

Silica-Alumina-Supported, Tungsten-Based Heterogeneous Alkane Metathesis Catalyst: Is it Closer to a Silica- or an Alumina-Supported System?

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Abstract: Grafting of $[W(\equiv C-t-Bu)(CH_2-t-Bu)_3]$ (**1**) on silica-alumina partially dehydroxylated at 500 °C generates a surface complex $[(\equiv SiO)W(\equiv C-t-Bu)(CH_2-t-Bu)_3]$ (**2**) as evidenced by mass balance analysis, IR, and NMR spectroscopy. Upon treatment of this species under H_2 , a tungsten hydride derivative, $[(\equiv SiO)(EO)W(H)_x]$ (**3**), ($E = Si$ or Al), is formed. Both of these complexes are active as alkane metathesis catalysts. The activity of this hydride is similar

to that observed for the tungsten hydride-supported on alumina and much greater than that obtained on silica. Noteworthy are the selectivities in higher alkane homologues, that is $C_{n+1} > C_{n+2}$, which are fully consistent with olefin metathesis being the key homologation process.

Keywords: alkanes; hydrides; metathesis; silica-alumina; tungsten

Introduction

Conversion of alkanes is still of major interest in the petrochemical industry, and the current oil prices and the expected future situation in terms of supply and demand make the efficient use and transformation of this natural resource of major importance.^[1,2] Since the early 1990s, we have developed a series of oxide-supported metal hydrides^[3–6] for the low temperature alkane transformation.^[7–9] In contrast to hydrogenolysis, alkane metathesis allows both lower and higher homologues to be obtained, and we have shown recently through a combination of structure-reactivity^[10] and kinetic^[11] studies that the key carbon-carbon cleavage and formation process involves olefin metathesis. Other approaches have been investigated to carry out alkane metathesis. For instance, Chevron has been using a combination of processes in a single reactor based on dehydrogenation-hydrogenation catalysts in the presence of olefin metathesis catalysts,^[12] and recently a homogeneous catalytic system based on the same principle has been reported.^[13] In all

cases reported so far, activity and stability of the systems are still a challenge.

We have recently developed W-based systems, giving higher turnover numbers and having a greater stability than the corresponding Ta-based systems. Nonetheless, in the case of W, it is necessary to use an alumina support because the silica-supported systems are either inactive or less active. In fact, it has not been possible to prepare a silica-supported W hydride so far; one reason being the sintering during the treatment under hydrogen of W-supported species. We report below the grafting and the characterization of $[W(\equiv C-t-Bu)(CH_2-t-Bu)_3]$, **1**, on silica-alumina, the preparation of the corresponding hydride without sintering, and the activity of these silica-alumina-supported species in alkane metathesis compared to the corresponding silica- and alumina-supported systems.

Results and Discussion

Monitoring the reaction of $[W(\equiv C-t-Bu)(CH_2-t-Bu)_3]$ (**1**) with $SiO_2-Al_2O_{3-(500)}$ by IR spectroscopy shows the following features: a pale yellow colouring of the disk, a disappearance of the band associated with the isolated silanol [$\nu_{(SiOH)}=3747\text{ cm}^{-1}$, Figure 1 a and b), the appearance of (i) a broad band at 3700 cm^{-1} consistent with the presence of remaining silanols in interactions with the grafted organometallic moieties^[14–16] and (ii) two groups of bands in the $3000\text{--}2700\text{ cm}^{-1}$ and $1470\text{--}1330\text{ cm}^{-1}$ regions assigned to $\nu_{(CH)}$ and $\delta_{(CH)}$ vibrations of perhydrocarbyl ligands.

