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# Synthesis of an oxo trialkyl tungsten fluoride complex and its dual reactivity with silica dehydroxylated at high temperature

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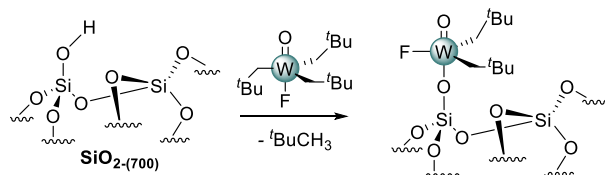
**Keywords:** olefin metathesis, surface chemistry, catalysis, tungsten, oxo ligand

**Abstract:** The novel complex  $\text{W(=O)Np}_3\text{F}$  has been prepared by fluorination of the corresponding chloride counterpart with  $\text{AgBF}_4$ . The reactivity of this complex with silica dehydroxylated at 700 °C afforded a well-defined silica supported monopodal tungsten oxo trialkyl surface species  $(\equiv\text{SiO})\text{W(=O)Np}_3$ . The reaction proceeds both through silanolysis of the W-F bond and opening of a siloxane bridge, with formation of a Si-F fragment, thanks to the affinity of silicon for fluoride. The resulting surface species was characterized by elemental analysis, DRIFT, solid state NMR and EXAFS spectroscopy. This material presenting fluorine on its surface shows an enhanced catalytic activity in propylene self-metathesis compared to its monopodal counterpart  $(\equiv\text{SiO})\text{W(=O)Np}_3$  (prepared from  $\text{W(=O)Np}_3\text{Cl}$ ) suggesting that the Si-F in a close vicinity to the W decreases the electron density of the W and thus increases its reactivity towards the olefinic substrate.

## 1. Introduction

The industrial olefin metathesis catalysts  $\text{WO}_3/\text{SiO}_2$  discovered in the 1960's was put into operation less than a decade after in the multi-ton Phillips Triolefin Process, which converts propylene into ethylene and butene, and is still a source of intense research interest.<sup>1,2</sup> This is mainly driven by the high economic impact of the reverse reaction commercialized as ABB Lummus Olefins Conversion Technology®, due to propylene shortage combined to the high abundance of ethylene from shale gas cracking. A noticeable number of recent publications are dedicated to the elucidation of the nature of the active sites.<sup>3–6</sup> Evidences are pointing towards an isolated bipodal tungsten oxo carbene surface species arising from a bipodal tungsten bis oxo sites by a pseudo Wittig reaction, even if an alternative mechanism involving a reduction of the metal center cannot be ruled out.<sup>5</sup> The inherent difficulty for studying these systems is due not only to their heterogeneity, but also to the fact that among the different species present on the surface of the catalyst classically prepared by wetness impregnation, only a small fraction of the metal centers is active in olefin metathesis.<sup>3,4,7</sup> To overcome this difficulty, we rely on the surface organometallic chemistry strategy, which leads to well defined single atoms surface species by reacting organometallic precursors with silica surface silanol group and by entering directly into the catalytic cycle, or its immediate precursor.<sup>8</sup> The podality of the resulting surface species is usually dependent on the silanol concentration, which is controlled by the temperature used during the partial dehydroxylation of the silica used as support. Using this methodology, we have reported the preparation of well-defined monopodal tungsten oxo alkyl species amenable to carbene formation.<sup>9–12</sup> Then, the same approach has further led to the preparation of the first bipodal tungsten oxo bis alkyl species as well as the unprecedented selective synthesis of the bipodal bis oxo tungsten surface species  $(\equiv\text{SiO})_2\text{W}(=\text{O})_2$ , a postulated precursor to the active sites.<sup>13,14</sup> These systems, which are realistic models of the industrial catalyst, show sustained activity in olefin metathesis. A further increase of the activity was achieved by the preparation of molybdenum analogues or by the modification of the supported tungsten oxo tris alkyl species with one equivalent of phenol, in particular with electron withdrawing fluorinated phenol.<sup>15–17</sup>

In light of these results, we were interested in replacing the pending neopentyl ligand with an even more electron withdrawing group as increased electrophilicity of the metal center is often correlated to improved catalytic activity.<sup>18</sup> As we targeted  $(\equiv\text{Si-O})\text{W}(=\text{O})(\text{X})(\text{Np})_2$  surface species as precursor to tetrahedral  $(\equiv\text{Si-O})\text{W}(=\text{O})(\text{X})(=\text{CH}t\text{Bu})$ , a selective and irreversible grafting reaction with the silica surface silanols was necessary. This ruled out the use of chloride and alkoxide derivatives, as we have already demonstrated that the chlorine and alkoxyde react with silanol groups.<sup>10,11,13,14,17</sup> We considered to reach our objective through grafting of the fluoride complex  $\text{W}(=\text{O})(\text{F})(\text{Np})_3$  (**1**) as W-F are expected to be more stable toward protonolysis and hence would favor tungsten–alkyl silanolysis as the only reaction between the molecular precursor and the silica support (Scheme 1).

