several ways: either selectively via one process of the two possible pathways or via both competing pathways. The grafting mechanisms are typically investigated as follows: (1) using



Scheme 3.



Scheme 4.

deuterated silica and monitoring where the deuterium ends in the products, (2) monitoring the ligands exchange before and after grafting by combining labelling studies (^{13}C labelled or different types of ligands) and solid state NMR spectroscopy, and (3) using soluble molecular models of silica, based on molecular silanols, *i.e.* polyoligomeric silsesquisiloxane (POSS-OH) or $(t\mathrm{BuO})_3\mathrm{Si{-}OH}$, to obtain mechanistic insight through monitoring the reaction of molecular silanols by solution NMR.

First, in the case of $[\mathrm{Ta}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_3]$, grafting on deuterated silica yields mainly undeuterated 2,2-dimethylpropane and the surface complex $[(\equiv\mathrm{SiO})\mathrm{Ta}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_2]$ (having the C—H alkylidene and CH_2 alkyl partially deuterated): this is consistent with a two-step mechanism (Scheme 4, pathway 2) involving the formation of a penta-coordinated complex $[(\equiv\mathrm{SiO})\mathrm{Ta}(\mathrm{CH}_2t\mathrm{Bu})_4]$, which then decomposes via α-H abstraction into $[(\equiv\mathrm{SiO})\mathrm{Ta}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_2]$. In fact, it has been possible to observe the NMR signature for this surface complex, and complementary experiment using POSS-OH as a molecular model for silica shows that $[\mathrm{Ta}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_3]$ selectively yields $[(\mathrm{POSS{-}O})\mathrm{Ta}(\mathrm{CH}_2t\mathrm{Bu})_4]$, which is then converted into $[(\mathrm{POSS{-}O})\mathrm{Ta}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_2]$ [14].