When grafting of **1**, $[W(\equiv C-t-Bu)(CH_2-t-Bu)_3]$, was performed on larger quantities of $SiO_2-Al_2O_{3-(500)}$ in the absence of solvent at 66°C , a pale yellow solid was obtained after washing the excess of **1** with anhydrous pentane and drying under vacuum. The percentage of grafted W typically ranges between 7.5 and 8.3%, that is $0.40\text{--}0.45\text{ mmol g}^{-1}$ of solid, which shows that 50% of the initial OH of silica-alumina (0.88 mmol OH/g) have been consumed in agreement with what has been observed by IR spectroscopy. During this process, an average of 0.9 equivs. of 2,2-dimethylpropane ($t-BuCH_3$) evolved per grafted W, in agreement with the loss of one neopentyl ligand,

which would have been replaced by a siloxy ligand of the surface. Moreover, treatment under H_2 of this solid leads to the formation of methane and ethane through hydrogenolysis of the perhydrocarbyl ligands, and their amount shows that the solid contained an average of 14–15 carbons per grafted W. Overall, the data are consistent with the loss of approximately one equivalent of 2,2-dimethylpropane during the grafting process, leaving on average 3 “neopentyl-like” ligands around the metal centre as expected for the formation of **2**, $[(\equiv SiO)W(\equiv C-t-Bu)(CH_2-t-Bu)_2]_{SA}$ (Scheme 1).

Moreover, the 1H and ^{13}C solid state NMR spectra of this solid (Figure 2 a) display the same signals as those observed for $[(\equiv SiO)W(\equiv C-t-Bu)(CH_2-t-Bu)_2]_{SiO_2}$, prepared by grafting of **1** on $SiO_{2-(700)}$.^[17] In the 1H NMR, the broad signal centred at 1.1 ppm is assigned to the methyl protons of $t-Bu$ fragments, and one shoulder is also observed at 2.0 ppm, which can be attributed to the methylene protons of the neopentyl ligand according to 2D HETCOR solid state NMR spectroscopy (see Supporting Information, Figure S1)^[18,19] and by analogy with the corresponding silica-supported complex (Figure 2 a).^[17] Similarly, the ^{13}C NMR spectrum of 10% ^{13}C enriched $[W(\equiv C^*-t-Bu)(C^*H_2-t-Bu)_3]$ grafted on $SiO_2-Al_2O_{3-(500)}$ (Figure 2 b) displays four signals at 318, 95, 52 and 32 ppm, as-

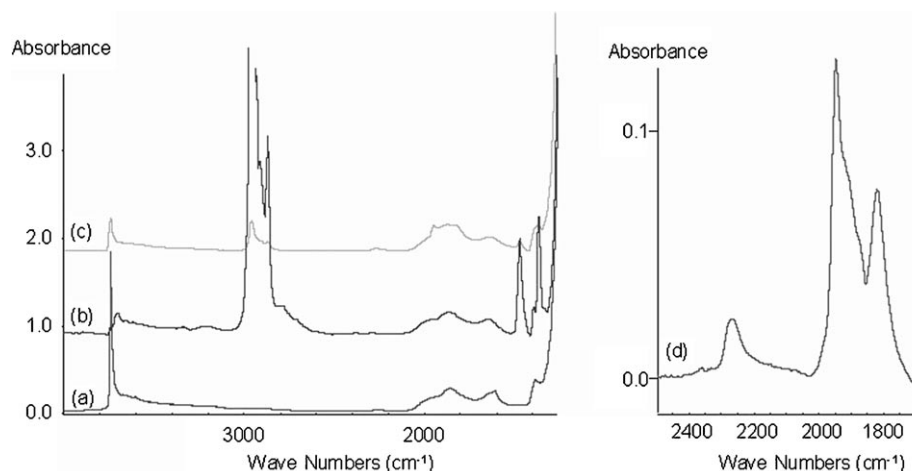
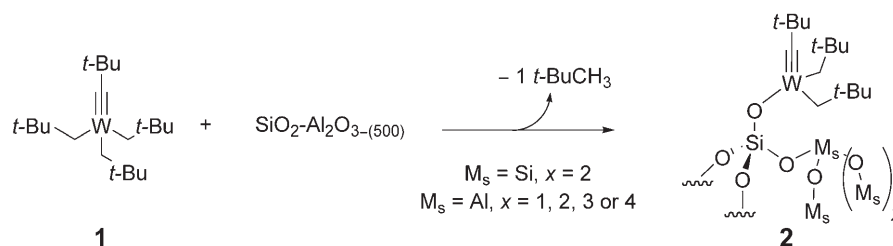


Figure 1. Monitoring the formation of tungsten hydride supported on $SiO_2-Al_2O_{3-(500)}$ (**3**) by IR spectroscopy: a) Silica-alumina dehydroxylated at 500°C . b) $[(\equiv SiO)W(\equiv C-t-Bu)(CH_2-t-Bu)_2]_{SA}$. c) After treatment under H_2 at 150°C for 12 h. d) Subtraction of a) from c), zoom of the $2500\text{--}1700\text{ cm}^{-1}$ region.