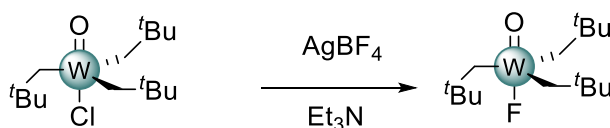


**Scheme 1.** Grafting strategy of **1** onto silica 700

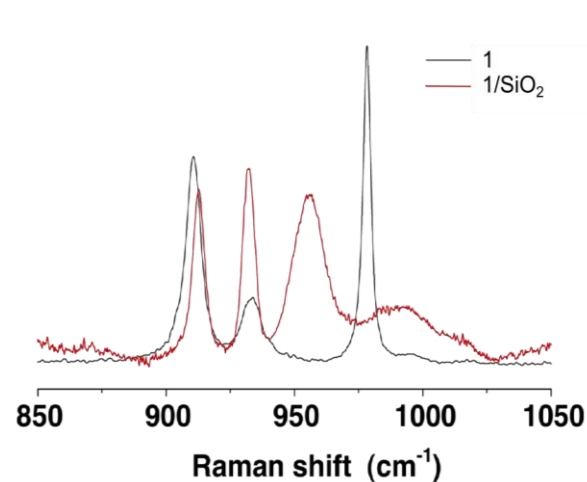
Along these lines, we disclose here the synthesis, characterization and grafting of the new complex  $W(=O)NP_3F$  **1**, giving **1/SiO<sub>2</sub>-700** which has also been fully characterized. The generated surface species demonstrated outstanding catalytic performances in propene metathesis without addition of a Lewis acid activator. Remarkably, as expected from previous related SOMC examples, mere exposure to the olefinic substrate is shown to trigger the generation *in situ* of the active carbene species.

## 2. Results and discussion

Molecular precursor **1** has been synthesized in high yield (95%) from the known chloride analogue following a two-step, one-pot procedure developed for the synthesis of a related species  $W(=N(2,6\text{-}^i\text{PrC}_6\text{H}_3))(F)(\text{Np})_3$ .  $\text{AgBF}_4$ -mediated chloride abstraction afforded the  $\text{BF}_4$  adduct from which  $\text{BF}_3$  was extracted upon addition of an excess of triethylamine.<sup>19</sup> Raman spectrum displays a characteristic sharp  $W=O$  stretching band at  $975\text{ cm}^{-1}$  (Figure 1 and S1).  $^1\text{H}$  NMR features of **1** are indicative of  $C_{3v}$  geometry, as the reported  $W(=O)(X)(\text{Np})_3$  derivatives ( $X = \text{Cl}, \text{Br}, \text{ONp}$ ).<sup>20,21</sup> This is evidenced by the doublet observed at 2.13 ppm for the methylenic protons coupled to the fluoride ligand ( $^3J_{\text{H-F}} = 8.6\text{ Hz}$ ), with satellites due to coupling to the tungsten center ( $^2J_{\text{H-W}} = 10.1\text{ Hz}$ ). Noteworthy, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum shows a multiplet centered at 94.9 ppm with the expected W satellites ( $^1J_{\text{C-W}} = 46\text{ Hz}$ ,  $^2J_{\text{C-F}} = 6.3\text{ Hz}$ ), accounting for the methylenic carbons. The  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum consists in a singlet with the  $^{183}\text{W}$  satellites centered at -0.6 ppm ( $^1J_{\text{F-W}} = 82.2\text{ Hz}$ ) (Figure S2). Elemental analysis, revealing 4.72 wt% of fluorine also corroborates the formation of the fluorinated complex.

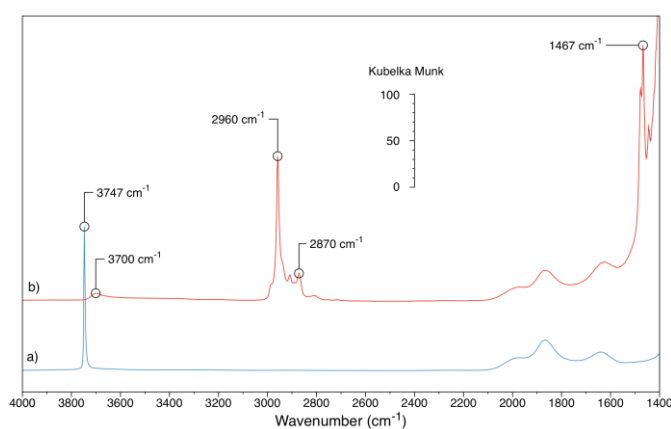


**Scheme 2.** Synthesis of **1** by fluorination



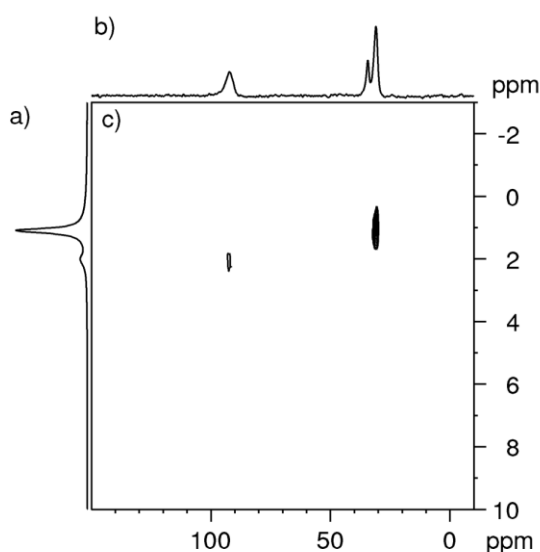
**Figure 1:** Raman spectrum of **1** and **1/SiO<sub>2</sub>-(700)**

