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Olefin Metathesis by Group VI (Mo, W) Metal Compounds

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Abstract

Olefin metathesis is an important reaction not only in petroleum chemistry but also in fine chemistry. Professors Grubbs, Schrock, and Chauvin obtained the Nobel Prize in 2005 for the development of this reaction (determination of the mechanism and synthesis of homogeneous catalysts). This reaction can be described as the redistribution of carbon chains of olefins via a breaking of their C=C double bonds. It is catalyzed by metal carbenes and the catalytic cycle passes through a metallacyclobutane. The purpose of this chapter is to give an overview of catalysts based on tungsten or molybdenum active for this reaction. Numerous tungsten and molybdenum organometallic complexes displaying a carbene functionality were synthesized. Some of them are highly active in olefin metathesis. Industrially, tungsten oxide on silica is used as a precursor of the propene production by olefin metathesis of but-2-ene and ethylene. However, the active sites are not well known but they can be modeled by grafting, via surface organometallic chemistry, perhydrocarbyl complexes of molybdenum or tungsten on oxide surfaces. After a review of the complexes used in homogeneous catalysis, a review of the industrial catalysts and their models will be given.

Keywords: olefin metathesis, molybdenum, tungsten, heterogeneous catalysis

1. Introduction

Olefin metathesis can be described as the redistribution of the two fragments obtained by breaking the double bond of an olefin (**Figure 1**). This reaction is of great interest not only for industry (for example, for the production of propene from ethylene and butene) but also for organic chemistry, mainly for the formation of cycles [1].

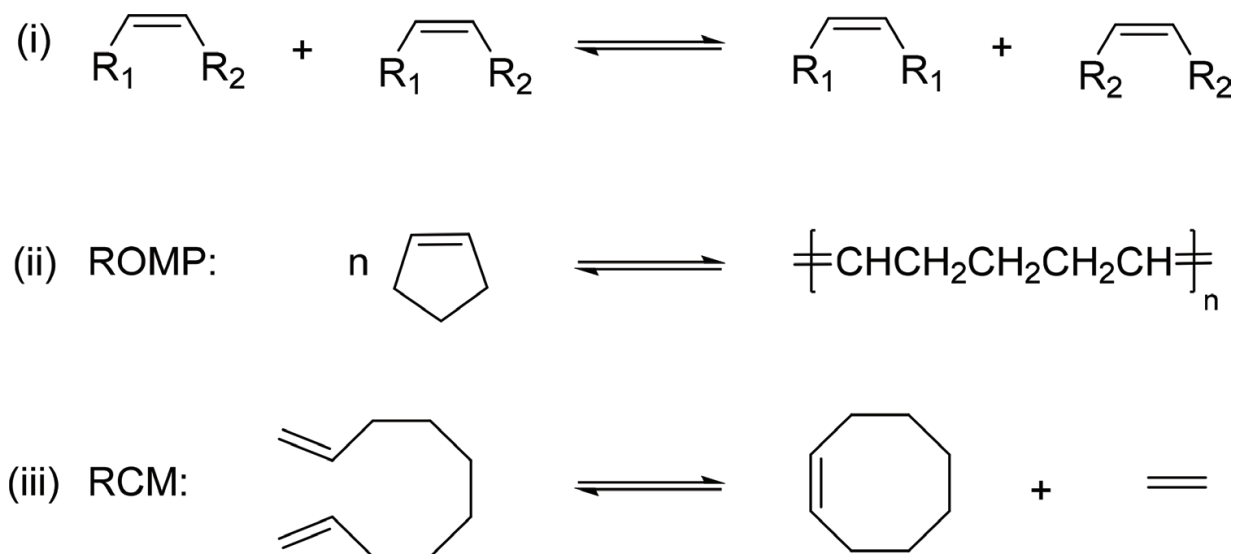


Figure 1. The three olefin metathesis reactions.

Historically, the reaction was not recognized as a metathesis reaction. At the end of the 1950s, there were many studies in industrial laboratories on the catalytic effects of systems containing transition metal ions on unsaturated hydrocarbons. These works had been initiated partly by the results of Ziegler and Natta in the field of ethylene and propene polymerization and partly by those obtained by Phillips and Standard Oil in ethylene polymerization by heterogeneous systems. Many observations were made which could not be explained by the reactions known at this period. Finally, it was really Calderon and Ofstead, at Goodyear, who obtained the first conclusive results, which led to the formulation of metathesis as a general principle of reversible scission and recombination of carbon-carbon double bonds.

The olefin metathesis reaction can be divided into three different reactions (**Figure 1**): (i) the homo-metathesis and the cross-metathesis which involve the exchange of fragments of acyclic olefins; (ii) the ring opening metathesis polymerization (ROMP), which involves the opening of a cyclic olefin, and (iii) the ring closing metathesis (RCM), which corresponds to the formation of a cyclic olefin by reaction of a diene. Three other classes of olefin metathesis are (iv) ring-opening metathesis polymerization, (v) acyclic diene metathesis, and (vi) ethenolysis.

The mechanism of the olefin metathesis reaction remained unknown for several years and various intermediates were postulated. In 1968, Calderon proposed a cyclobutane coordinated to the metal as an intermediate species (**Figure 2**) [2]. Pettit proposed the formation of a tetramethylene complex [3], while Grubbs postulated the formation of a metallacyclopentane [4].

Finally, Chauvin proposed the now admitted and experimentally proved mechanism of the olefin metathesis reaction and obtained the Nobel Prize in 2005 with Grubbs and Schrock for this discovery [5]. This mechanism necessitates the presence of a metallocarbenic species which can coordinate an olefin, leading to the formation of a metallacyclobutane. Upon rearrangement this cycle will lead to the formation of a new olefin and restore the metal carbene species (**Figure 3**).

This mechanism implies that the reactions are equilibrated and the metallacyclobutane can lead to new products (productive metathesis) or to the starting olefins (degenerative metathesis).

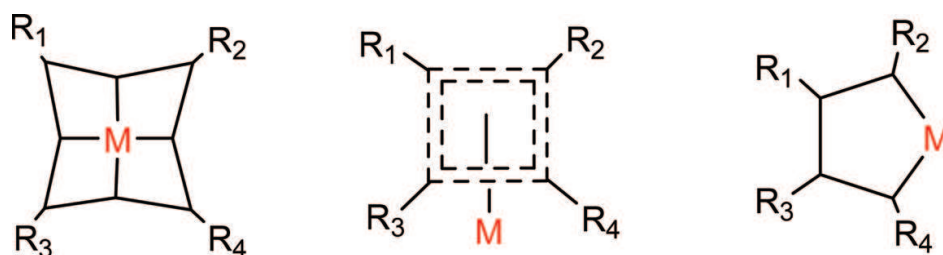


Figure 2. Intermediates proposed for the olefin metathesis reaction.

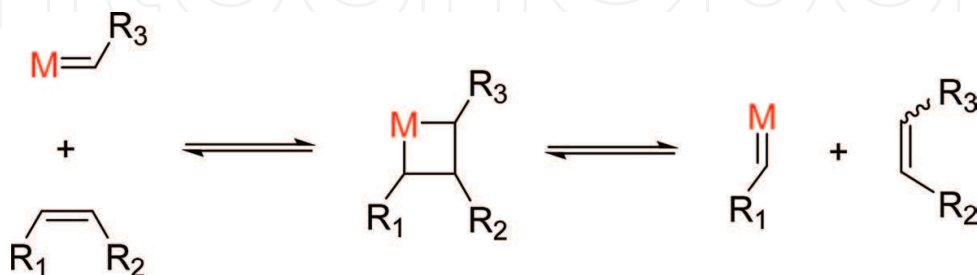


Figure 3. Mechanism of the olefin metathesis reaction.

This mechanism has been confirmed by the synthesis of homogeneous complexes containing a nucleophilic carbenic function and the formation of a metallacyclobutane by their reaction with an olefin [6, 7]. These species display a good activity in the olefin metathesis reaction, in agreement with a mechanism involving them. In addition, numerous complexes with metallacyclobutane intermediates were isolated and gave additional proofs to the Chauvin's mechanism [8, 9]. During last years, the development of highly active homogeneous and heterogeneous catalysts made the olefin metathesis reaction a powerful tool in numerous domains such as petrochemistry, polymers synthesis, fine chemistry, and synthesis of natural products.

Usually, olefin metathesis catalysts contain elements from groups 6 to 8, typically molybdenum, tungsten, rhenium, and ruthenium. While catalysts based on ruthenium are widely used in organic synthesis at the laboratory scale, molybdenum and tungsten are used industrially at a larger scale. Systems based on rhenium were developed but their use remains marginal.

Due to the importance of catalysts based on group (VI) elements, this review will be limited to them, with the aim to have a better understanding of the nature of the active sites in the industrial systems.

2. Group VI complexes used in homogeneous catalysis

The first homogeneous catalytic systems using group VI metals (W or Mo) were ill-defined Ziegler-Natta type compounds, formed *in situ* by contacting a precatalyst and a cocatalyst [10]. The first example of olefin metathesis was described in 1955 by Anderson and Merckling who observed the formation of polynorbornene during the reaction of norbornene and $\text{TiCl}_4/\text{LiAl}(\text{heptyl})_4$ [11]. Two other catalytic systems based on quite the same elements ($\text{WCl}_6/\text{AlEt}_3$

and $\text{MoCl}_5/\text{AlEt}_3$) were described by Natta et al. in 1964 [12]. Depending on the catalytic system used, trans- or cis-polymers were obtained by polymerization of cyclopentene and tungsten leading to the trans compound. Later, various catalysts based on tungsten combined to an alkylating agent were described such as $\text{WCl}_6/\text{EtOH}/\text{EtAlCl}_2$, $\text{WCl}_6/\text{SnBu}_4$, or $(\text{ArO})_4\text{WCl}_2/\text{SnMe}_4$ and are active for the metathesis of internal olefins such as cis-pent-2-ene [13–15]. Systems based on the combination of nitrosyl complexes of molybdenum or tungsten with alkylaluminum species were developed for the metathesis of terminal olefins (pent-1-ene, oct-1-ene) [16–19]. In parallel, many academic researchers tried to synthesize metal alkylidene species which should be active for olefin metathesis as proposed by Chauvin. Casey et al. isolated in 1973 the first electrophilic metal alkylidene, $[(\text{CO})_5\text{W}=\text{C}(\text{C}_6\text{H}_5)_2]$, which is of the Fisher type and is active in olefin metathesis at room temperature without any cocatalyst [20]. After 1980, Schrock has prepared all a family of molybdenum and tungsten complexes with nucleophilic carbene functions. The general formula of these complexes, which are highly active in olefin metathesis, is $[\text{M}(=\text{CHCMe}_2\text{Ph})(=\text{N}-\text{Ar})(\text{OR}')_2]$ where R' and Ar are sterically encumbered groups. The structure of some of these complexes is depicted in **Figure 4**.