Scheme 1. Grafting of $[W(\equiv C-t-Bu)(CH_2-t-Bu)_3]$ (**1**) onto $SiO_2-Al_2O_{3-(500)}$.

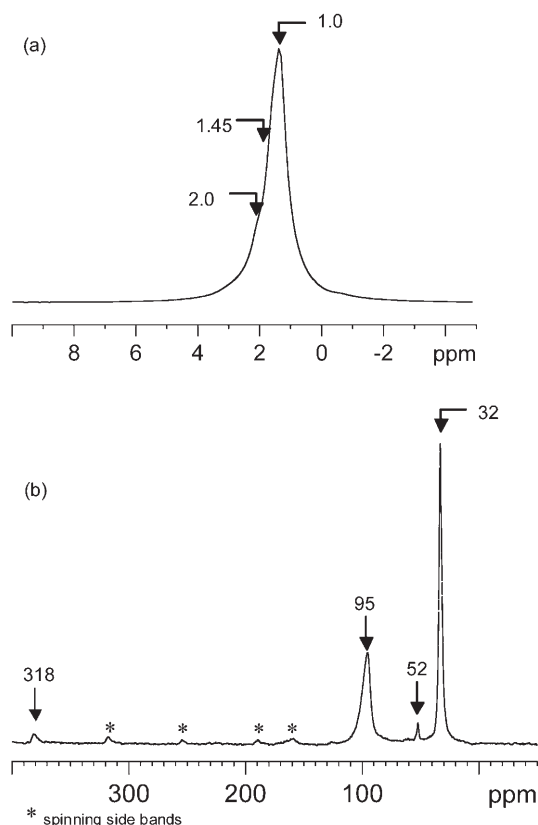


Figure 2. a) Solid-state ^1H MAS NMR spectrum of **2**. The spectrum was recorded with 8 scans and a relaxation delay of 1 s. No line broadening was applied before Fourier transform. b) ^{13}C CP/MAS solid-state NMR spectrum of **2**. The spectrum was recorded with 7000 scans, a relaxation delay of 1 s and a CP contact time of 1 ms. An exponential line broadening of 80 Hz was applied before Fourier transform.

signed respectively to the carbynic ($\text{W}\equiv\text{C}$), the methylene ($\text{W}-\text{CH}_2-t\text{-Bu}$), the quaternary carbon of the neopentylidene ligand ($\text{W}\equiv\text{CCMe}_3$) and the methyl groups of the $t\text{-Bu}$ [$\text{C}(\text{CH}_3)_3$], respectively.^[17]

In summary, the reaction of $[\text{W}(\equiv\text{C}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_3]$ (**1**) with $\text{SiO}_2\text{-Al}_2\text{O}_{3-(500)}$ leads to the formation of a supported organotungsten species whose general structure can be formulated as $[(\equiv\text{SiO})\text{W}(\equiv\text{C}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2]_{\text{SA}}$ (**2**) in which the tungsten atom is grafted to the surface *via* one covalent bond ($\equiv\text{SiO}-\text{W}$) as evidenced by mass balance analysis, IR and NMR spectroscopy. Moreover, the structure of $[\text{1/SiO}_2\text{-Al}_2\text{O}_{3-(500)}]$ was reported earlier to be an alkylidene W complex because of its high performances in olefin metathesis.^[20] Here, we show that it is in fact a well-defined alkylidyne complex, and the necessary propagating alkylidene ligand^[21] is probably generated in the presence of olefins as already proposed for other oxide supported group 6 alkylidyne complexes.^[17,18,22,23]