**1** was reacted with silica dehydroxylated at 700 °C (SiO<sub>2</sub>-(700)), which solely bears isolated silanol groups on its surface, a prerequisite for the targeted selective formation of monosiloxide surface species intermediate. Grafting proceeded efficiently, as demonstrated by consumption of the isolated silanol signal (at 3747 cm<sup>-1</sup>). We noted that there is still a significant amount of interacting SiOH with alkyl groups (peak centered at 3700 cm<sup>-1</sup>) on the infrared spectrum of the resulting material **1/SiO<sub>2</sub>-(700)**. Simultaneously, the stretching and deformation signals of alkyl groups (2990-2800 cm<sup>-1</sup> and 1460-1480 cm<sup>-1</sup>, respectively) appeared (Figure 2). ICP-AES analyses indicate a W loading of 4.43 wt%, and 4.27 wt% of carbon. The C/W ratio of 14.7 is close to the theoretical value of 15.0 for (≡Si-O)W(=O)(Np)<sub>3</sub>. Quantitative gas phase analysis by GC indicates the formation of only traces of neopentane. This result is comparable to the grafting of the chlorine analogue W(=O)Np<sub>3</sub>Cl, **2**, where only traces of neopentane have been observed. The only difference relies in the tungsten loading which is higher in the case of the fluorinated analogue (**1/SiO<sub>2</sub>-700**: 4.43 w%, **2/SiO<sub>2</sub>-700**: 4.02 w%).



**Figure 2:** IR Spectra of a) SiO<sub>2</sub>-(700) and b) **1/SiO<sub>2</sub>-(700)**

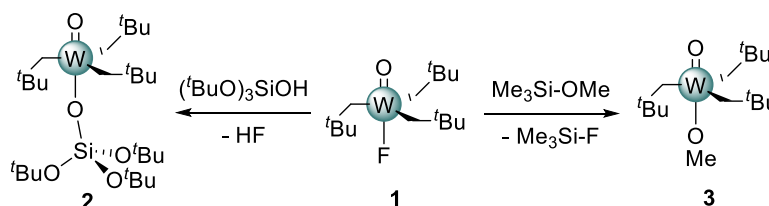
As shown in Fig. 1 and Fig. S2, the Raman spectrum of **1**/**SiO<sub>2</sub>**-(700) is quite similar to the one of the molecular precursor **1**. The modes related to neopentyl groups vibrations, detected at 905 and 935 cm<sup>-1</sup> in **1**, encounter significant changes in intensity, while their frequency is only slightly affected upon grafting. On the other hand, after grafting on silica, the band at 975 cm<sup>-1</sup> in **1** attributed to W=O, shifts to 960 cm<sup>-1</sup> as was already observed for (≡Si-O)W(=O)(Np)<sub>3</sub> (Figure 1 and S2).<sup>9</sup> **1**/**SiO<sub>2</sub>**-(700) was further characterized by multinuclear solid state NMR spectroscopy. The <sup>1</sup>H MAS NMR spectrum features two peaks, at 2.0 and 1.1 ppm, accounting for the methylene and methyl protons, respectively. Accordingly, the <sup>13</sup>C CP MAS NMR spectrum displays the expected signals for tungsten neopentyl fragments at 92.3, 34.5 and 31.0 ppm, for the methylene, tertiary and methyl carbons, respectively, as confirmed by the <sup>1</sup>H-<sup>13</sup>C HETCOR 2D spectrum (Figure 3). All these data are in line with the formation of (≡Si-O)W(=O)(Np)<sub>3</sub> as observed with W(=O)Np<sub>3</sub>Cl as precursor. However, the <sup>19</sup>F MAS NMR spectrum features a broad signal centered at -143 ppm. This marked shift compared to **1** (-0.6 ppm, Figure S2) is indicative of major structural changes. Such a shift is expected for a fluorinated silica with a <sup>19</sup>F signal assigned to isolated [≡Si-F] at -156 ppm.<sup>22</sup> Nevertheless, direct non-aqueous fluorination of the silica with HF is reported to leads to HF-silanol interaction from which Si-F can be formed only after calcination at 450 °C.<sup>23</sup>



**Figure 3:** a) <sup>1</sup>H, b) <sup>13</sup>C CP MAS and c) HETCOR NMR spectra of **1**/**SiO<sub>2</sub>**-(700)

In order to assign this signal in the <sup>19</sup>F MAS NMR spectrum as well as to rationalize the higher metal loading following the grafting of **1** compared to that obtained with **2**, a reactivity study was carried out both with a model of isolated silanol and of siloxane bridges (Scheme 3). First, when **1** is treated in a Young tap-sealed NMR tube in C<sub>6</sub>D<sub>6</sub> with one equivalent of (*t*BuO)<sub>3</sub>SiOH as a well-accepted model of isolated surface silanol, full conversion is achieved in less than 24 h at room temperature (Figure S3). New set of resonances corresponding to the neopentyl ligand are observed at 2.19 and 1.35 in the <sup>1</sup>H