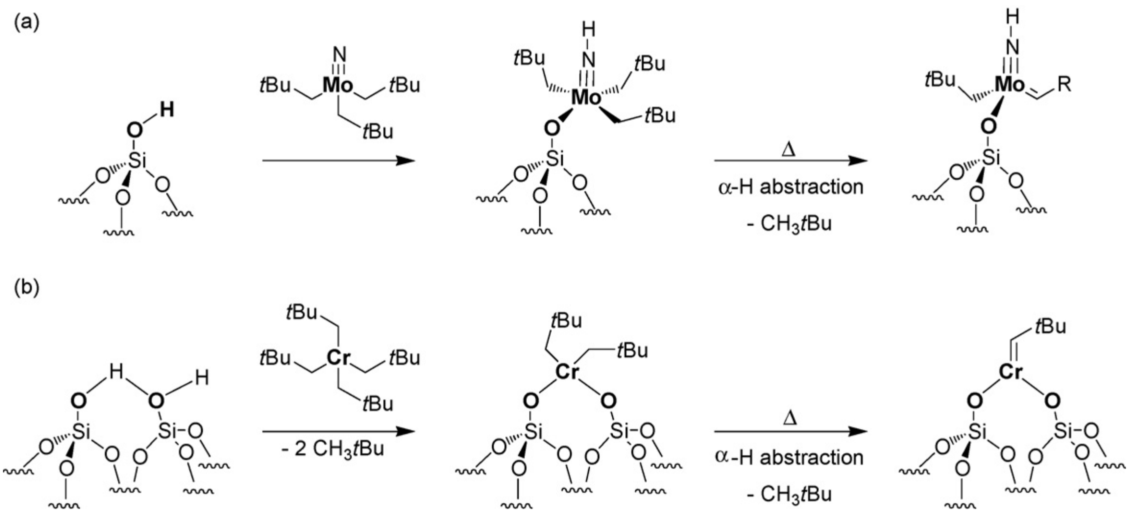
Second, in contrast to $[\mathrm{Ta}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_3]$, grafting of $[(\mathrm{R}^1\mathrm{N}\equiv)\mathrm{Mo}(=\mathrm{CHR}^2)(\mathrm{CH}_2\mathrm{R}^3)_2]$ on $\mathrm{SiO}_{2-(700)}$ selectively occurs via the cleavage of the M–alkyl bond (Scheme 4, pathway 1) as evidenced by deuterium labelling of silica, the use of complexes having different alkyl and alkylidene substituents ($\mathrm{R}^2 \neq \mathrm{R}^3$) or selectively labelled ligands and finally by monitoring the reaction in solution using molecular models of silica, POSS-OH or $(t\mathrm{BuO})_3\mathrm{SiOH}$ [15,16]. Note that it has been shown that the reaction of O—H with these complexes depends on its acidity, and for instance the OH groups of alcohols, which are less acidic than these of phenols, selectively react with the alkylidene ligand [7]. The observed grafting mechanism for silica is consistent with the fact that the $\mathrm{p}K_\mathrm{a}$ of silanols is close to this of phenols [17]. Additionally, amido and alkoxy complexes $[(\mathrm{R}^1\mathrm{N}\equiv)\mathrm{Mo}(=\mathrm{CHR}^2)(\mathrm{X})_2]$ ($\mathrm{X}=\mathrm{NR}_2$ or OR) selectively yields $[(\equiv\mathrm{SiO})(\mathrm{R}^1\mathrm{N}\equiv)\mathrm{Mo}(=\mathrm{CHR}^2)(\mathrm{X})]$ for $\mathrm{X}=\mathrm{NPh}_2$, pyrrolyl or O$t$Bu, but a mixture of $[(\equiv\mathrm{SiO})(\mathrm{R}^1\mathrm{N}\equiv)\mathrm{Mo}(=\mathrm{CHR}^2)(\mathrm{X})]$ and $[(\equiv\mathrm{SiO})(\mathrm{R}^1\mathrm{N}\equiv)\mathrm{Mo}(\mathrm{CH}_2\mathrm{R}^2)(\mathrm{X})_2]$ for X = 2,5-dimethylpyrrolyl. Note that, in this case, $[(\equiv\mathrm{SiO})(\mathrm{R}^1\mathrm{N}\equiv)\mathrm{Mo}(\mathrm{CH}_2\mathrm{R}^2)(\mathrm{X})_2]$ is not converted into $[(\equiv\mathrm{SiO})(\mathrm{R}^1\mathrm{N}\equiv)\mathrm{Mo}(=\mathrm{CHR}^2)(\mathrm{X})]$ even with a thermal treatment at 120 °C. These data suggest that grafting probably occurs via a direct electrophilic cleavage of the M–X bonds for amido and alkoxide complexes in most cases, with the exception of 2,5-dimethylpyrrolyl, for which the steric bulk of this ligand probably slows down this reaction (pathway 1) over the addition reaction (first step of pathway 2). In the case of isostructural W complexes, grafting of $[(\mathrm{R}^1\mathrm{N}\equiv)\mathrm{W}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_2]$ generates selectively $[(\equiv\mathrm{SiO})(\mathrm{R}^1\mathrm{N}\equiv)\mathrm{W}(=\mathrm{CH}t\mathrm{Bu})\,(\mathrm{CH}_2t\mathrm{Bu})]$ [18], while this of $[(\mathrm{R}^1\mathrm{N}\equiv)\mathrm{W}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{NR}_2)_2]$ (NR_2 = 2,5-dimethylpyrrolyl) yields a mixture of $[(\equiv\mathrm{SiO})(\mathrm{R}^1\mathrm{N}\equiv)\mathrm{W}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{NR}_2)]$ and $[(\equiv\mathrm{SiO})(\mathrm{R}^1\mathrm{N}\equiv)\mathrm{W}(\mathrm{CH}_2t\mathrm{Bu})\,(\mathrm{NR}_2)_2]$ [19]. While no detailed mechanistic study was undertaken in these cases, the formation of the same product as for the corresponding Mo complexes suggests that grafting probably occurs as described above for Mo. Finally, for $[(t\mathrm{BuC}\equiv)\mathrm{Re}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_2]$, while grafting on $\mathrm{SiO}_{2-(700)}$ yields a single species $[(\equiv\mathrm{SiO})(t\mathrm{BuC}\equiv)\mathrm{Re}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})]$, it occurs via both pathways (Scheme 4, pathways 1 and 2) and in fact through a statistical attack of the silanol towards the $\mathrm{Re{-}CH}_2t\mathrm{Bu}$ (pathway 1) and $\mathrm{M{=}CH}t\mathrm{Bu}$ (pathway 2) bonds [20,21].