The preparation of the corresponding hydride was then investigated. When $[(\equiv\text{SiO})\text{W}(\equiv\text{C}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2]_{\text{SA}}$

is heated under H_2 for 15 h at 150°C , the pale yellow solid darkens to brown, and the IR spectrum shows the following (Figure 1 c and d): i) the disappearance of 95 % of the $\nu_{(\text{C}-\text{H})}$ and $\delta_{(\text{C}-\text{H})}$ bands, ii) the re-appearance of a band at 3747 cm^{-1} associated with isolated silanols (20 %), iii) the appearance of bands at 2270 cm^{-1} and in the $1980\text{--}1800\text{ cm}^{-1}$ region.

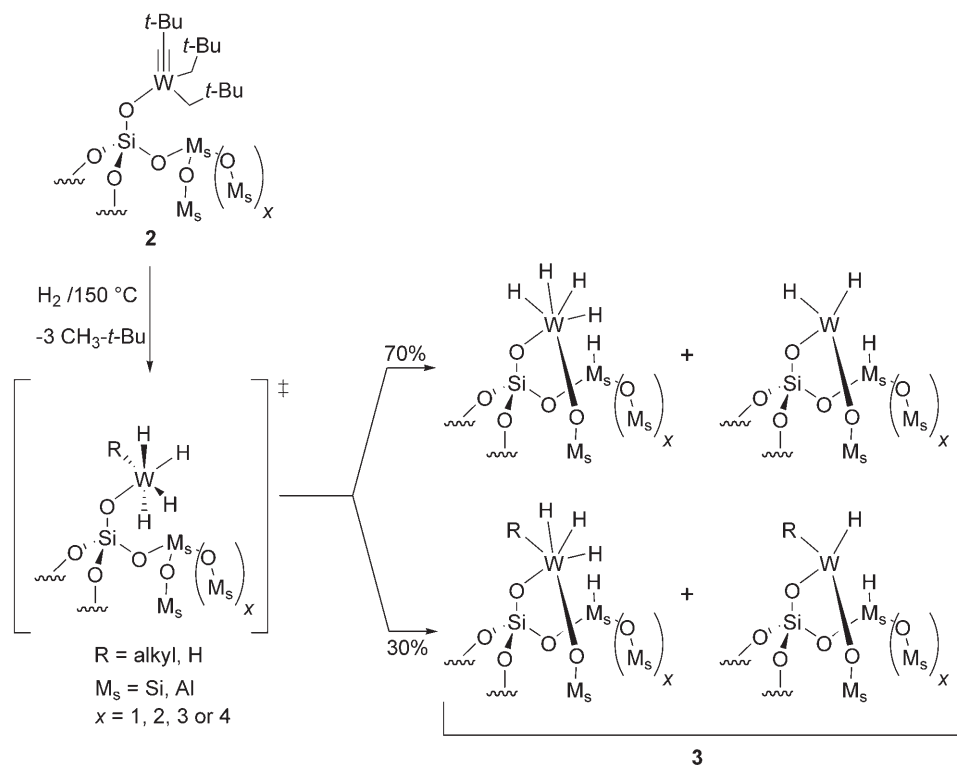
Treatment of this solid with D_2 at 80°C for 15 min leads to the disappearance of most of the bands in the $1980\text{--}1800\text{ cm}^{-1}$ region (90 %) (Supporting Information, Figure S2), which are regenerated (95 %) upon treatment with H_2 at 80°C . Therefore, these bands can be assigned to $\nu_{(\text{W}-\text{H})}$ vibrations. Moreover, one broad signal of weak intensity at 1910 cm^{-1} remains unchanged upon treatment under D_2 : it is assigned to a $\nu_{(\text{Al}-\text{H})}$ vibration by comparison with what is observed for the W hydride supported on alumina.^[6] Similarly, the band at 2270 cm^{-1} is not affected by this treatment, and can be assigned to a $\nu_{(\text{Si}-\text{H})}$.^[3-5] Additionally, the band at 2961 cm^{-1} associated with the residual alkyl ligands (5 %, Figure 1 c) are modified, while a weak band at 2214 cm^{-1} , consistent with $\nu_{(\text{C}-\text{D})}$ vibrations, appears: these C–H bonds are associated to remaining alkyl fragment probably bonded to W. These observations are already in sharp contrast to what has been observed upon treatment of $[(\equiv\text{SiO})\text{W}(\equiv\text{C}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2]_{\text{SiO}_2}$, for which silanols are regenerated and no or only weak bands around 1900 cm^{-1} , assigned to W–H, appear. Moreover, in contrast to the tungsten hydride supported on alumina,^[6] the IR spectrum of this supported tungsten hydride on silica-alumina, $[\text{W}-\text{H/SiO}_2\text{-Al}_2\text{O}_3]_{\text{SA}}$ (**3**) show several tungsten hydride bands, residual surface alkyl species as well as both Si–H and Al–H species. These latter hydride species are probably formed by the reaction of tungsten hydride intermediates with adjacent ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) and ($\equiv\text{Si}-\text{O}-\text{Al}_s$) bridges,^[3-5] thus providing bisgrafted species, $[(\equiv\text{SiO})_2\text{WH}_n]$ and $[(\equiv\text{SiO})(\text{Al}_s\text{O})\text{WH}_n]$ along with ($\equiv\text{Si}-\text{H}$) and (Al_s-H). The absence of SiH_2 species (not observed in the IR spectrum)^[4] suggests the absence of formation of trisgrafted species.