NMR spectrum and 92.3, 35.4 and 31.9 in  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum accompanied with *tert*-butoxy signals at 1.43 in the  $^1\text{H}$  NMR spectrum and 72.5 and 35.4 in  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum. No trace of neopentane was observed. Against our expectation, this set of signals corresponds to  $\text{W}(=\text{O})\text{Np}_3(\text{OSi}(\text{O}^t\text{Bu})_3)$ , **3**.<sup>11</sup> Noteworthy, under the same reaction condition with  $\text{W}(=\text{O})\text{Np}_3\text{Cl}$  (**2**), **3** was observed only at 60 °C and cooling to room temperature afforded back **2** and  $(t\text{BuO})_3\text{SiOH}$ .<sup>11</sup> Indeed this explains the formation of the same surface species obtained when  $\text{W}(=\text{O})\text{Np}_3\text{Cl}$  is reacted with silica under dynamic vacuum conditions to shift the equilibrium. Nevertheless, this reactivity does not account for the higher loading and the  $^{19}\text{F}$  NMR  $\equiv\text{Si-F}$  resonance. Thus we performed the reaction of **1** with an excess (20 equivalents) of  $\text{Me}_3\text{Si-OMe}$  in a Young tap-sealed NMR tube: The signals corresponding to **1** slowly (4 days) disappear whereas new signals accounting for the neopentyl ligand appear at 1.72 and 1.19 in the  $^1\text{H}$  NMR spectrum and 86.2, 34.83 and 33.06 in  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (Figure S4). Noteworthy a  $^{183}\text{W}$  coupling is present for the methylene ( $^2J_{\text{W-H}} = 11.6$  Hz,  $^1J_{\text{W-C}} = 96.5$  Hz) whereas the fluorine coupling disappears. the  $^{19}\text{F}\{^1\text{H}\}$  signals gradually shift from -0.6 to -157.8 ppm with a  $^1J_{\text{SiF}}$  value of 276 Hz, which is in agreement with the literature values for  $\text{Me}_3\text{SiF}$ .<sup>24</sup> From these evidences along with the appearance of a methoxy peak at 3.77 ppm and 56.9 ppm in the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra respectively, we can conclude that the reaction of **1** with  $\text{Me}_3\text{Si-OMe}$  leads to a fluorine transfer to the silicon with the concomitant formation of  $\text{W}(=\text{O})\text{Np}_3(\text{OMe})$ , **4**.

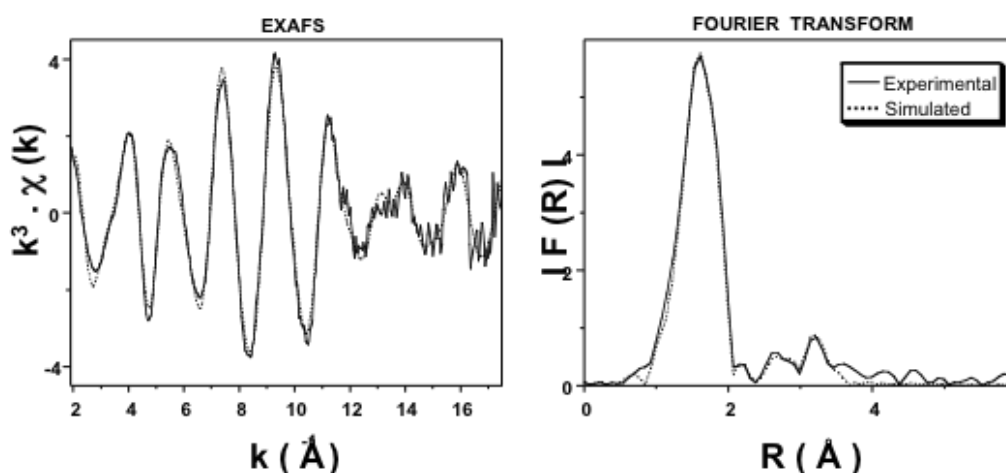


**Scheme 3.** Reaction of **1** with silica models

The structure of the supported tungsten complex **1**/ $\text{SiO}_2$ -(700) was further studied by analysis of the W  $L_{III}$ -edge extended X-ray absorption fine structure (EXAFS) data (Figure 4). The parameters extracted from the fit of the EXAFS spectrum (Table 1) are in fact quite similar to those published for  $[(\equiv\text{SiO})\text{WONp}_3]$ ,<sup>9,11</sup> and are consistent with a W coordination sphere comprising one oxygen atom at 1.703(8) Å, one oxygen at 1.98(2) Å and three carbons at 2.11(2) Å, assigned to an oxo ligand, two siloxide's  $\sigma$ -bonded oxygen, and three methylenic carbons from neopentyl ligands, respectively. These distances are similar to that found in  $[\text{W}_2\text{O}_3(\text{CH}_2^t\text{Bu})_6]$  where the  $\text{W}=\text{O}_{\text{terminal}}$  (1.676–1.736 Å),  $\text{W}-\text{O}_{\text{bridging}}$  (1.913–1.987 Å) and  $\text{W-C}$  (2.113–2.150 Å) and also to  $\text{W}=\text{O}$  1.686(5) and  $\text{W-C}$  2.118(9) distances found in  $(^t\text{BuCH}_2)_2\text{W}(\text{O})[\text{C}-(^t\text{Bu})(\text{Si}^t\text{BuPh}_2)]$ .<sup>25,26</sup> W-O distances for  $\sigma$ -bonded siloxide ligands are usually shorter, *e.g.* (1.876–1.882 Å) in the case of  $[\text{W}=\text{O}(^t\text{Bu}_3\text{SiO})_2(\text{C}_2\text{H}_5)_2]$ .<sup>27</sup> Moreover, the fit was improved when considering further layers of backscatterers: (i) three C atoms at 3.28(3) Å, assigned to the neopentyl