Silica supported metallocarbenes have also been obtained by thermolysis of surface alkyl complexes. For instance, a thermal treatment at 70 °C of $[(\equiv\mathrm{SiO})\mathrm{Mo}(=\mathrm{NH})(\mathrm{CH}_2t\mathrm{Bu})_3]$, obtained by grafting $[\mathrm{Mo}(\mathrm{N})(\mathrm{CH}_2t\mathrm{Bu})_3]$ on $\mathrm{SiO}_{2-(700)}$, gives $[(\equiv\mathrm{SiO})\mathrm{Mo}(=\mathrm{NH})(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})]$ as evidenced by reactivity studies (Scheme 5a) [22,23]. Similarly, $[(\equiv\mathrm{SiO})_2\mathrm{Cr}(\mathrm{CH}_2t\mathrm{Bu})_2]$, prepared by grafting $[\mathrm{Cr}(\mathrm{CH}_2t\mathrm{Bu})_4]$ on $\mathrm{SiO}_{2-(200)}$, yields $[(\equiv\mathrm{SiO})_2\mathrm{Cr}(=\mathrm{CH}t\mathrm{Bu})]$ upon thermal treatment at 70 °C (Scheme 5b) according to mass-balance analysis, IR spectroscopy, EXAFS and reactivity studies (reaction with $\mathrm{D}_2\mathrm{O}$, Br_2 and alkenes) [24,25].

2.3. *Catalytic reactivity of silica supported metallocarbenes*

2.3.1. *Alkene metathesis*

At the exception of $[(\equiv\mathrm{SiO})\mathrm{Ta}(=\mathrm{CH}t\mathrm{Bu})(\mathrm{CH}_2t\mathrm{Bu})_2]$ and $[(\equiv\mathrm{SiO})_2\mathrm{Cr}(=\mathrm{CH}t\mathrm{Bu})]$, all silica supported well-defined alkylidene complexes are highly active alkene metathesis catalyst precursors



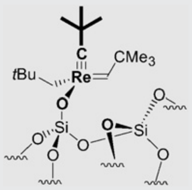
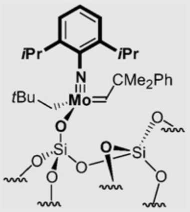
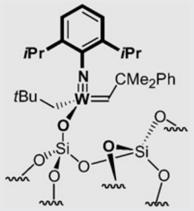
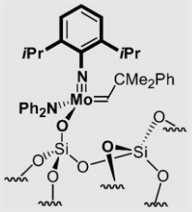
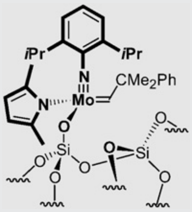
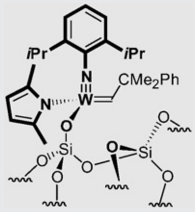
Scheme 5.

as evidenced by high TON in the metathesis of propene as a test substrate (Table 1). The first fully characterized silica supported system was $[(\equiv SiO)(tBuC\equiv)Re(=CHtBu)(CH_2tBu)]$, and it displayed a higher activity than both homogeneous and heterogeneous Re-based catalysts (Table 1) [20]. It is noteworthy that its activity was similar to the best homogeneous catalysts based on d^0 metal complexes, including $Mo(NAr)(=CHtBu)(OR)_2$. However, besides 2-butenes, this system also unexpectedly generates 1-butene (4%) as a primary product of propene metathesis, and it undergoes a fast deactivation via de-grafting [26]. Concerning reactivity, computational studies have shown that the high reactivity of this system is associated with the dissymmetry at the metal centre, *i.e.* presence of one strong (alkyl) and one weak σ-donor (siloxy) ligands [10,11]. This ligand combination both lowers the activation energy for the coordination of the alkene to the metal complex, which needs to undergo a distortion from a tetrahedron to a trigonal prism, and destabilizes the metallacyclobutane intermediates, hence the overall higher reactivity. Moreover, computational studies also point out that deactivation and by-product formation (1-butene) is probably due to β-H transfer at the metallacyclobutane intermediate [26].

These studies have been further exploited by generating well-defined isoelectronic Mo imido surface complexes $[(\equiv SiO)(R^1N\equiv)Mo(=CHR^2)(X)]$ ($R^1 = 2,6$-di-i-PrC_6H_4, $R^2 = tBu$ or $=CMe_2Ph$ and $X=CH_2tBu$ or amido ligands: diphenylamido, pyrrolyl or 2,5-dimethylpyrrolyl). First, for $X=CH_2tBu$, while the initial rates are not improved by comparison with the Re complex, both the selectivity and the stability are improved (Table 1). Replacing the pendant alkyl ($X=CH_2tBu$) by an amido or an alkoxy ligand [27] further improved the catalysts, giving overall higher initial rates, stability and selectivity (no 1-butene). The best system has been obtained for X = 2,5-dimethylpyrrolyl and with an optimised imido ligand where R^1 = adamantyl, and it displays a reactivity far greater than the equivalent homogeneous catalysts: 780 mol/mol Mo/min, 275,000 ton and >99.9% selectivity. This gain of activity is not limited to propene, and in fact the performances in ethyl

Table 1

Representative examples of propene metathesis catalyst precursors and their performances (initial activity, overall turnover numbers after 1500 min and selectivity).