Hydrolysis of these hydrides by reaction with H_2O vapour (30 Torr, 60 equivs.) at room temperature gives 1.9 ± 0.2 equivs. of H_2/W and 0.3 ± 0.1 equivs. of $t\text{-BuCH}_3/\text{W}$. Moreover, the reaction with 50 equivs. of CH_3I at room temperature gives 0.9 ± 0.1 equivs. of CH_4 and 0.9 ± 0.2 equivs. and H_2 per W. Hydrolysis of the resulting powder gives 0.01 H_2/W , 0.03 CH_4/W and 0.02 $t\text{-BuCH}_3/\text{W}$, which shows that the reaction of the metal hydrides with CH_3I is complete, and that CH_3I does not react to give a (hydrolysable) $\text{W}(\text{CH}_3)\text{I}$ fragment. Overall, the reaction of CH_3I shows that the number of H atoms/W is about 2.7 ($0.9\text{ CH}_4/\text{W} + 1.8\text{ H}_2/\text{W}$), some of which can be readily released as H_2 and could be associated to $\text{W}(\eta^2\text{-H}_2)$ species. Moreover, the presence of remaining alkyl ligands, *ca.* 0.3

$\text{CH}_3\text{-}t\text{-Bu/W}$, point out that there are on average 3.0 (H/R) ligands/W. Hydrolysis data (1.9 equivs. of H_2/W) are also consistent with this hypothesis if one considers that half of the measured H_2 (0.95 H_2) has been released by de-coordination of H_2 from $\text{W}(\eta^2\text{-H}_2)$ species and the other half from hydrolysis of W-H species (0.95 H_2). Note that a small amount of H_2 probably comes from the hydrolysis of Al-H species (small amount according to IR spectroscopy, see Supporting Information Figure S2). Since bisgrafted surface complexes are probably the major species (absence of SiH_2 species), it is therefore possible to propose an idealized view of surface species as a 1:1 mixture of a dihydrido and a tetrahydrido species, some of which (*ca.* 30%) having an alkyl ligand in place of a hydride with some W atoms attached to a bisiloxy system and others to one siloxy and one aluminoxy (Scheme 2).