ligands' quaternary carbons, corresponding to a  $126 \pm 8^\circ$  W-C-C angle, in agreement with the  $123.7\text{--}127.4^\circ$  range found for  $[\text{W}_2\text{O}_3(\text{CH}_2\text{tBu})_6]$ ; (ii) one silicon at  $3.54(3)$  Å, (iii) some contribution of fluorine atoms at  $2.51(7)$  Å which can be in interaction with the tungsten as the W-F distance is quite long for a covalent bond.

**Figure 4:** Tungsten  $L_{\text{III}}$ -edge  $k^3$ -weighted EXAFS (left) and corresponding Fourier transform (right) with comparison to simulated curves for the W-containing surface species in **2**. Solid lines: experimental; dashed lines: spherical wave theory.

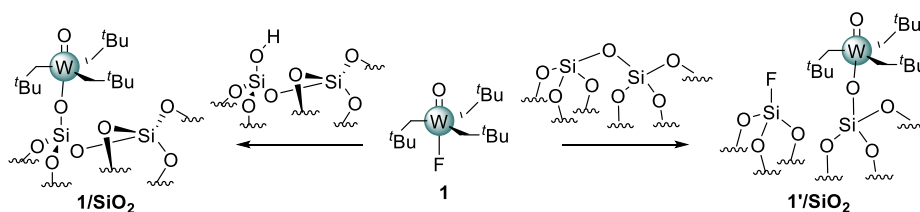


**Table 1.** EXAFS parameters for supported complex **1**/ $\text{SiO}_2$ - $(700)^{\text{a}}$

Type of neighbour	Number of neighbours	Distance (Å)	$\sigma^2$ (Å <sup>2</sup> )
<b>W=O</b>	1.0	1.703(8)	0.0021(6)
<b>W-O</b> Si≡	1.0(7)	1.98(2)	0.0015(12)
<b>W-CH<sub>2</sub>C</b> Me <sub>3</sub>	3.0(7)	2.11(2)	0.0024(5)
<b>W-CH<sub>2</sub>C</b> Me <sub>3</sub>	3.0 <sup>b</sup>	3.28(3)	0.0042(20)
<b>W-O</b> Si≡ <sup>c</sup>	1.0 <sup>b</sup>	3.54(3)	0.009(5)
<b>W--F</b>	0.3	2.51(7)	0.008(7)

The errors generated by the EXAFS fitting program "RoundMidnight" are indicated in parentheses. <sup>a</sup>  $\Delta k$ :  $[1.9 - 17.4 \text{ Å}^{-1}]$  -  $\Delta R$ :  $[0.4\text{--}3.6 \text{ Å}]$  ( $[0.4\text{--}2.3 \text{ Å}]$ , when considering only the first coordination sphere);  $S_0^2 = 1.02$ ;  $\Delta E_0 = 8.3 \pm 2 \text{ eV}$  (the same for all shells); Fit residue:  $\rho = 3.8 \%$ ; Quality factor:  $(\Delta\chi)^2/\nu = 2.13$  ( $\nu = 18 / 33$ ) ( $[(\Delta\chi)^2/\nu]_1 = 3.43$  with  $\nu = 14 / 22$ , considering only the first coordination sphere). <sup>b</sup> Shell constrained to a parameter above. <sup>c</sup> Two (W-O-Si) types multiple scattering pathways (3 and 4 legs) have also been considered in the fit but not mentioned in this table.