			
Initial rates (min^{-1})	120	120	8.4
TON	6,000	22,000	6,000
Selectivity	96%	99.4%	99.4%
			
Initial rates (min^{-1})	374	320	24
TON	138,000	101,000	25,000
Selectivity	>99.9%	>99.9%	>99.9%

oleate metathesis are also greatly improved upon using the silica-supported systems. Overall, these performances are far greater than those obtained with the corresponding homogeneous catalysts [28].

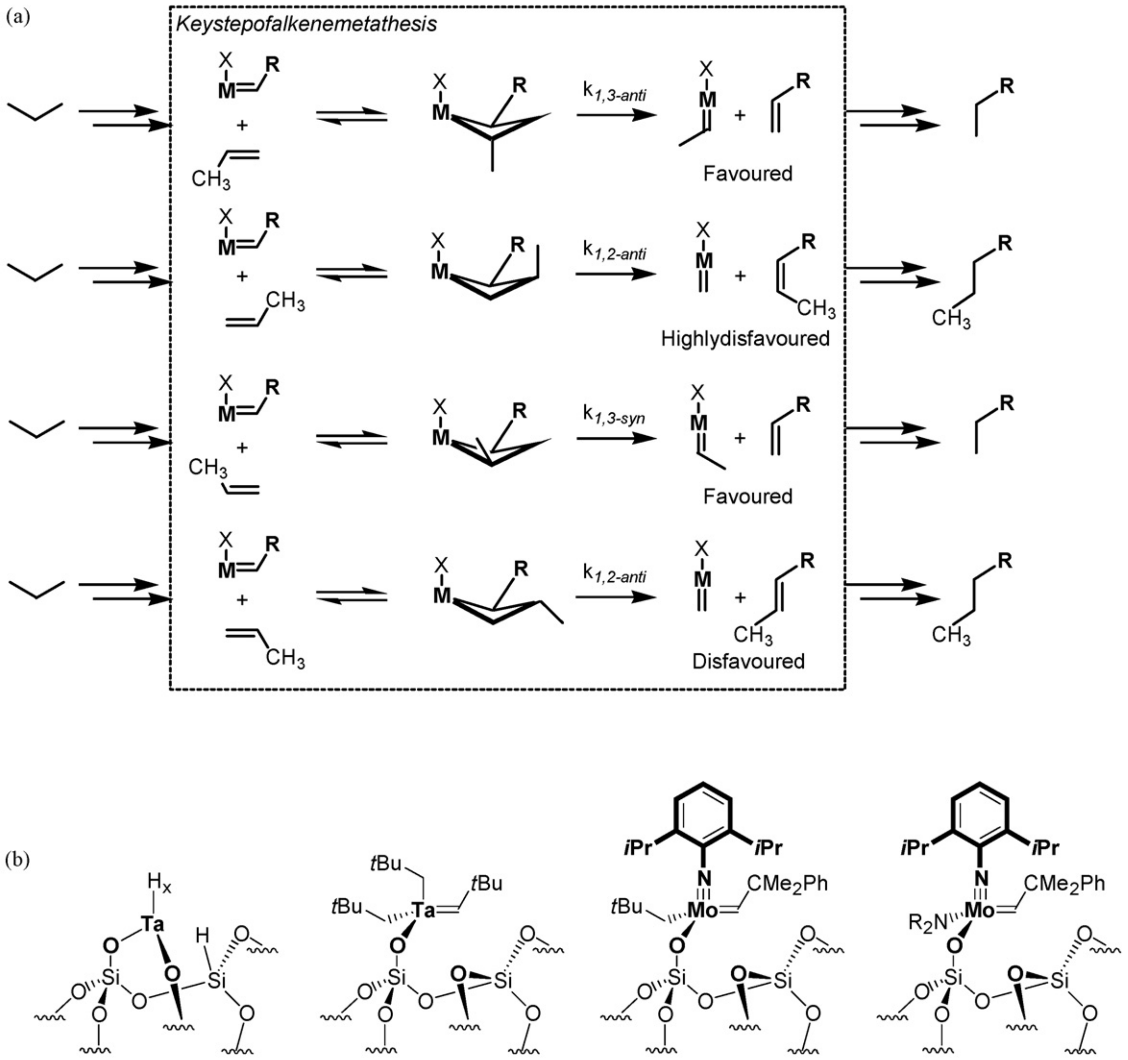
In the case of the W imido surface complexes, it is noteworthy that the activity decreases by one order of magnitude compared to the corresponding Mo complexes, and that the selectivity is directly related to the type of ligand: selectivity of 99.4% for X=CH_2*t*Bu and >99.9% for X = 2,5-dimethylpyrrolyl, for W [18,19] as already observed for the corresponding Mo complexes. However, while less active, the W complexes are more stable as evidenced by the good TON despite low rates (Table 1). This better stability has allowed the observation of the actual alkene metathesis intermediates, *i.e.* the methylidene and the metallacyclobutanes, and particularly the latter as a mixture of both square based pyramid and trigonal bipyramid isomers. It is noteworthy that these species have the same reactivity as the catalyst precursors, which shows that they are the actual reaction intermediates of the catalytic cycle.