The reactivity of these species is also noteworthy. Firstly, $[(\equiv\text{SiO})\text{W}(\equiv\text{C-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})_2]_{\text{SA}}$ (**2**) is an active catalyst precursor for the metathesis of propane under standard reaction conditions (Table 1, see Supporting Information Table S1 for experimental details). The initial rate is 0.7 mol propane (P)/mol W/h, and 30 TON have been reached after 120 h. These catalytic performances (activity/selectivity) are similar to those of the corresponding alumina-supported complex $[(\text{Al}_2\text{O})\text{W}(\equiv\text{C-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})_2]_{\text{Al}_2\text{O}_3}$,^[6] while the corresponding silica-supported system is inactive

even if the spectroscopic features of **2**, $[(\equiv\text{SiO})\text{W}(\equiv\text{C-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})_2]_{\text{SA}}$, are identical to these of $[(\equiv\text{SiO})\text{W}(\equiv\text{C-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})_2]_{\text{SiO}_2}$ and somewhat different from these of $[(\text{Al}_2\text{O})\text{W}(\equiv\text{C-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})_2]_{\text{Al}_2\text{O}_3}$. Secondly, for $[\text{W-H/SiO}_2\text{-Al}_2\text{O}_3]_{\text{SA}}$ (**3**) the initial rate after 1 h and the number of turnovers after 120 h are 8.5 mol P/mol W/h and 123, respectively. Again, the silica-alumina-supported tungsten hydride (**3**) displays catalytic performances (activity/selectivity) similar to those of the alumina supported W hydrides (Supporting Information, Figure S3).^[6] In contrast, the corresponding silica-supported tungsten hydride system is not very active (10 TON/ W_{total}), but in this case, the presence of only a low amount of active sites, due to sintering during the preparation, might be the main origin of this difference. In addition, as observed previously, linear alkanes are favoured over branched ones independently of the catalysts used (**2** or **3**), and the selectivities of higher homologues are as follows: $\text{C}_{n+1} > \text{C}_{n+2} \gg \text{C}_{n+3}$. The observed selectivities are very close to those observed for alumina supported W-based systems and are fully consistent with the model proposed earlier (Scheme 3),^[10,11] which is based on olefin metathesis intermediates and which predicts that the favoured pathway for the formation of higher homologues involves a [1,3]-disubstituted metallacyclobutane rather than a [1,2]-disubstituted one (Scheme 3).^[24] The higher selectivity of linear versus branched compounds is also consistent with this



Scheme 2. Proposed structures for tungsten hydrides supported on silica-alumina.

Table 1. Propane metathesis: activity (TON) and product selectivities of tungsten perhydrocarbyl species supported on oxide and their corresponding hydrides after 120 h of reaction in a batch reactor (see Table S1 for experimental details).

Pre-catalysts;	Initial rate [mol P/mol W/h]	TON (conversion) ^[a]	Product selectivity [%] ^[b]	Butanes ^[c]	Pentanes ^[d]	Hexanes ^[e]
$[(\equiv\text{SiO})\text{W}(\equiv\text{C}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2]_{\text{SA}} \text{ (2)}$	0.7	29 (3.3)	1.6	61.7	25.7/3.4	5.5/1.3
$[(\equiv\text{SiO})\text{W}(\equiv\text{C}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2]_{\text{SiO}_2}$	-	0 (0)	-	-	-	-
$[(\text{Al}_2\text{O})\text{W}(\equiv\text{C}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2]_{\text{Al}_2\text{O}_3}$	1.8	28 (3.2)	2.7	65.4	20.7/2.9	5.3/1.5
$[\text{W}-\text{H}/\text{SiO}_2-\text{Al}_2\text{O}_3]_{\text{SA}} \text{ (3)}$	8.5	123 (21)	1.9	58.0	28.9/3.2	5.2/1.4
$[\text{W}-\text{H}/\text{SiO}_2]_{\text{SiO}_2}$	-	8 (1.2)	5.7	56.0	29.0/2.8	5.1/1.4
$[\text{W}-\text{H}/\text{Al}_2\text{O}_3]_{\text{Al}_2\text{O}_3}$	8.5	121 (18)	2.4	57.3	28.9/3.7	5.0/1.3

^[a] TON is expressed in mol of propane transformed/mol of W. The numbers in parenthesis are the conversion after 120 h.^[b] The selectivities are defined as the amount of product(i) over the total amount of products.^[c] $\text{C}_4/i\text{-C}_4$.^[d] $\text{C}_5/i\text{-C}_5$.^[e] Selectivity of the sum of all C_6 isomers.^[f] Not determined.

model since the latter would involve the less reactive disubstituted carbenes. Note also the low amount of methane, which shows that W-based catalysts are more selective than the corresponding Ta ones, probably because they do not catalyze the competitive reaction of alkane hydrogenolysis.^[9]

These results show that attaching W to a siloxy group does not prevent to obtain highly active catalysts, but that alumina, whether as a bulk or in a silica-alumina, plays a crucial role. One possibility is that alumina prevents the mobility of surface species (sintering), and could stabilize surface intermediates in alkane metathesis.