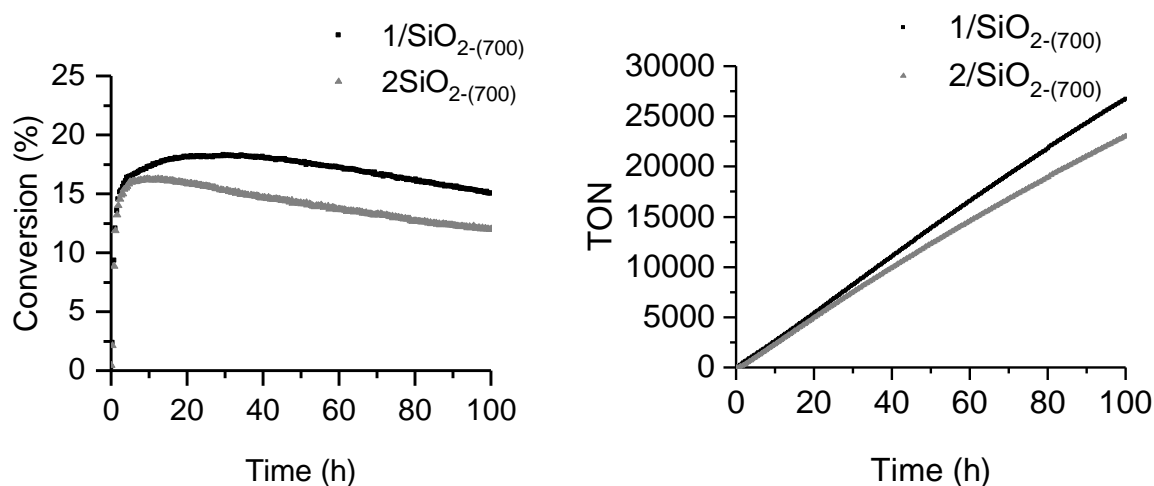




**Scheme 4.** Grafting reactions of **1** onto SiO<sub>2-700</sub>

Exposure of **1/SiO<sub>2</sub>** at 80 °C to 40 equivalents of propene in a batch reactor leads to the formation of an equilibrated mixture of metathesis products: propene, ethylene and 2-butene (*cis/trans* ratio of 2.3), along with  $0.9 \pm 0.1$  equivalent of neopentane per tungsten and small amounts of neohexene along with other *t*Bu-containing metathesis products that are however not volatile enough in these condition to be properly quantified. The first compound may be ascribed to the formation of the carbenic catalytic active species, while the second one stems from the first catalytic cycle which generates a tungsten oxo-propylidene. Donor-triggered formation of carbene species of thermally stable dialkyl species is well documented for a variety of metal centres including pentacoordinated tungsten.<sup>28–33</sup> One of the best examples is given by Cp<sup>\*</sup>Nb(NAr)(CH<sub>2</sub>Ph)<sub>2</sub> (Ar = 2,6-*i*PrC<sub>6</sub>H<sub>3</sub>) which is indefinitely stable at 100 °C in hydrocarbon solution but cleanly gives Cp<sup>\*</sup>Nb(NAr)(=CHPh)(PMe<sub>3</sub>) at 65 °C in the presence of PMe<sub>3</sub>.<sup>30</sup> Even though the basic PMe<sub>3</sub> ligand is used in most cases in order to also stabilize the newly formed coordinatively unsaturated carbene species, Schrock *et al.* showed that less basic donors such as acetonitrile or even MeOH are also able to induce the  $\alpha$ -abstraction in Re( $\equiv$ C*t*Bu)(CH<sub>2</sub>*t*Bu)<sub>3</sub>(X) (X = OTf, BF<sub>4</sub>, BAr<sup>F</sup><sub>4</sub>) to yield Re( $\equiv$ C*t*Bu)(=CH*t*Bu)(CH<sub>2</sub>*t*Bu)(X)L<sub>n</sub> (L = pyridine, MeCN, MeOH).<sup>33</sup>

In a further step, catalytic performances of **1/SiO<sub>2-700</sub>** were probed under dynamic conditions: with a flow of 20 mL.min<sup>-1</sup> of propene, a steady 18% conversion of propene was obtained. The selectivity remained constant with time on stream, with equimolar quantities of ethylene and 2-butenes, no other alkene was detected. After the onset of the catalysis, the *trans/cis* 2-butene selectivity kept to a constant value of 1.8 (therm. eq. = 2.3) (Figure 5). Furthermore, **1/SiO<sub>2-700</sub>** exhibited sustained activity with respect to time on stream, contrary to the imido counterpart which deactivated rapidly under the same condition.<sup>8</sup> Under these mild conditions, turnover numbers of 25200 after 95 hours have been reached without marked deactivation. Comparison with the monopodal surface species ( $\equiv$ SiO)W(=O)Np<sub>3</sub> **2/SiO<sub>2-700</sub>** shows a beneficial effect of the presence of fluorine on the surface, possibly from the weak interaction with the surrounding fluorine as evidenced by EXAFS spectroscopy.



**Figure 5.** Conversion vs. time (left) and cumulated TON vs. time of **1/SiO<sub>2</sub>-(700)**, and **2/SiO<sub>2</sub>-(700)** in propene metathesis (80 °C, 20 mL.min<sup>-1</sup>)

#### 4. conclusion

The complex W(=O)Np<sub>3</sub>F has been synthesized and characterized. The reactivity of this complex with highly dehydroxylated silica and representative models of silica (namely, (tBuO)<sub>3</sub>SiOH) and Me<sub>3</sub>SiOMe) has been studied. Grafting of **1** onto a silica partially dehydroxylated at 700 °C leads to the previously reported monopodal surface species (≡SiO)W(=O)Np<sub>3</sub> by reaction of the W-F moiety with silanol, and by fluorine transfer reaction with strained siloxane bridges. In both cases, the overall reaction consists of cleavage of W-F bond and formation of a W-OSi fragment. This surface species is more active in propene metathesis than the previously reported monopodal counterpart **2/SiO<sub>2</sub>-(700)**. The presence of fluorine on the surface is believed to increase the activity of our system by electronic effect. This suggests that the presence of the Si-F fragment in a close vicinity to the W center decreases the electron density of the W and thus increases its reactivity towards the olefinic substrate. These elements illustrate the importance of the second coordination sphere surrounding the surface organometallic centers on the resulting catalytic performances. Thus, thanks to the surface organometallic chemistry, some degree of improvement can be achieved by relying on such subtle factors, laying the basis for future directions in catalytic materials fine tuning.