As these complexes are not very sensitive to functional groups, their use was then extended to fine chemistry [21, 22], oleochemistry [23], and to the synthesis of functional polymers [24] while during many years olefin metathesis was confined to nonfunctional olefins. In these complexes, the metal is surrounded by the carbene moiety and by various electro-attractor and/or sterically encumbered ligands allowing a good stability in solution and good activity, selectivity, and stability. For example, complex **6**, which contains an imido group and a binaphthyl

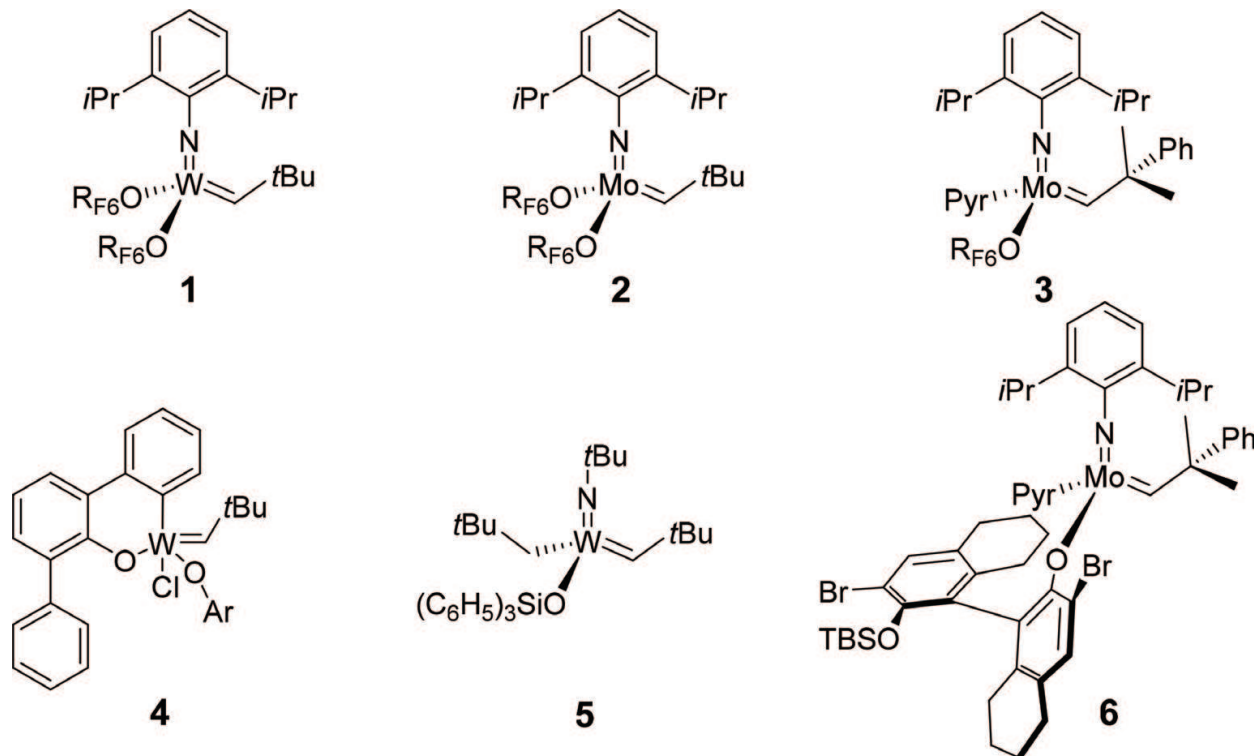


Figure 4. Some W(VI) and Mo(VI) complexes bearing imido, aryloxy, and carbenic functions highly active in olefin metathesis.

ligand, is able to perform the cross-metathesis of methyl oleate with ethylene (**Figure 5**) with a good yield (Turnover number (TON) = 4750) [23]. The reaction products, dec-1-ene and methyl decen-9-oate, are important intermediates in the chemical industry and are used for the preparation of polyolefins, surfactants, and lubricating compounds. The TON can be considerably increased (up to 50,000) upon addition of $\text{Al}(\text{octyl})_3$ [25].

Osborn et al. have developed another family of complexes where the imido group is replaced by an oxo ligand. For that purpose, they prepared oxo alkyl complexes of molybdenum and tungsten. The idea was that these species were not stable, due to the small energy of the metal-carbon bond, and should lead to the formation of the carbenic complex upon α -H abstraction. Oxo complexes of molybdenum and tungsten with neopentyl and/or neosilyl ligands were prepared (**Figure 6**) [26] and are active in the metathesis of linear, cyclic, and functional olefins, but in presence of Lewis acids such as AlCl_3 , SnCl_4 , or GaCl_3 [27, 28].

Later, Schrock et al. have synthesized pentacoordinated complexes of tungsten(VI) with oxo and alkylidene groups stabilized by phosphine ligands (**Figure 7**) [29, 30]. These systems are active in metathesis of terminal and internal olefins in presence of a Lewis acid such as AlCl_3 [31].

Complex **9**, which contains two chloro ligands, has been used as a precursor for the preparation of numerous oxo carbenic complexes where chlorine was replaced by other ligands such as phenoxide, pyrrolidyl, thiophenoxide, or siloxide. By this way, Schrock et al. have studied the effect of the modification of the coordination sphere of this complex on its activity and selectivity in metathesis of terminal olefins and ROMP of norbornene derivatives. For example, $\text{W}(=\text{O})(\text{CHCMe}_2\text{Ph})-(\text{Me}_2\text{Pyr})(\text{OAr})$ (Me_2Pyr = 2,5-dimethylpyrrolide, OAr = aryloxide) **13** is active in ROMP of 2,3-dicarbomethoxynorbornadiene (DCMNBD) and leads selectively to the cis syndiotactic polymer while complex $\text{W}(=\text{O})(\text{CHCMe}_2\text{Ph})(\text{OR})_2$ **10** leads selectively to the cis isotactic polymer [32]. Addition of a Lewis acid such as $\text{B}(\text{C}_6\text{F}_5)_3$ leads to a considerable increase of both the activity and the selectivity.

Complexes with thiophenoxide ligands were also prepared and their activity in metathesis of oct-1-ene and polymerization of DCMNBD was compared to that of the corresponding

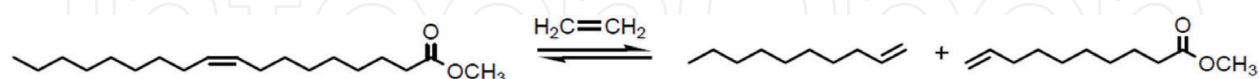


Figure 5. Cross-metathesis of ethylene and methyl oleate.

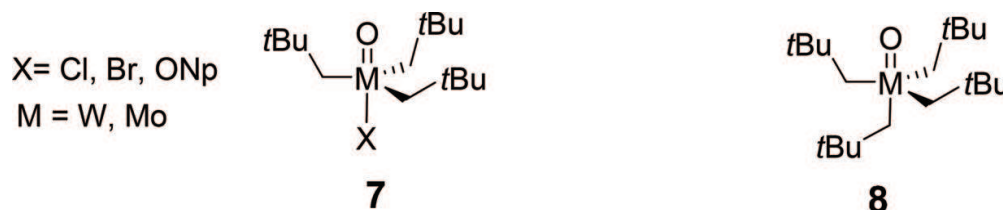


Figure 6. Oxo alkyl complexes synthesized by Osborn et al.

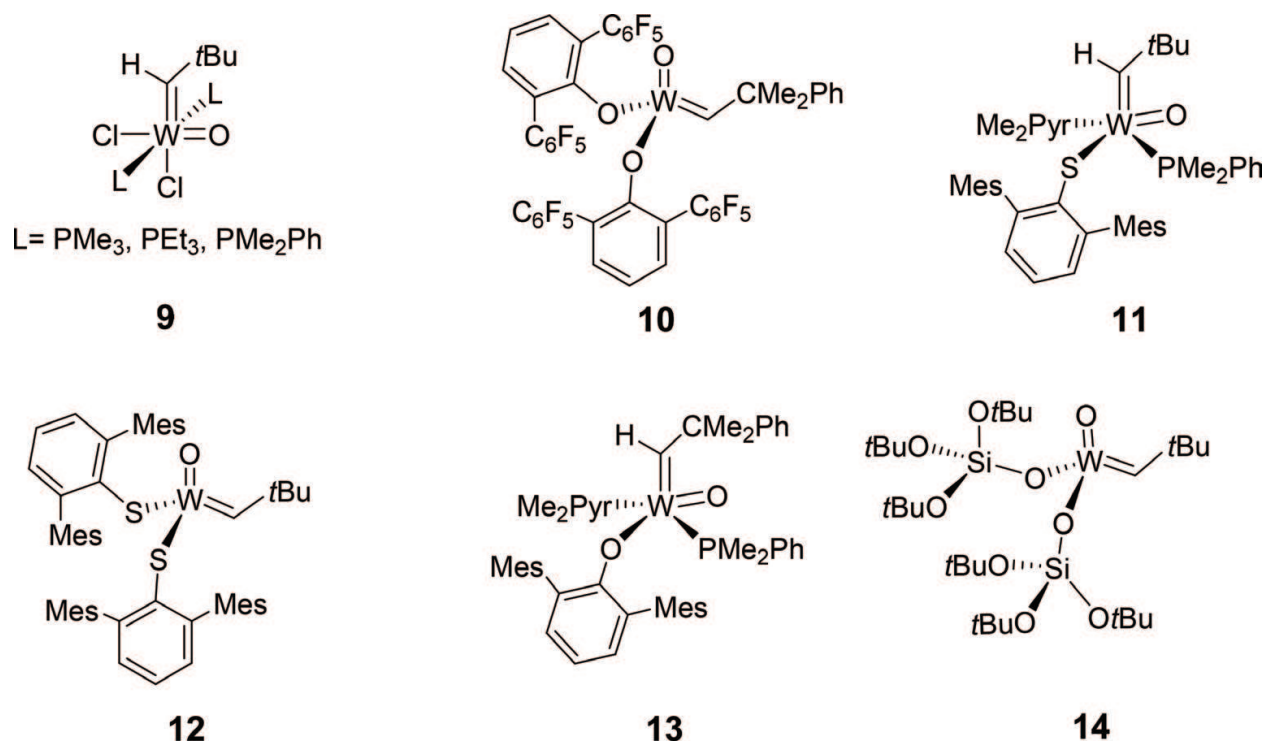


Figure 7. Oxo carbenic complexes synthesized by Schrock et al.