Conclusions

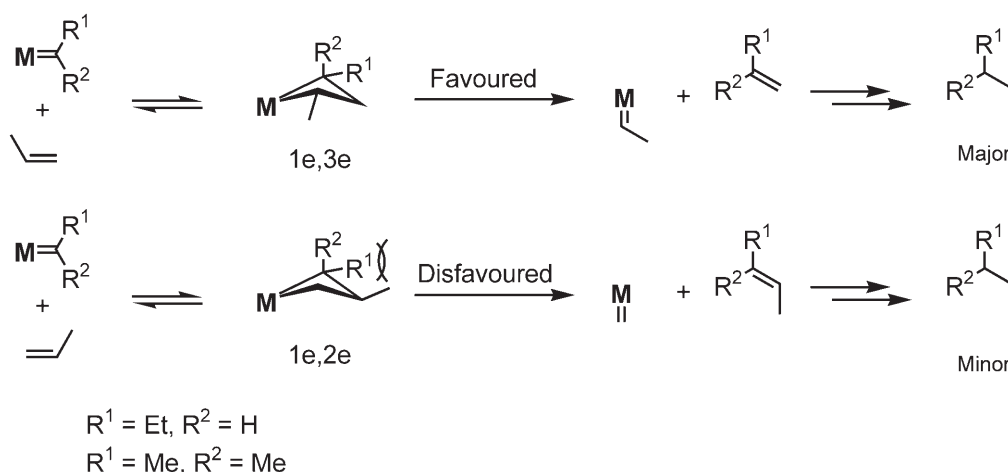
In conclusion, we have shown that **1** reacts selectively on the silanol of a silica alumina partially dehydroxylated at 500 °C to provide a well-defined surface species **2** $[(\equiv\text{SiO})\text{W}(\equiv\text{C}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2]_{\text{SA}}$ as evidenced by IR and NMR spectroscopies. Upon treatment with H_2 , this surface species further reacts with the oxide surface to generate probably bisgrafted species according to reactivity studies with H_2O and CH_3I . The major surface species are best described as a 1:1 mixture of a bis- and a tetrahydride W surface species. Both species are alkane metathesis catalyst precursors, with activities and selectivities similar to those observed for the corresponding alumina supported species, which shows that alumina has a critical role in the W based systems and could possibly prevent the mobility of reactive surface species. Further studies along this line are currently under investigation.

Experimental Section

General Procedures

All experiments were carried out under controlled atmosphere, using Schlenk and glove-box techniques for the organometallic synthesis. For the synthesis and treatments of the surface species, reactions were carried out using high-vacuum lines (1.34 Pa) and glove-box techniques. Argon, hydrogen and propane were purified over molecular sieve and deoxo catalysts. Pentane was distilled over Na/K amalgam. Before use, silica-alumina (HA-S-HPV from Akzo-Nobel: $\text{Si}/\text{Al} = 3$ and $390 \text{ m}^2\text{g}^{-1}$) was calcined under N_2/O_2 and partially dehydroxylated under vacuum at 500 °C ($\text{SiO}_2\text{-Al}_2\text{O}_{3-(500)}$). $[\text{W}(\equiv\text{C}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_3]$ (**1**) was synthesised as described in the literature.^[25]

The preparation of **1*** was performed according to the same procedure as that used for **1**, but starting with a 90:10 mixture of non-labeled $t\text{-BuCH}_2\text{Cl}$ and (99 % atom ^{13}C) monolabeled $t\text{-BuC}^*\text{H}_2\text{Cl}$ to form $t\text{-BuCH}_2\text{MgCl}$ (10 % ^{13}C labelled) as alkylating agents (yield 80–85 %); the 99 % ^{13}C monolabeled $t\text{-BuC}^*\text{H}_2\text{Cl}$ was prepared as previously described.^[19]



Scheme 3.