#### 4. Experimental

##### 4.1 General procedures

All experiments were carried out by using standard Schlenk and glove-box techniques. Solvents were purified and dried according to standard procedures. C<sub>6</sub>D<sub>6</sub> (SDS) was distilled over Na/benzophenone and stored over 3Å molecular sieves. WOnp<sub>3</sub>Cl was synthesized following the literature procedure.<sup>20</sup> Propene was dried and deoxygenated before use by passing it through a mixture of freshly regenerated molecular sieves (3A) and R-3-15 catalysts (BASF). SiO<sub>2-(700)</sub> was prepared from Aerosil silica from Degussa (specific area of 200 m<sup>2</sup>.g<sup>-1</sup>), which was partly dehydroxylated at 700 °C under high vacuum (10<sup>-5</sup> Torr) for 15 h to give a white solid having a specific surface area of 190 m<sup>2</sup>.g<sup>-1</sup> and containing 0.7 OH nm<sup>-2</sup>. Gas-phase analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionisation detector and an Al<sub>2</sub>O<sub>3</sub>/KCl on fused silica column (50 m X 0.32 mm). Elemental analyses were performed at the CNRS Central Analysis Department of Solaize (metal analysis) or in the LSEO (Dijon, for C, H analysis). IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer by using a DRIFT cell equipped with CaF<sub>2</sub> windows. The samples were prepared under Ar within a glove-box. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm<sup>-1</sup>). Confocal Raman spectra were acquired using the 488 nm line of an Ar-ion laser. The excitation beam was focused on the sample by a 50X long working distance microscope and the scattered light was analyzed by an air-cooled CCD (Labram HR, Horiba Jobin Yvon). The fluorescence was subtracted from the spectra for clarity. Solution NMR spectra were recorded on an Avance-300 Bruker spectrometer. All chemical shifts were measured relative to residual <sup>1</sup>H or <sup>13</sup>C resonance in the deuterated solvent: C<sub>6</sub>D<sub>6</sub>, δ 7.16 ppm for <sup>1</sup>H, 128.0 ppm for <sup>13</sup>C. <sup>1</sup>H and <sup>13</sup>C solid-state NMR spectra were acquired on an Avance-500 spectrometer with a double-resonance 4 mm CP-MAS probe. The spinning frequency was 10 kHz. Chemical shifts were given in ppm with respect to TMS as external reference. <sup>19</sup>F solid-state NMR spectra were recorded on a DSX400 with a double-resonance 2.5 mm CP-MAS probe at the Institut de Recherches sur la Catalyse et l'Environnement de Lyon. Rotation frequencies were set for 27 kHz. Chemical shifts are given with respect to CFCl<sub>3</sub> as external reference. Procedures related to Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) are described in detail below.

#### 4.2. Preparation of WO(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>F.

WO(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl (1.5 g, 3.34 mmol) and AgBF<sub>4</sub> (0.65 g, 3.34 mmol) were stirred in 20 mL of toluene for one hour at room temperature. The reaction mixture was then filtered to remove the insoluble AgCl, and NEt<sub>3</sub> (1.1 ml, 7.70 mmol) was added. The resulting solution was stirred for 16 h at room temperature and the reaction mixture was filtered over celite. The solvent was then removed *in vacuo* to leave a white solid. The crude material was sublimed at 60 °C under reduced pressure (3.10<sup>-5</sup> Torr) to yield 1.13 g of pure product (78 % yield). δ(<sup>1</sup>H, C<sub>6</sub>D<sub>6</sub>): 2.12 [6 H, m, CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>, *J*(WH), 12.6 Hz, *J*(FH), 8.9 Hz], 1.14 (24 H, s, CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>). δ(<sup>13</sup>C{<sup>1</sup>H})(C<sub>6</sub>D<sub>6</sub>): 95.3 [m, CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>, *J*(WC), 94.5 Hz, *J*(FC) 6.5 Hz], 35.9 [d,

$\text{CH}_2\text{C}(\text{CH}_3)_3$ ,  $J(\text{FC})$  3.2 Hz], 33.0 (s,  $\text{CH}_2\text{C}(\text{CH}_3)_3$ ).  $\delta(^{19}\text{F}, \text{C}_6\text{D}_6)$ : -0.33 [1 F, m,  $J(\text{WH})$ , 163.2 Hz,  $J(\text{FH})$ , 8.9 Hz]. Anal. Calcd for  $\text{C}_{15}\text{H}_{33}\text{OFW}$ : C, 41.69; H, 7.69; F, 4.42 %. Found: C, 41.47; H, 7.89; F, 4.72%.

#### 4.3. Preparation of $\text{SiO}_{2-(700)}$

Aerosil silica from Degussa with a specific area of  $200 \text{ m}^2 \text{ g}^{-1}$ , was partly dehydroxylated at  $700^\circ\text{C}$  under high vacuum ( $10^{-5}$  Torr) for 15 h to give a white solid having a specific surface area of  $190 \text{ m}^2 \text{ g}^{-1}$  and containing  $0.7 \text{ OH nm}^{-2}$ .