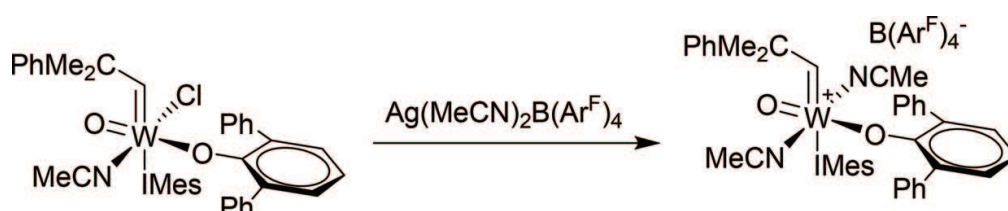


Figure 8. Synthesis of the cationic tungsten(VI) complex.

phenoxide complexes. They are less active and less selective. This was attributed to a higher electronic density around the metal, due to a stronger σ -donor effect of thiophenoxides compared to phenoxides [33]. The bis-siloxy oxo alkylidene tungsten complex **14** has been described recently. However, it displays a low initial activity (Turnover frequency (TOF) = 12 min^{-1}) in metathesis of cis oct-4-ene at 80°C. This low activity has been explained by the low thermal stability of this complex in absence of phosphine ligands [34].

Buchmeiser et al. have increased the catalytic activity of these oxo complexes by increasing the electrophilicity of the metal by transforming them into cationic species. They have reported recently the synthesis and X-ray structure of the first stable cationic complex of tungsten by removing chlorine of the W—Cl bond by reaction with $\text{Ag}(\text{MeCN})_2\text{B}(\text{Ar}^F)_4$ (Figure 8). This complex is highly active (the TONs can reach 10,000) in metathesis of olefins functionalized by nitrile, sec-amine, or thioether groups [35].

3. Solids containing group VI (Mo, W) metal ions used in heterogeneous catalysis

Oxides of group VI (molybdenum and tungsten) and group VII (rhenium) are often used in industrial processes when they are supported on silica or alumina. The triolefin process, developed by Phillips (**Figure 9**), was the first commercial application using WO_3 supported on silica for olefin metathesis [36]. Initially, this process was developed in order to convert propene into ethylene and but-2-ene. Later, due to the increasing request of propene for the synthesis of numerous chemicals (polypropylene, acrylonitrile, propene oxide, cumene, and acetone), new processes were developed for the production of propene.

Actually, the propene production by metathesis is mainly made by use of the OCT (Olefins Conversion Technology) process, developed by ABB Lummus Technology at Houston. This reaction is the reverse of the triolefin process, with quite the same catalyst [37, 38]. It produces ca. 6% of the world production (6.5 Mtons/year in 2014). The SHOP (Shell Higher Olefins Process) is one of the main industrial processes using olefin metathesis for the production of α -olefins, which are precursors for plasticizers and detergents [37, 39]. The catalyst is based on $\text{MoO}_3/\text{Al}_2\text{O}_3$ or WO_3/SiO_2 , the production ability being ca. 1.2 Mtons/year [37]. Another industrial process using olefin metathesis is the synthesis of neohexene from di-isobutene and ethylene (**Figure 10**). Neohexene is mainly used for perfumes where it is a starting material for the obtention of synthetic musks [40].

The main application of these heterogeneous systems is in petrochemistry and their use in other domains such as organic synthesis, oleochemistry, or polymerization remains very limited, mainly due to the drastic conditions which are required and to their intolerance of functional groups. The most often used catalyst is WO_3/SiO_2 , due to the following reasons: (i) it is resistant to poisoning by oxygenated and sulfided compounds due to the high reaction temperature (more than 350°C) [41, 42]; (ii) even if the coke formation is important at high temperature, the catalyst can be regenerated easily by calcination in air [42], without decomposition of the active sites, in

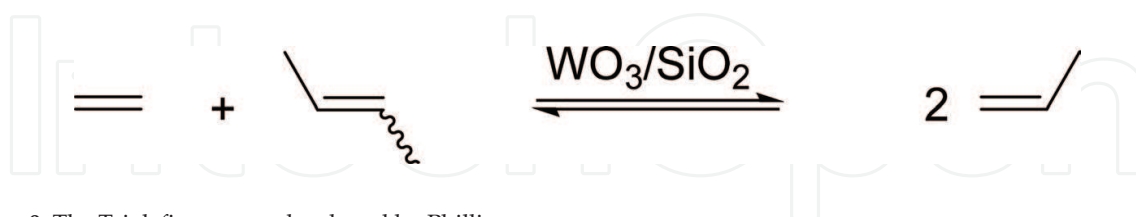


Figure 9. The Triolefin process developed by Phillips.

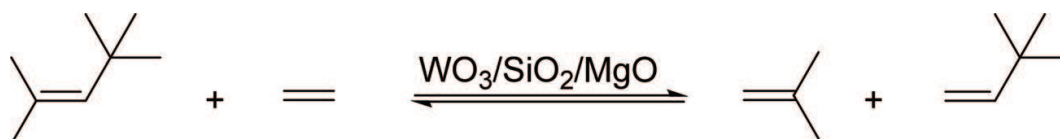


Figure 10. Synthesis of neohexene by olefin metathesis.

contrast to other systems such as $\text{MoO}_3/\text{Al}_2\text{O}_3$ or $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$; and (iii) its preparation is easy, by impregnation of a high surface area silica by an aqueous solution of ammonium metatungstate $[(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}]$.

A lot of studies were made on the WO_3/SiO_2 system, before and after activation by propene, by using various spectroscopic methods such as Raman, UV-visible, EPR, XANES, and EXAFS. The first studies were made by Raman and led to the conclusion that the active site was an isolated surface complex of tungsten but of unknown structure [43]. The first postulated surface species was a pentacoordinated tungsten complex but no experimental justification was given [44].

In 1991, Basrur et al. have proposed that the active species of the WO_3/SiO_2 catalyst was a bis-oxo bis-siloxy tungsten complex $[(\text{=SiO})_2\text{W(=O)}_2]$ and that the activation by propene led to a reduction of tungsten and formation of acetone or to a transformation of the W=O double bond into a metal-carbene bond with liberation of acetaldehyde [45]. A characterization by EXAFS at room temperature of WO_3/SiO_2 has shown that polytungstic species are present on the surface of silica [46]. By using a combination of Raman and UV-visible spectroscopies *in situ*, Wachs et al. have shown that, at room temperature, the tungsten oxide phase is composed of nanoparticles of WO_3 and of polyoxotungstate clusters $(\text{W}_{12}\text{O}_{39})^{6-}$, **17** (Figure 11). After dehydration at 450°C under air, these polyoxotungstate clusters evolve into bis-oxo bis-siloxy tungsten species **15** and mono-oxo tetra-siloxy tungsten species **16** while the nanoparticles remain unchanged [47, 48].

Some authors have studied propene metathesis on WO_3/SiO_2 and have shown that the reaction rate is linearly dependent on the propene partial pressure [49]. It has also been reported that the amount of surface tungsten and the treatment of the catalyst by an inert gas (nitrogen, argon, helium) [45] or by hydrogen [50] have a significant effect on the catalytic activity.

Recently, Wachs et al. have studied the effect of the WO_3 amount on silica on the catalytic activity in propene metathesis at 300°C . The results are depicted in Figure 12. The catalytic activity increases with the amount of WO_3 until a value of ca. 8 wt.% and then remains quite constant. These results were explained as follows: At low coverage ($\text{WO}_3 < 8 \text{ wt.}\%$) the catalytic activity is proportional to the amount of isolated mono-oxo and di-oxo species (which are all assumed to be active in olefin metathesis). At high coverage, the reaction rate is not dependent on the tungsten loading, due to the formation of WO_3 crystallites which are inactive [51]. There is also an effect of the WO_3 loading on the amount to ethylene and butenes.

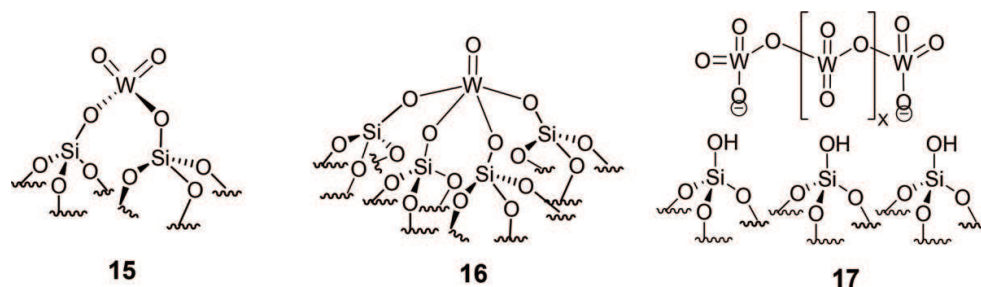


Figure 11. Proposed molecular structures for WO_3/SiO_2 .

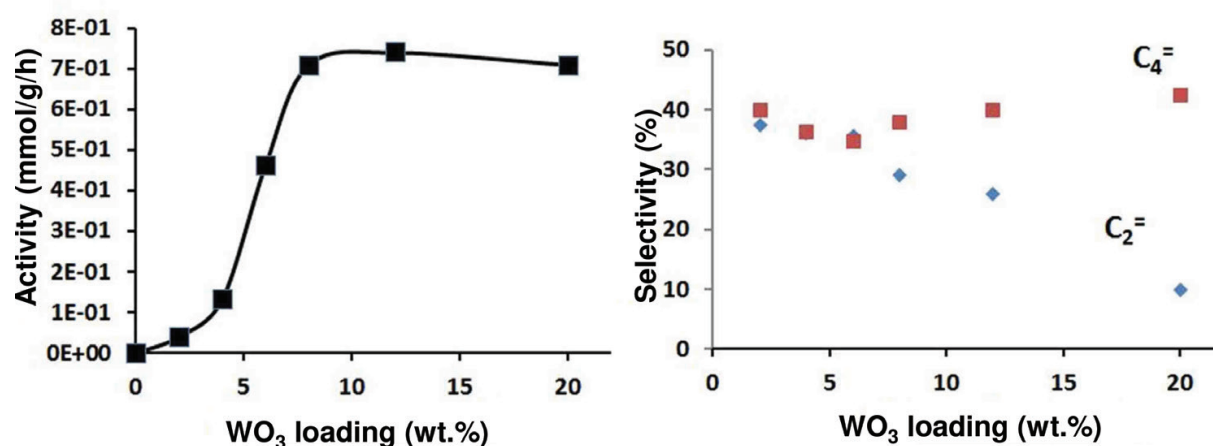


Figure 12. Conversion and ethylene/butene ratio as a function of the WO₃ loading during propene metathesis at 300°C.

At low coverage, the ethylene/butene ratio is equal to ca. 1 as expected while at high coverage it decreases strongly, due to the formation of C₄–C₆ alkanes. This was interpreted as due to the presence of Brönsted acid sites on the WO₃ crystallites (or nanoparticles), which led to oligomerization and cracking [51].