2.3.2. Alkene polymerization

In the specific case of [(≡SiO)$_2$Cr(=CH*t*Bu)], while alkenes react stoichiometrically via cross-metathesis, this species is a highly active ethene polymerization catalyst precursor [24]. It has therefore been proposed to be a good model for the active sites (or the resting state) of Phillips polymerization catalyst.

2.3.3. Alkane metathesis

While [(≡SiO)Ta(=CH*t*Bu)(CH_2*t*Bu)$_2$] is not a good alkene metathesis precursor, it was the first well-defined metallocarbene [29,30], displaying activity in alkane metathesis with performances close to those of the parent silica supported tantalum hydride [31,32]. Additionally, the formation of the two cross-metathesis products, *t*BuCH_2–Me and *t*BuCH_2–Et, in the metathesis of propane, with a ratio similar to this obtained for the cross-metathesis products of propene with [(≡SiO)(*t*BuC≡)Re(=CH*t*Bu)(CH_2*t*Bu)] was a clear indication that alkene metathesis was probably the key step of alkane metathesis (Scheme 6a) [30]. This, in combination with kinetic studies [33], also led to propose that alkylidene hydride



TON@120h	65	34	55	<1
Activityin mol/mol M/h	0.5	0.6	1	0

Scheme 6.

species could be one of the key intermediates in alkane metathesis (X═H in Scheme 6). This has been used to develop new types of catalysts based on group 6 metals, which are known to be better alkene metathesis catalysts, either based on tungsten hydrides [34] or on well-defined silica supported metallocarbenes [35,36]. Therefore, using [(≡SiO)(R^1N≡)Mo(═CHR^2)(X)] as alkane metathesis precursor, it was clearly shown that the pendant ligand was key: the precursor must have X = alkyl [35,36], even though the best activity and stability in alkene metathesis is associated with amido ligands, *i.e.* X═NR_2 (Scheme 6b). The necessity of the pendant alkyl ligand is in fact consistent with the proposed alkylidene hydride intermediates, since the pendant alkyl group is probably the source of H [36].

3. Conclusion

Well-defined silica supported metallocarbenes are easily accessible. They are obtained by grafting on $SiO_{2-(700)}$ well-defined molecular metallocarbene complexes, which contain a labile ligand such as an alkyl, an alkoxide or an amido. These systems are highly active alkene metathesis catalyst precursors, which display higher stability than their molecular equivalent. This is due to (1) the asymmetric metal centre, which is linked to both a strong σ-donor (alkyl > amido > alkoxy) and a weak σ-donor (siloxy) ligands, and (2) site isolation on the silica surface, which increase the lifetime of reactive species. This has also allowed the characterization of the actual intermediates of the alkene metathesis catalytic cycle in the specific case of [(≡SiO)(ArN≡)W(═CH*t*Bu)(2,5-dimethylpyrrolyl)]. Similarly, it has also permitted a better understanding of alkane metathesis, which specifically requires the presence of an alkylidene and an alkyl ligands as in [(≡SiO)Ta(═CH*t*Bu)(CH_2*t*Bu)$_2$] and [(≡SiO)(ArN≡)Mo(═CH*t*Bu)(CH_2*t*Bu)] in agreement with the proposed active sites based on alkylidene hydride species. Finally, in the specific case of [(≡SiO)$_2$Cr(═CH*t*Bu)], prepared by thermolysis of [(≡SiO)$_2$Cr(CH_2*t*Bu)$_2$], its high activity in alkene polymerization suggests that the active sites of the Phillips catalysts could be, in fact, based on Cr^{IV} alkylidene complexes.

Acknowledgements

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