#### 4.4. Preparation and characterization of $1/\text{SiO}_{2-(700)}$

##### 4.4.1. Grafting of **1** onto $\text{SiO}_{2-(700)}$

A mixture of **1** [ $\text{WO}(\text{CH}_2\text{CMe}_3)_3\text{F}$ ] (500 mg, 1.2 mmol) in pentane (10 ml) and  $\text{SiO}_{2-(700)}$  (2 g) was stirred at  $25^\circ\text{C}$  overnight. After filtration, the solid was washed 5 times with pentane and all volatile compounds were condensed into another reactor (of known volume) in order to quantify neopentane evolved during grafting. The resulting white powder was dried under vacuum ( $10^{-5}$  Torr). Analysis by gas chromatography indicated the formation of  $290 \mu\text{mol}$  of neopentane during the grafting ( $1.0 \pm 0.1 \text{ NpH/W}$ ). Elemental analysis of: W 4.43 % wt; C 4.27 % wt.  $^1\text{H}$  MAS solid state NMR (500 MHz)  $\delta$  2.0, 1.1 ppm.  $^{13}\text{C}$  CP/MAS solid state NMR (125 MHz)  $\delta$  92, 3, 34.5 and 31.0 ppm.  $^{18}\text{F}$  MAS solid state NMR (376 MHz)  $\delta$  -143 ppm.

##### 4.4.2. EXAFS characterization of $1/\text{SiO}_{2-(700)}$

X-ray absorption spectra were acquired at the SRS of the CCLRC in Daresbury (UK), using beam-line 9.3 (project # 50049), at room temperature at the tungsten  $\text{L}_{\text{III}}$  edge, with a double crystal  $\text{Si}(111)$  monochromator detuned 70% to reduce the higher harmonics of the beam (Figure S4). The spectra were recorded in the transmission mode between 10.05 and 11.45 keV. The supported W sample was packaged within a nitrogen filled dry box in a double air-tight sample holder equipped with kapton windows. This type of cell has already been used and proved to be very efficient for air-sensitive compounds. The spectra analyzed were the results of four such acquisitions and no evolution could be observed between the first and last acquisition. The data analyses were performed by standard procedures using in particular the program “Athena”<sup>34</sup> and the EXAFS fitting program “RoundMidnight”,<sup>35</sup> from the “MAX” package.

The program FEFF8 was used to calculate theoretical files for phases and amplitudes based on model clusters of atoms.<sup>36</sup> The value of the scale factor,  $S_0^2 = 1.02$ , was determined from the spectrum of a reference compound, diluted in BN,  $\text{FW}(=\text{O})\text{Np}_3$  (one oxygen at  $1.708(7) \text{ \AA}$ , one fluorine at  $1.942(8) \text{ \AA}$  and three carbon atoms at  $2.10(1) \text{ \AA}$  in the first coordination sphere). The refinements were performed by fitting the structural parameters  $N_i$ ,  $R_i$ ,  $\sigma_i$  and the energy shift,  $\Delta E_0$  (the same for all shells). The fit residue,  $\rho$  (%), was calculated by the following formula:

$$\rho = \frac{\sum_k [k^3 \chi_{\text{exp}}(k) - k^3 \chi_{\text{cal}}(k)]^2}{\sum_k [k^3 \chi_{\text{exp}}(k)]^2} * 100$$

As recommended by the Standards and Criteria Committee of the International XAFS Society,<sup>37</sup> the quality factor,  $(\Delta\chi)^2/\nu$ , where  $\nu$  is the number of degrees of freedom in the signal, was also calculated and considered.

## 4.5. Propene metathesis

### 4.5.1. Procedure in a batch reactor

**1/SiO<sub>2</sub>** (100 mg) and propene were heated at 80 °C in a batch reactor of known volume (500 mL). Aliquot were drawn and analysed by gas chromatography every 2 hours.

### 4.5.2. Procedure in a flow reactor:

A stainless-steel half-inch cylindrical reactor that can be isolated from ambient atmosphere was charged with **1/SiO<sub>2</sub>-(700)** (128 mg, % W = 4.43 %, 30 mol<sub>C<sub>3</sub>H<sub>6</sub></sub>.mol<sub>W</sub><sup>-1</sup>.min<sup>-1</sup>) or catalyst **2/SiO<sub>2</sub>-(700)** (135 mg, % W = 4.02 %, 30 mol<sub>C<sub>3</sub>H<sub>6</sub></sub>.mol<sub>W</sub><sup>-1</sup>.min<sup>-1</sup>) in a glovebox. After connection to the gas lines and purging of the tubing, a 20 mL.min<sup>-1</sup> flow of propylene was passed over the catalyst bed at 80°C. Hydrocarbon products were analyzed online by GC (HP 8890 chromatograph fitted with an Al<sub>2</sub>O<sub>3</sub>/KCl 50 m x 0.32 mm capillary column, FID detector).

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## Appendix A. Supplementary data.

Supplementary data related to this article can be found at

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