Recently operando methods (UV-Vis, Raman, XANES/EXAFS) were used in order to characterize the catalyst during its pretreatment and in presence of propene, the aim being to establish a structure-activity relationship. Wachs et al. studied by Raman the effect of the pretreatment in air on a WO₃/SiO₂ catalyst as a function of the oxide loading [51]. For low coverages, the Raman spectrum shows new bands at 1016 and 958 cm⁻¹, which were attributed to the symmetric vibrations of di-oxo and mono-oxo species, respectively. The di-oxo species displays also an asymmetric vibration band at 968 cm⁻¹. The absence of the W–O–W band at 200–300 cm⁻¹ confirms the absence, at low coverage, of WO₃ aggregates. These results are in agreement with the UV-visible results. When the tungsten amount is higher than 0.6%, the Raman peak at 990 cm⁻¹ increases with the amount of tungsten. At high loadings, three new bands appear at 270, 720, and 805 cm⁻¹, characteristic of tungsten oxide nanoparticles. The main conclusion of this study is that tungsten is well dispersed on the silica surface for WO₃ loadings below 8 wt.%.

The catalyst containing 4 wt.% was also studied by operando Raman spectroscopy during the metathesis reaction of propene (1% in argon) at 300°C. The bands characteristics of the mono-oxo and di-oxo species (which are the sole species on the solid) decrease simultaneously with time and disappear after 100 minutes [51]. This proves that the two species were activated by propene and led to the formation of carbene species with elimination of oxygen from the coordination sphere of tungsten (Figure 13). After reoxidation by an O₂/Ar mixture, the initial bands of the tungsten oxide species are restored with their intensity and no formation of nanoparticle is detected by Raman. For catalysts with high loadings (8 wt.% WO₃), the activation under propene leads to a strong decrease of the bands characteristic of the nanoparticles with formation of oxygenates such as formaldehyde or acetaldehyde but no acetone is formed. In addition, a study by ESR and UV-visible spectroscopy has shown that tungsten is mainly in the +VI oxidation state.

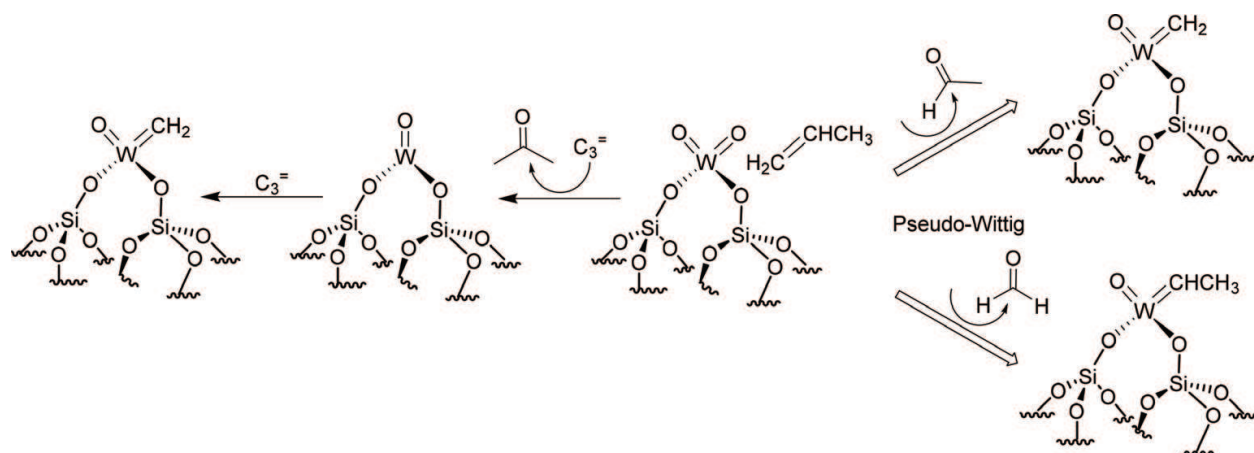


Figure 13. Possible mechanisms for the activation of the di-oxo tungsten species by propene.

However, Bell et al. [52] have recently shown by an *in situ* XANES study that there is a reduction of W(VI) to W(IV) during the activation of WO_3/SiO_2 at 500°C . This result is in agreement EXAFS data and with the formation of acetone during the activation (**Figure 13**). The amount of evolved acetone shows that for a catalyst containing 5.4 wt. only 5% of tungsten atoms are active in olefin metathesis. This value is similar to what had been reported for MoO_3 supported on silica [53] and that proposed by Wachs et al. for WO_3 on silica [51]. Unfortunately, no mechanism was proposed to explain the transformation of the mono-oxo tungsten (IV) species into the bisiloxy-oxo-carbene $(\equiv\text{SiO})_2(\text{O})\text{W}=\text{CHR}$ ($\text{R} = \text{H}, \text{CH}_3$). Very recently Stair et al. have observed, during a Temperature Programmed Reduction (TPR) study of WO_3/SiO_2 in presence of propene, the formation of a mixture of methane, carbon monoxide, and hydrogen [54]. They proposed that the activation at 700°C is made via a pseudo-Wittig reaction with evolution of aldehydes, not stable at high temperature and which decompose into small molecules (**Figure 13**).

EXAFS spectra of a pretreated 5.4 wt.% WO_3/SiO_2 catalyst show the presence of mono-oxo and di-oxo tungsten species with contributions in the Fourier transform at 0.12 nm ($\text{W}=\text{O}$) and 0.16 nm ($\text{W}-\text{O}$) (the true distances take into account a phase correction and are slightly larger by 0.04 nm than those deduced from the Fourier transform). After treatment at 600°C under inert gas (helium), Bell et al. observed a decrease of the peak at 0.16 nm [52]. This decrease was attributed to the transformation of the mono-oxo species into the di-oxo one (**Figure 14**). This increase of the di-oxo concentration could explain the higher activity of this system compared to that obtained after activation under air.

Stair et al. reported recently that a pretreatment at high temperature of the WO_3/SiO_2 catalyst by a gas containing propene increased by two to three orders of magnitude its activity at low temperature [54]. Surprisingly, these catalysts can be regenerated by a treatment under nitrogen at high temperature.

Even if some tentative structure-activity relationships were made for the MO_3/SiO_2 ($\text{M} = \text{Mo}, \text{W}$) catalysts, the structure of the true active species is not really known up to now. The main problem is due to the low amount of active sites. Spectroscopic methods such as in-operando Raman,

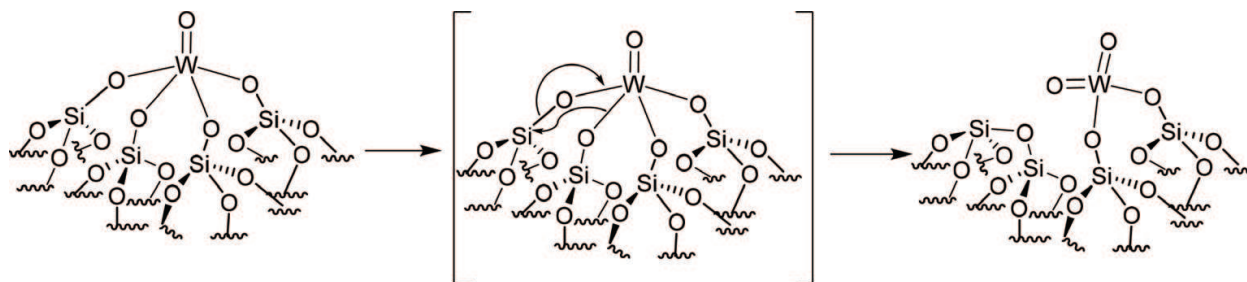


Figure 14. Conversion of the mono-oxo tungsten(VI) species into the di-oxo one.

UV-Vis, XANES, or EXAFS show all surface species, not only those which are active in olefin metathesis. As a consequence, it is very difficult to understand the activation mechanism of the catalyst (and also its deactivation).

The preparation of systems containing a higher amount of active sites could lead to more active (and easily regenerated) systems and could allow a better characterization and mechanistic study of the initiation and deactivation steps and their rationalization in terms of classical organometallic chemistry. Surface organometallic chemistry (SOMC) is a choice method for the preparation of silica supported complexes. Numerous tungsten complexes with a variety of ligands (alkyl, carbene, carbyne, oxo, imido, aryloxy, etc.) were immobilized on oxide supports in order to obtain single site species which can be applied for the valorization of hydrocarbons via various reactions (alkane or alkene metathesis, methane coupling, etc.) [55, 56]. These materials can be characterized by the same spectroscopic methods than the conventional catalysts (solid-state NMR, EXAFS, DRIFT, ESR, UV-Vis, etc.).

4. Supported tungsten catalysts prepared by SOMC

SOMC can be considered as a bridge between homogeneous and heterogeneous catalysis [55–57]. Its aim is to graft organometallic complexes on oxide surfaces (silica, alumina, titania, zirconia, etc.) or on metal surfaces. In the case of oxides, the complex can be linked to the support by one or more bonds with surface oxygen atoms. When the support has been previously functionalized, the bonding can be made via other atoms such as P, N, Si, etc. As it is the case in homogeneous catalysis, these surface organometallic species can be defined by their ligands around the metal. Two types of ligands can be considered, those which will be involved in the catalytic cycle and those which are only spectators (such as oxo, alkoxo, amido, or imido groups). The modification of both types of ligands can have a drastic effect on the activity and selectivity of a given catalytic reaction, allowing to establish structure-activity relationships. For example, pretreatment of the support at different temperatures will lead to the synthesis of surface complexes with one, two, or three bonds with the surface. This new approach has many advantages:

- The catalyst can be easily separated from the reaction products and recycled.
- The catalysts are single sites, as in homogeneous catalysis.

- The metal complexes have a limited mobility on the surface, avoiding the bimolecular decomposition reactions which are often observed in homogeneous catalysis [58].
- The catalysts can be characterized easily by use of spectroscopic methods, as all species are identical.
- The good knowledge of the structure of the active site allows to propose a reasonable catalytic cycle and to determine how deactivation and regeneration will proceed.

A lot of organometallic complexes of groups 4–8 were grafted on a variety of surfaces such as amorphous inorganic oxides [55], zeolites [59], or metals [60, 61]. This methodology led to numerous applications in fine chemistry and/or petrochemistry including reactions which were not known up to now. This is mainly due to a combination of organometallic synthesis and surface science. The catalytic efficiency of the materials prepared by this way depends on the coordination sphere around the metal, on the number, and the character (ionic or covalent) of the bonds with the support and on the nature of the oxide support (silica, alumina, silica-alumina, etc.).

In the case of tungsten SOMC, the choices of the organometallic precursor and of the support are mainly dependent on the expected catalytic reaction and on the intermediates involved in the postulated catalytic cycle. The high oxidation state of tungsten (VI) allows the possibility of a number of ligands in the coordination sphere leading to both spectators and reactive species in the catalytic cycle. The reactive species will be hydrides, alkyl, carbenes, and carbynes. During the last few years, many studies were made with such surface complexes in olefin metathesis. We will review here only those containing the oxo ligand as they could be considered as models of the industrial heterogeneous catalysts. There are two principal methodologies which have been developed to achieve well-defined tungsten oxo species on oxide: (i) grafting of a reactive tungsten carbyne complex followed by transfer of oxygen from the support and (ii) grafting of an organometallic complex bearing oxo ligand.