Analyses by gas chromatography were performed using a KCl/Al₂O₃ column (50 m, 0.32 mm) equipped with an FID detector.

Infrared spectra were recorded on a Nicolet Magna 550 FT spectrometer equipped with a cell designed for *in situ* reactions under controlled atmosphere. Elemental analyses were performed at the Service Central d'Analyses of CNRS in Solaize.

¹H MAS and ¹³C CP-MAS solid state NMR spectra were recorded on a Bruker Avance-500 spectrometer with a conventional double resonance 4 mm CP-MAS probe. The samples were introduced under Ar in a zirconia rotor, which was then tightly closed. In all experiments, the rotation frequency was set to 10 kHz. Chemical shifts were given with respect to TMS as external references for ¹H and ¹³C nuclei.

Monitoring the Grafting of [W(≡C-*t*-Bu)(CH₂-*t*-Bu)₃] on Silica-Alumina and the Formation of the Hydride by IR Spectroscopy

Silica-alumina (20–50 mg) was pressed into an 17 mm self-supporting disk, adjusted in the sample holder, and put into a glass reactor (300 mL) equipped with CaF₂ windows. The support was calcined under N₂/O₂ and partially dehydroxylated under vacuum at 500 °C, SiO₂-Al₂O₃₋₍₅₀₀₎. The compound **1** was then sublimed under dynamic vacuum at 70–80 °C onto the oxide disk, which typically turned orange-yellow. The solid was then heated at 80 °C for 2 h, and the excess of **1** was removed by reverse sublimation at 70–80 °C and condensed into a lateral tube cooled in liquid N₂, which was then sealed off using a torch. After evacuation under vacuum for 30 min, a large excess of anhydrous H₂ (77,330 Pa) was introduced, and the solid was heated at 150 °C for 15 h. The gaseous products were analysed by GC, and evacuated. An IR spectrum was recorded after each step.

Representative Procedure for Grafting of **1** on SiO₂-Al₂O₃₋₍₅₀₀₎ on a Larger Scale [1/SiO₂-Al₂O₃₋₍₅₀₀₎] (**2**)

A mixture of **1** (815 mg, 1.75 mmol, 1.2 equivs.) and SiO₂-Al₂O₃₋₍₅₀₀₎ (3.0 g) was stirred at 66 °C for 4 h. All volatile compounds were condensed into another reactor (of known

volume around 5 L) in order to quantify 2,2-dimethylpropane evolved during grafting. Analysis by gas chromatography indicated the formation of 1.45 ± 0.05 mmol of 2,2-dimethylpropane (0.9 ± 0.1 CH₃-*t*-Bu/W). Pentane (10 mL) was introduced into the reactor by distillation, and the solid was washed three times. After evaporation of the solvent, the resulting brown powder was dried under vacuum to yield 3.6 g of [1/SiO₂-Al₂O₃₋₍₅₀₀₎] (**2**). Elemental analysis: W 8.3 %_{wt}.

Preparation of the W-H/SiO₂-Al₂O₃ (**3**)

The solid **2** [1/SiO₂-Al₂O₃₋₍₅₀₀₎] (0.50 g) was heated at 150 °C in the presence of a large excess of anhydrous H₂ (77 330 Pa) in a glass reactor of 500 mL. After 15 h, the gaseous product was quantified by GC. After evacuation of the gas phase, a second treatment under H₂ is performed under the same experimental conditions.

Representative Procedure for Propane Metathesis

In a glove-box, the solid **2** (45 mg, 20.1 μmole) was introduced in a batch reactor of 500 mL. After evacuation of Ar, dry propane was added (600 Torr; sub/cat=876), and the reaction mixture was heated at 150 °C. To monitor the reaction, aliquots were expanded in a small volume, brought to atmospheric pressure with air and analysed by GC. Similar procedures were used with solid **3** and other catalysts mentioned in Table 1 (see Supporting Information Table S1 for experimental details).

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