4.1. Supported tungsten complexes with oxo and hydride ligands

The first carbynic complex of tungsten(VI), $[W(=CtBu)(CH_2tBu)_3]$, was synthesized in 1978 by Clark and Schrock [62]. Later, various complexes of the same type were synthesized, for example, $[W(=CtBu)X_3]$ ($X = Cl, OtBu, N^iPr_2$) [63, 64]. Some of these complexes (mainly those with a pronounced electrophilic character such as $[W(=CtBu)(OtBu)_3]$) displayed a moderate activity in alkynes metathesis. Unfortunately, these systems deactivated rapidly by a bimolecular reaction leading to a dinuclear tungsten complex with a $W=O$ triple bond [65, 66]. In order to avoid this deactivation, these complexes were heterogeneized. $[W(=CtBu)X_3]$ ($X = Cl, OtBu, CH_2tBu$) was grafted on silica partially dehydroxylated at 500°C. Weiss et al. proposed that there was formation of the carbenic species $[(=SiO)W(=CtBu)X_3]$ ($X = Cl, tBu$) by addition of the Si–OH bond of silica on the carbyne bond [67]. The carbenic ligand was evidenced by its reactivity with acetone via a pseudo-Wittig reaction and indirectly by the catalytic activity in olefin metathesis. $[W(=CtBu)(CH_2tBu)_3]$ was then grafted on silica, dehydroxylated at 200°C (SiO_{2-200}) and at 700°C (SiO_{2-700}). When silica was treated at 700°C the main reaction product was $[(=SiO)W(=CtBu)(CH_2tBu)_2]$ **18**, while $[(=SiO)_2W(=CtBu)(CH_2tBu)]$ **19** was formed on silica treated at 200°C (**Figure 15**) [68].

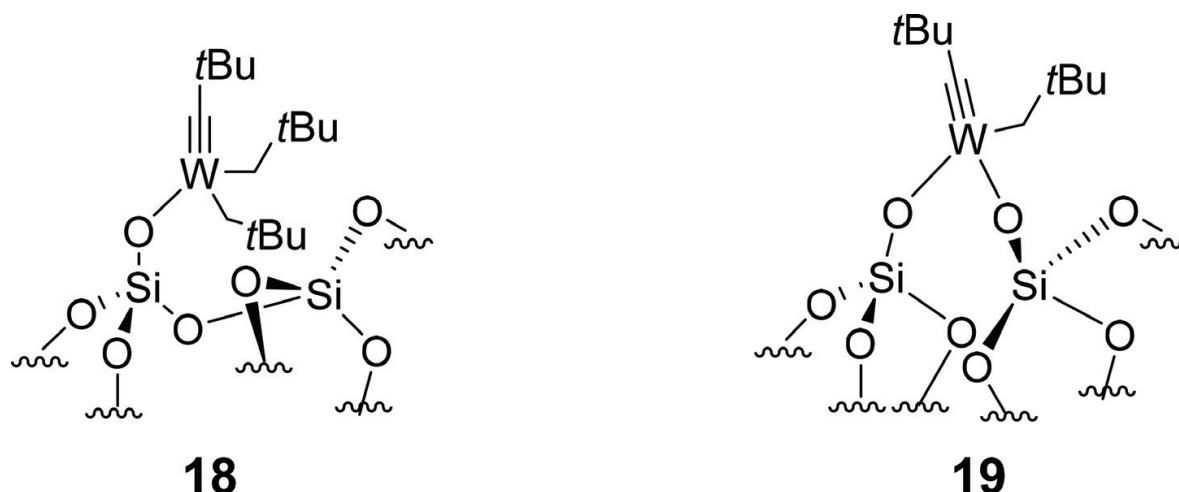


Figure 15. Species formed during the reaction of $[W(\equiv CtBu)(CH_2tBu)_3]$ with SiO_{2-200} and SiO_{2-700} .

The structures of species **18** and **19** were confirmed by solid-state NMR (1H , ^{13}C , HETCOR, J-resolved). The interaction with the silica surface was studied by ^{17}O MAS NMR by using enriched silica [69]. This study showed the existence of interactions between protons of residual hydroxyl groups and the alkyl ligands of the supported species.

Species **18** shows a good activity in propene metathesis (initial TOF 5.5 min^{-1} , TON = 11,000 after 40 h) [68]. Two mechanisms were proposed explaining the formation of the carbenic ligand. The first one is a α -H transfer from the alkyl ligand to the carbyne during the coordination of the olefin and formation of a bis-alkylidene complex [70]. The other possibility is to form directly the carbene by metathesis between the olefin and the carbyne: a metallacyclobutene is formed which decomposes into a carbene-alkenyl tungsten complex (**Figure 16**).

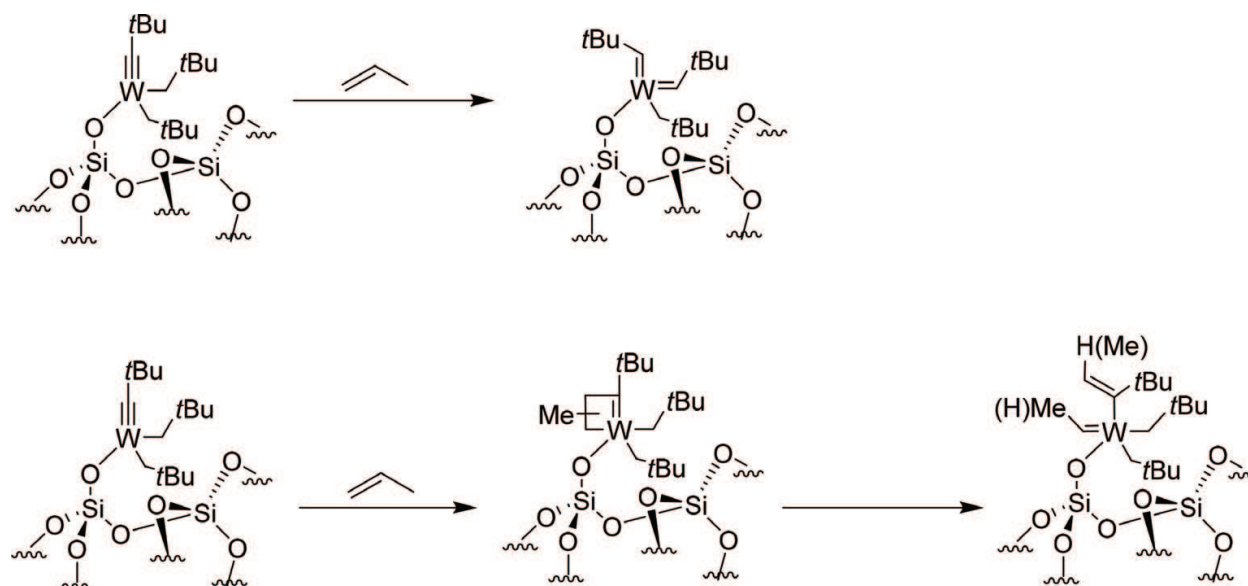


Figure 16. Possible mechanisms of formation of a carbene from the surface carbyne.

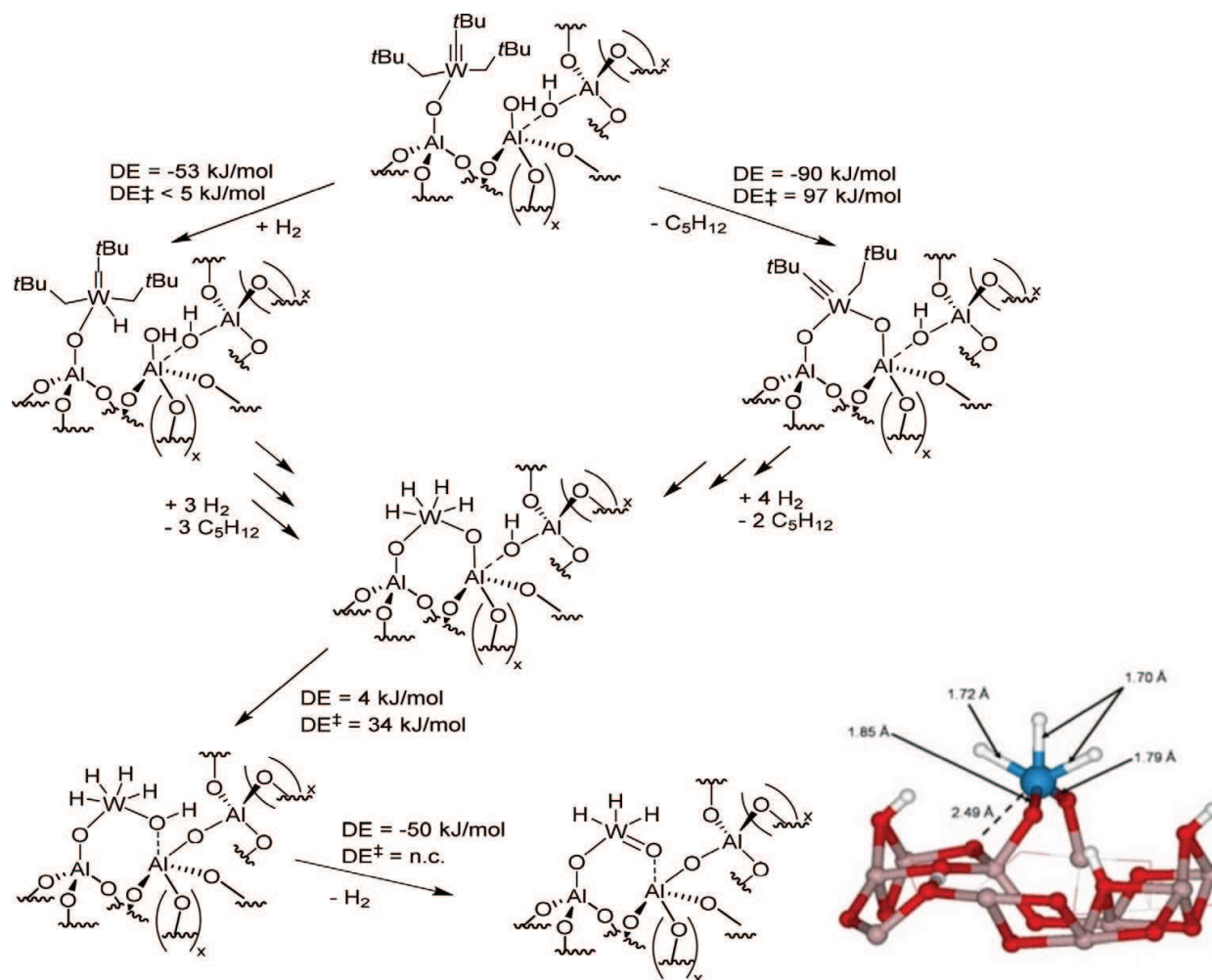


Figure 17. Mechanism proposed for the formation of the oxo hydride tungsten species on alumina.

The grafting reaction of $[W(\equiv C tBu)(CH_2 tBu)_3]$ was also studied on alumina dehydroxylated at 500°C . Alumina is a complex support as aluminum can be tetra-, penta-, or hexacoordinated and its surface hydroxyl groups can be bound to one, two, or three aluminum atoms. As a result, there is a great variety of hydroxyl groups with variable acidity. The determination of the surface complexes obtained after grafting needed the use of a variety of experimental (DRIFT, solid-state NMR, EXAFS) and theoretical (DFT calculations) methods [71]. The evolved gas (one neopentane per grafted tungsten) and microanalysis were in agreement with the formation of a complex having only one covalent bond with the surface, $[(Al_5O)W(\equiv C tBu)(CH_2 tBu)_2]$ **20**. The infrared study showed that there is a partial consumption of the hydroxyl groups and that only those linked to one tetrahedral aluminum have reacted [72]. The ^{13}C CP-MAS NMR spectrum of $[(Al_5O)W(\equiv C tBu)(CH_2 tBu)_2]$ shows only a broad signal between 50 and 110 ppm for the $W-CH_2$ -carbon atoms. DFT calculations show that this broadening is due to an interaction between these methylene groups and the residual surface aluminum groups.

In contrast to complexes **18** and **19** formed on silica, complex **20** has a good activity in propane metathesis at 150°C with an initial TOF equal to 1.8 h^{-1} [73]. The mechanism of this reaction

involves three steps: dehydrogenation of the alkane, olefin metathesis, and hydrogenation of the resulting olefin. This example shows that the support can have a nonnegligible effect on the catalysis. Treatment under hydrogen at 150°C of the complexes obtained on silica and alumina leads also to completely different species. On silica sintering is observed and TEM shows that tungsten particles (size 0.1–0.2 nm) are formed [71]. On alumina no sintering is observed and a hydride species is obtained [71, 73]. This hydride species is characterized by a small peak at 10.0 ppm in ^1H MAS NMR and by two infrared bands at 1903 and 1804 cm^{-1} . The attribution of the two infrared bands was confirmed by isotopic exchange W–H/W–D upon addition of deuterium [71]. In addition, EXAFS showed the presence of a W=O double bond [74]. All these data combined to DFT calculations allowed to propose that the surface hydride is a tris-hydride oxo tungsten(VI) complex stabilized by coordination of the oxo ligand to one surface aluminum (**Figure 17**) [75].

The mechanism of formation of this surface species was elucidated by use of DFT calculations. These calculations suggested that the oxo species is formed by reaction of an unstable tungsten hydride species with one oxygen atom of the alumina surface. Such a phenomenon is prohibited on silica surfaces due to the stability of the Si–O bond. This oxo-hydride tungsten is more active than the industrial WO_3/SiO_2 catalyst for the cross-metathesis of ethylene and but-2-ene to propene. For example, at 120°C the TON can reach 9000 and at 150°C 16,000 after 48 h. At 200°C the TON increases to 22,000 but a rapid deactivation of the catalyst is observed [76].

While an excess of ethylene is needed in the case of the industrial WO_3/SiO_2 catalyst to achieve a good selectivity to propene [77], the tungsten hydride on alumina is very selective (more than 98%) even for ethylene/butene ratios lower than 1. From a mechanistic point of view, the initiation step occurs via the insertion of three ethylene molecules in the W–H bonds, leading to a tris-ethyl tungsten surface complex (the insertion of ethylene is more favorable from both thermodynamic and kinetic points of view than that of but-2-ene [78, 79]). The next step is the elimination of ethane (which can be detected by gas chromatography) by a α -H abstraction, leading to the active ethyl-ethylidene oxo tungsten complex (**Figure 18**) [76].

More interestingly, this system is also active for the direct conversion of ethylene to propene with a very good selectivity (more than 95%). The TON can reach 1120 after 120 h [80]. The

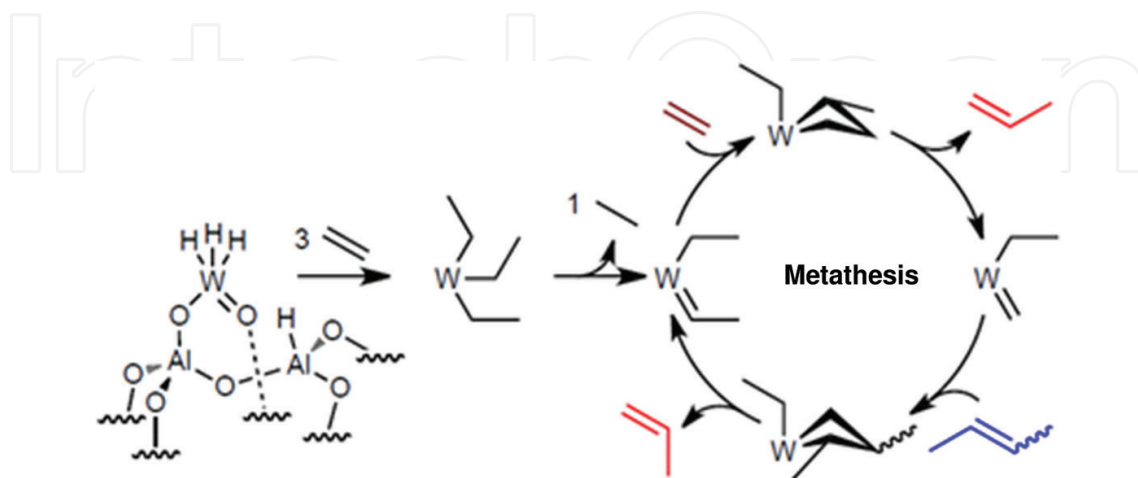


Figure 18. Formation of the active species from tungsten hydride and catalytic cycle for ethylene/but-2-ene cross-metathesis.

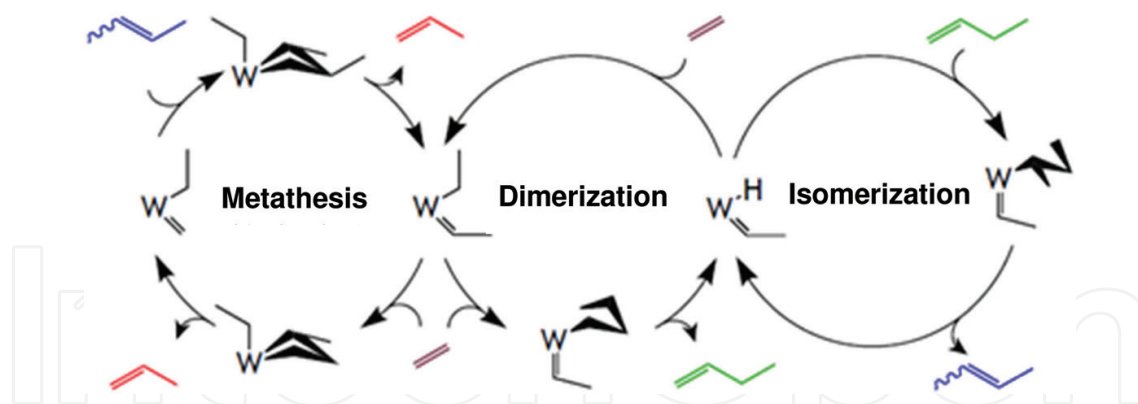


Figure 19. Proposed mechanism for the direct conversion of ethylene to propene.

mechanism of this reaction passes probably via the same ethyl ethylidene oxo tungsten complex than above as ethane is also detected at the first stages of the reaction. This complex can then convert ethylene to propene via three successive reactions: (i) dimerization of ethylene to but-1-ene; (ii) isomerization of but-1-ene to but-2-ene; and (iii) cross-metathesis between ethylene and but-2-ene (**Figure 19**).

This hydride species displays also a good activity in the metathesis of isobutene into 2,3-dimethylbutenes with a relative selectivity reaching 92% [81, 82]. It is the first example of use of a supported tungsten complex for this reaction, which is very difficult, due to the high steric hindrance in the gem-tetra-substituted metallocyclobutane intermediate. All these works show the beneficial effect of the oxo ligand (even if it is only spectator) in the coordination sphere of tungsten for metathesis of olefins. In this case, the oxo ligand was formed by extraction from the surface of alumina toward the xophilic tungsten center after its reduction under hydrogen.

4.2. Supported oxo-alkyl and oxo-carbene tungsten complexes

As shown above, the industrial WO_3/SiO_2 catalyst contains only a very small amount of really active sites, rendering their characterization by spectroscopic methods very difficult. However, it has been proposed by several authors that the active site is a tungsten(VI) complex with the formula $[(\equiv\text{Si}-\text{O})_2\text{W}(=\text{O})(=\text{CHR})]$ and containing two siloxy ligands, one oxo ligand and a carbene. However, oxo alkylidene tungsten complexes are very unstable and there are only few reports on them. The first supported tungsten oxo alkyl species active in olefin metathesis was achieved by grafting reaction of the complexes synthesized by Osborn et al. (**Figure 6**) [26]. Upon α -H abstraction, these complexes can lead to supported oxo-alkylidene species. The first oxo-alkyl complex of tungsten supported on silica was prepared by reaction of $\text{W}(=\text{O})(\text{CH}_2t\text{Bu})_4$ with silica dehydroxylated at 700°C [83]. The reaction occurs via breaking of a $\text{W}-\text{C}$ bond and leads selectively to $[(\equiv\text{SiO})(\text{W}=\text{O})(\text{CH}_2t\text{Bu})_3]$ **22** (**Figure 20**). This complex has been fully characterized by DRIFT, Raman spectroscopy, solid-state NMR, and EXAFS. The Raman spectrum displays a band at 935 cm^{-1} which is characteristic of the $\text{W}=\text{O}$ bond. EXAFS indicates that the supported complex has a bipyramidal trigonal structure with the oxo ($d(\text{W}=\text{O}) = 0.171\text{ nm}$) and siloxy ligands ($d(\text{W}-\text{O}) = 0.197\text{ nm}$) in axial position while the

three neopentyl groups are located in equatorial position (**Figure 20**). These results were also comforted by DFT calculations.

Complex **22** was used in propene metathesis at 80°C. The evolution of one neopentane molecule per grafted complex and the detection of the olefin metathesis products (ethylene and but-2-ene) are in agreement with the formation of the $[(\equiv\text{SiO})(\text{W}=\text{O})(\text{CH}_2t\text{Bu})(=\text{CH}t\text{Bu})]$ surface complex (**Figure 21**). This species is formed *in situ* by coordination of propene to tungsten (which is electro-deficient), leading to a hexacoordinated complex with a great steric hindrance which will favor the α -H abstraction. DFT calculations show that the formation of the carbene species is thermodynamically favored, the energy barrier being $\Delta E = -29 \text{ kJ.mol}^{-1}$ [83].

The catalytic performances of **22** were compared to those of the supported imido-carbene complex $[(\equiv\text{SiO})(\text{W}=\text{N}(2,6\text{-}i\text{PrC}_6\text{H}_3)(\text{CH}_2t\text{Bu})(=\text{CH}t\text{Bu}))]$ **23** in propene metathesis. The initial activities are quite similar for the two surface species: $4.5 \text{ mol}_{\text{C}_3\text{H}_6}.\text{mol}_\text{W}^{-1}.\text{min}^{-1}$ for **23** and $4.9 \text{ mol}_{\text{C}_3\text{H}_6}.\text{mol}_\text{W}^{-1}.\text{min}^{-1}$ for **22**. The main difference is the evolution with time of stream: Complex **23** deactivates rapidly (**Figure 22a**) while complex **22** remains stable. As a result, after 95 h the TON is 22,000 for **22** and ca. 2,500 for **23** [83]. In terms of selectivity, complex **22** is stable with equimolar amounts of ethylene and but-2-ene while in the case of compound **23** isobutene and higher olefins (pentenes and hexenes) are also formed (**Figure 22b**).

In the case of the imido complex, the deactivation mechanism has been determined: It is due to the decomposition of the 2-methyltungstocyclobutane by β -H transfer, leading to a

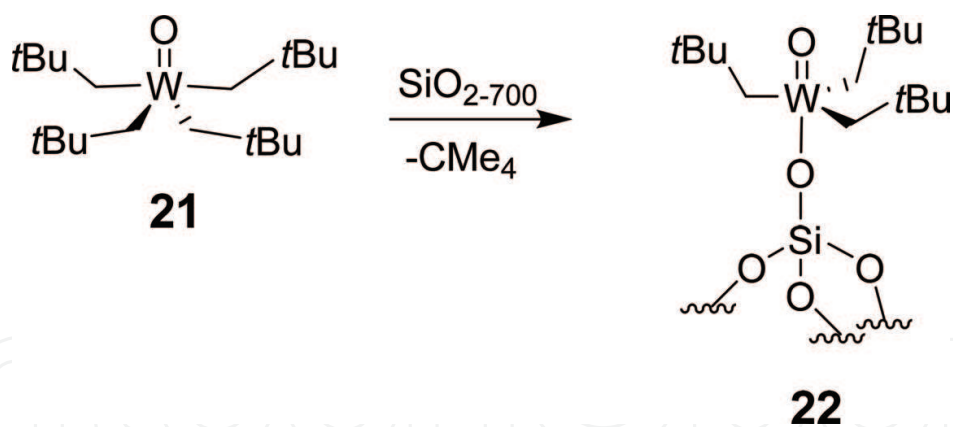


Figure 20. Grafting reaction of complex **21** on dehydroxylated silica.

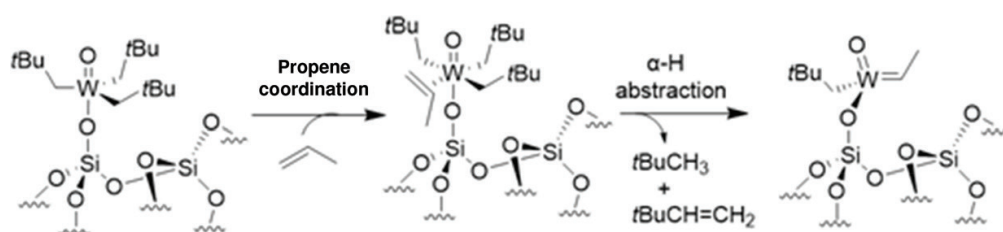


Figure 21. Mechanism of formation of the surface oxo-carbene species.

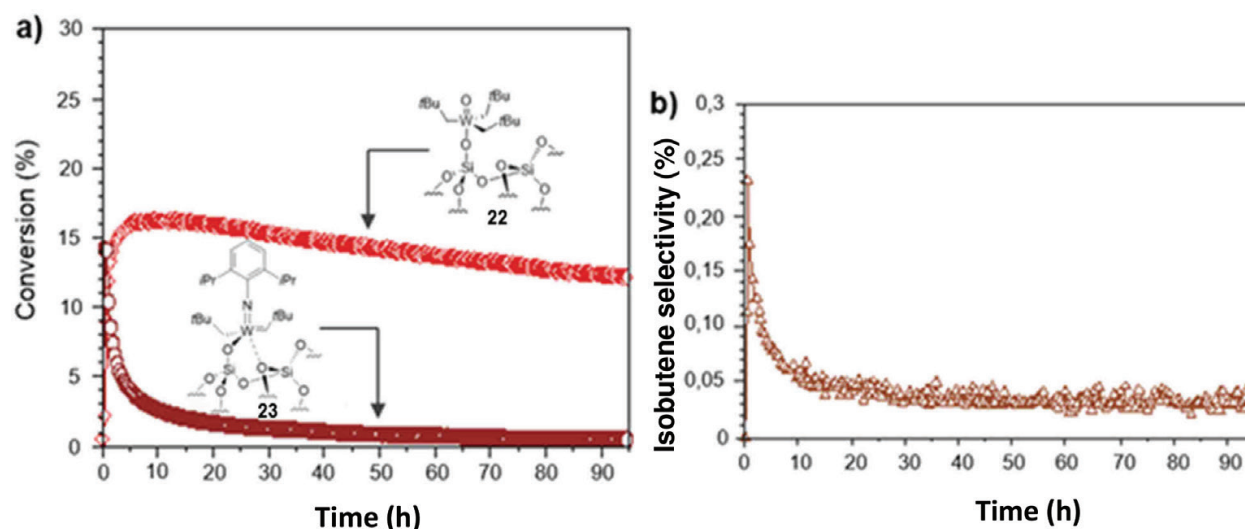


Figure 22. Metathesis of propene catalyzed by complexes **22** and **23**: (a) Conversion as a function of time; (b) isobutene selectivity as a function of time for complex **23**.

meta-allyl-tungsten hydride. This hydride is then converted into an inactive tungsten(IV) species with the evolution of isobutene by reductive elimination (**Figure 23**) [83].

The variation of the isobutene selectivity is quite the same than that of the conversion (**Figure 22a** and **b**) in agreement with a deactivation mechanism implying isobutene. This result shows also that the oxo ligand has a nonnegligible effect on the activity and stability of the tungsten catalysts. Recently, Eisenstein et al. performed DFT calculations on these compounds and found that replacement of the imido ligand by an oxo one increases the energy barrier of the β -H transfer in the mechanism of **Figure 23** and so stabilizes the catalyst [84]. $[(\equiv\text{SiO})\text{W}(=\text{O})(\text{CHtBu})_3]$ was the first reported model of the WO_3/SiO_2 industrial catalyst. The latter surface compound is monopodally anchored to the surface, which is different from the proposed active site in the industrial WO_3/SiO_2 catalyst precursor. However, the real model for the industrial catalyst (being a bipodal tungsten oxo carbene species) was not achieved with the former organometallic complex grafted on SiO_{2-200} (support that frequently yields bipodal species). The expected W—C silanolysis step does not occur (**Figure 24**), even after thermal treatment. Such reactivity is reminiscent of tungsten aqueous organometallic chemistry described by Schrock and Lippard [85, 86]. Indeed, the coordination environment of **22**

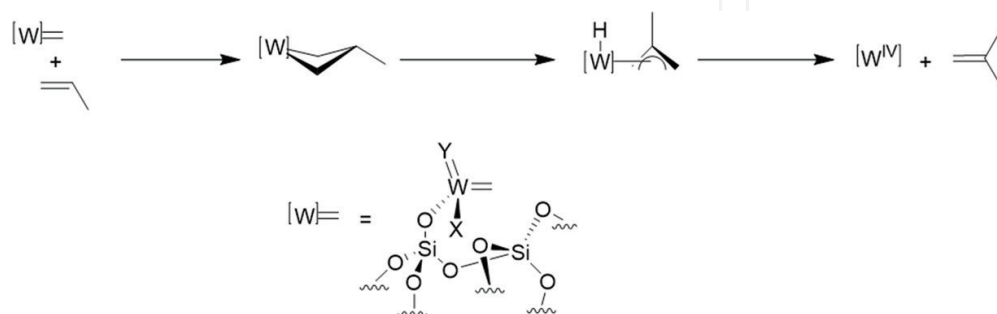


Figure 23. Mechanism of deactivation of the tungsten catalyst.

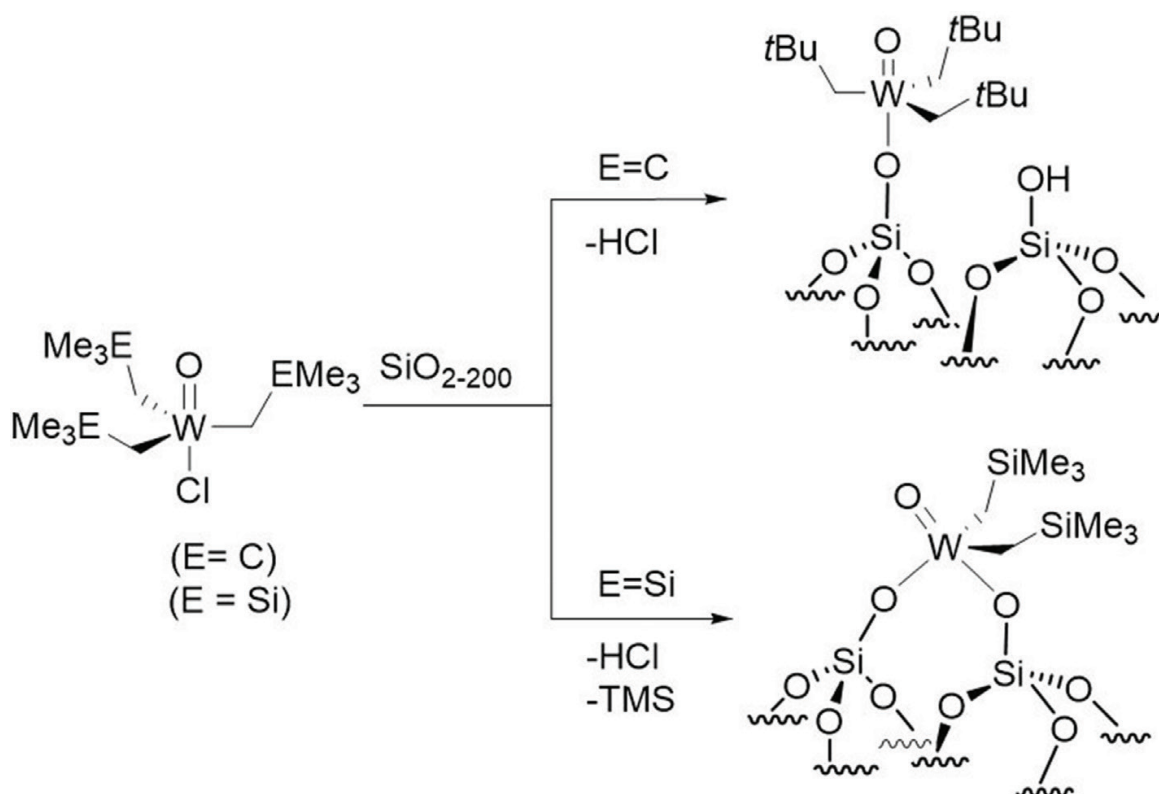


Figure 24. Reaction of $\text{W}(\text{=O})(\text{CH}_2\text{tBu})_4$ and $\text{W}(\text{=O})\text{Cl}(\text{CH}_2\text{SiMe}_3)_3$ with $\text{SiO}_2\text{-200}$.

is very similar to that of the trisoxo alkyl dinuclear complex $[\text{O}(\text{WONp})_2]$ which is stable toward excess water. In order to push forward the second protonolysis step, the neopentyl ligand needs to be replaced by a more reactive fragment. Interestingly, Xue et al. have recently studied the reactivity of $[\text{W}(\text{=CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_3]$ with H_2O and found a different behavior compared to $[\text{W}(\text{=CtBu})\text{Np}_3]$ [87]. When $[\text{W}(\text{=CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_3]$ reacts with water, the authors observed mainly two products: tungsten bis-oxo bis-neosilyl trimer and $[\text{WO}(\text{OSiMe}_3)(\text{CH}_2\text{SiMe}_3)_3]$.

Then, the new complex $[\text{WOCl}(\text{CH}_2\text{SiMe}_3)_3]$ was obtained in 70% yield from $[\text{W}(\text{=CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_3]$ by hydrolysis at -78°C with 2 eq. of H_2O in THF (resulting in the formation of the unstable intermediate $[\text{WO}(\text{OSiMe}_3)(\text{CH}_2\text{SiMe}_3)_3]$ as reported by Xue) followed by reaction with 1 eq. of $\text{Me}_3\text{SiCl}/\text{HCl}$. Thus, grafting of $[\text{WO}(\text{CH}_2\text{SiMe}_3)_3\text{Cl}]$ onto silica dehydroxylated at 200°C yields the well-defined bipodal species $[(\text{=SiO})_2\text{WO}(\text{CH}_2\text{SiMe}_3)_2]$ **24** via consecutive HCl and SiMe_4 release. This was demonstrated by mass balance analysis, elemental analysis, IR, advanced solid-state NMR (^1D and $2\text{D } ^1\text{H}$, ^{13}C , ^{29}Si and ^{17}O), and EXAFS. Furthermore, DFT calculations allowed understanding and rationalizing the experimental results regarding grafting selectivity of $[\text{WO}(\text{CH}_2\text{SiMe}_3)_3\text{Cl}]$ compared to its neopentyl counterpart [88].

More recently, Schrock et al. synthesized new oxo tungsten complexes bearing various ligands and studied their grafting on silica dehydroxylated at 700°C . Ligands such as 2,6-mesitylphenoxy, 2,6-diadamantyl-methylphenoxy, thio-2,6-mesitylphenoxy, or tris(tert-butoxy)siloxy were used and the corresponding carbenes were synthesized (**Figure 25**) [34, 89–91].

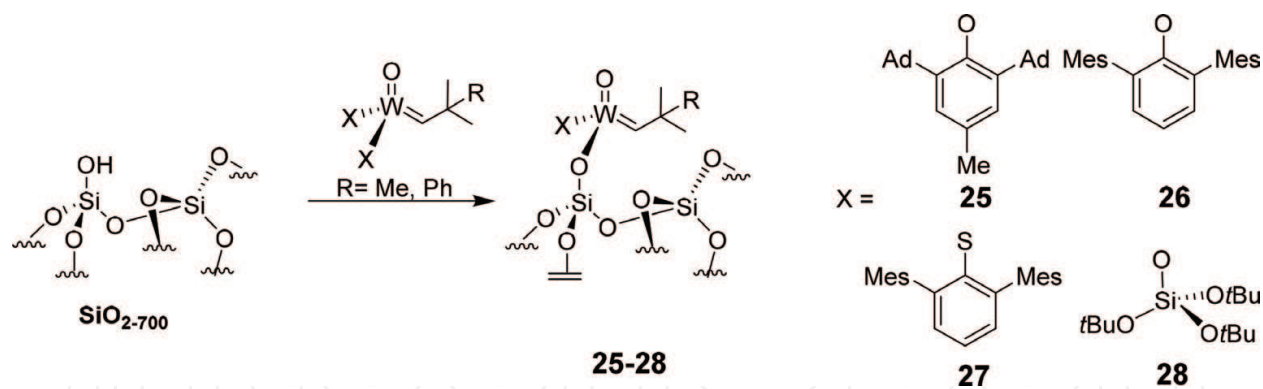


Figure 25. Grafting reaction of oxo-carbene tungsten complexes on silica.

The characterization of the grafted materials by infrared spectroscopy, chemical analysis, and solid-state NMR shows that the presence of these sterically encumbered ligands leads to a nonselective grafting reaction. For example, $[W(=O)(=CHtBu)(O\text{-}2,6\text{-mesitylphenoxide})_2]$ leads mainly (ca. 80%) to $[(\equiv SiO)W(=O)(=CHtBu)(O\text{-}2,6\text{-mesitylphenoxide})]$, formed by σ metathesis between the silanol group and the W–Ar ligand. The minor product, $[(\equiv SiO)W(=O)(CH_2tBu)(O\text{-}2,6\text{-mesitylphenoxide})_2]$, is formed by protonation of the carbene moiety by the silanol group [90].

In order to reveal the stability and robustness of the real model of industrial catalyst **24** (being a supported bipodal tungsten oxo species active in olefin metathesis) with respect to the iso-electronic monopodal tungsten oxo aryloxy species, **25**, both materials were exposed to a continuous flow of propylene with a molar flow rate of $60 \text{ mol}_{C_3H_6} \cdot \text{mol}_W^{-1} \text{ min}^{-1}$ ($20 \text{ mL}_{C_3H_6} \text{ min}^{-1}$; 80°C , 1 bar). Both materials gave only metathesis products (equimolar amounts of ethylene and 2-butenes). **25** presents a very fast deactivation, affording a TON = 3,000 after 25 h on stream. Conversely, **24** efficiently performs propene metathesis with sustained activity over 24 h operating time (TON = 24,000). Although **24** (after activation with the olefinic substrate) and **25** have the same coordination environment and both catalysts are active in propylene metathesis, there is a remarkable difference in stability. The local structure of **24** closely resembles the proposed industrial WO_3/SiO_2 catalyst and showed a fairly stable catalytic activity with time on stream of propylene. On the other hand, **25** belongs to “model of model” rather than a true and robust catalyst, deactivated rapidly with time on stream. The huge difference in the catalytic performance may be due to the importance of the bipodal nature of **24**, or the presence of a bulky organic ligand in **25**, which can gradually undergo intramolecular C–H activation with time and loss of the active tungsten alkylidene sites.

5. Conclusion

As shown above, there is a great interest to the study of olefin metathesis, not only by academics but also by industry. Indeed, this reaction can be considered as a key step in many

processes of fine chemistry, polymerization, or petrochemistry. This reaction can be catalyzed by homogeneous or heterogeneous systems.

Table 1 lists all well-defined systems reviewed in this chapter.

The homogeneous systems are well-described and structure-activity relationships were made allowing defining the best ligands and oxidation state of the metal for example. The heterogeneous systems, in contrast, are ill-defined even if they are preferred by industrials, due to their easy separation and recycling. Actually, WO_3/SiO_2 is often used by industry but the exact structure of the active species, which is in a small proportion, remains unknown even if it is generally accepted that it should be a species like $[(\text{Si}-\text{O})_2\text{W}(\text{=O})(\text{=CHR})]$. This model was then modeled by grafting organometallic complexes of tungsten containing an oxo ligand and able to give carbene species on the surface. These systems can be considered as models of the active site of WO_3/SiO_2 but their synthesis remains very complicated and up to now only few examples of such catalysts were reported, preventing the attainability of structure-activity relationships.

Catalyst	Reference
Homogeneous catalysts	
$[(\text{CO})_5\text{W}=\text{C}(\text{C}_6\text{H}_5)_2]$	Casey et al. [20], 31
$[\text{M}(\text{=CHCMe}_2\text{Ph})(\text{=N-Ar})(\text{OR}')_2]$ M = Mo, W	Malcolmson et al. [21], 30; Schrock and Czekelius [22], 107; Marinescu et al. [23], 108; Schrock [24], 109
$\text{M}(\text{=O})(\text{CH}_2\text{C}(\text{CH}_3)_3)_X$ M = Mo, W; X = Cl, Br, ONp, Np	Kress et al. [26], 111
$\text{W}(\text{=O})\text{Cl}_2\text{L}(\text{=CH-}t\text{Bu})$ L = PMe_3 , PEt_3 , PMe_2Ph	Wengrovius and Schrock [29], 118; Wengrovius et al. [30], 117
$\text{W}(\text{=O})(\text{=CHCMe}_2\text{Ph})-(\text{Me}_2\text{Pyr})(\text{OAr})$ (Me_2Pyr = 2,5-dimethylpyrrolide, OAr = aryloxide)	Wengrovius and Schrock [29], 118; Wengrovius et al. [30] 117
$\text{W}(\text{=O})(\text{=CHCMe}_2\text{Ph})(\text{OR})_2$	Wengrovius and Schrock [29], 118; Wengrovius et al. [30] 117
$\text{W}(\text{=O})(\text{=CHCMe}_3)(\text{OSi}(\text{OtBu})_3)_3$	Mougel and Coperet [34], 122
$[\text{W}(\text{=O})(\text{=CHCMe}_2\text{Ph})(\text{Mes})(\text{OAr})(\text{NCMe})_2]^+$	Schowner et al. [35], 123
Heterogeneous catalysts	
$[(\text{=SiO})\text{W}(\text{=C}t\text{Bu})\text{X}_3]$ (X = Cl, $t\text{Bu}$)	Weiss and Lössel [67], 61
$[(\text{=SiO})\text{W}(\text{=C}t\text{Bu})(\text{CH}_2t\text{Bu})_2]$	Le Roux, 2005 [68], 62
$[(\text{=SiO})_2\text{W}(\text{=C}t\text{Bu})(\text{CH}_2t\text{Bu})]$	Le Roux, 2005 [68], 62
$[(\text{Al}_s\text{O})\text{W}(\text{=C}t\text{Bu})(\text{CH}_2t\text{Bu})_2]$	Le Roux, 2005 [71], 68
$[(\text{=SiO})(\text{W=O})(\text{CH}_2t\text{Bu})_3]$	Mazoyer, 2010 [74], 94
$[(\text{=SiO})(\text{W=N}(2,6\text{-}i\text{PrC}_6\text{H}_3)(\text{CH}_2t\text{Bu})(\text{=CH}t\text{Bu}))]$	Mazoyer, 2010 [74], 94
$[(\text{=SiO})_2\text{WO}(\text{CH}_2\text{SiMe}_3)_2]$	Grekov et al. [88], 162
$[(\text{=SiO})\text{W}(\text{=O})(\text{=CH}t\text{Bu})(\text{O-2,6-mesitylphenoxide})]$	Conley et al. [90], 156

Table 1. Some representative metathesis catalysts listed in this review.

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