

Development of the first well-defined tungsten oxo alkyl derivatives supported on silica by SOMC: towards a model of WO₃/SiO₂ olefin metathesis catalyst†‡

Etienne Mazoyer,^a Nicolas Merle,^a Aimery de Mallmann,^a Jean-Marie Basset,^{*ab} Elise Berrier,^c Laurent Delevoe,^c Jean-François Paul,^c Christopher P. Nicholas,^d Régis M. Gauvin^{*c} and Mostafa Taoufik^{*a}

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A well-defined, silica-supported tungsten oxo alkyl species prepared by the surface organometallic chemistry approach displays high and sustained activity in propene metathesis. Remarkably, its catalytic performances outpace those of the parent imido derivative, underlining the importance of the oxo ligand in the design of robust catalysts.

Tungsten oxide supported on silica is an efficient catalyst for olefin metathesis used in industrial processes since the 1960s.¹ Several elements point to isolated metal centers as the active sites,² and from the Chauvin mechanism,³ it is reasonable to expect that carbene species are involved, possibly bearing an oxide ligand in the metal's ligand sphere. Owing to the strategic importance of olefins as building blocks for the world chemical industry, development of efficient processes is of utmost relevance. More specifically, tailored heterogeneous catalysts with known structure–activity relationships may improve lifetimes and have higher numbers of active sites.⁴

From the homogeneous catalysis point of view, tungsten oxo-alkylidene derivatives and their alkyl precursors have attracted early attention. The first example was provided by Schrock *et al.*, who reported that (WO)Cl₂(=CHR)(PR'₃)_n derivatives catalyze olefin metathesis in the presence of a Lewis acid.⁵ Osborn and Kress *et al.* described that base-free tungsten oxotrisalkyl complexes (WO)XNp₃ (**1-X**, Np = CH₂-*t*Bu, X = Cl, Br, ONp) are efficient metathesis catalysts with high, sustained activity upon activation by Lewis acids and photoinitiation.⁶ Following these results, considerable attention turned to compounds bearing the isoelectronic imido ligand. Indeed, due to their easier synthesis, enhanced stability and high activity in olefin metathesis in the absence of cocatalysts, this approach proved to be rewarding both for homogeneous and heterogenized systems.⁷

When considering the WO₃/SiO₂ catalyst, and in the view of developing realistic model surface species, we targeted, as W molecular precursors, oxo carbenes or their alkyl precursors that are amenable to carbene generation upon α -H abstraction. Among the rare examples of such compounds,^{6,8} the **1-X** oxo alkyls devoid of inhibiting coordinated Lewis base appear as promising candidates for this purpose.

When considering the design of single-site heterogeneous catalysts with a controlled coordination sphere, surface organometallic chemistry (SOMC) has emerged as a powerful approach. The reaction of molecular species with a silica surface may be understood by comparison to their known reactivity in solution, and therefore targeted species may be obtained through judicious selection of the molecular precursors. The key step in grafting, namely formation of the metal-support bond by protonolysis, must occur irreversibly with high selectivity. This rules out the use of halide or alkoxides as the X species in **1-X**, as competition between W–C and W–X bond protonolysis may occur upon grafting: see for example the formation of binuclear W₂O₃Np₆ from hydrolysis of **1-Cl**.⁹

We thus turned our attention to the tetraalkyl derivative (WO)Np₄ (**1-Np**). Indeed, upon immobilization, the sole reactivity pathway available for reaction with silanols would be protonolysis of a W–C bond. As **1-Np** has not been isolated yet,^{6b} we revisited its synthesis. Inspired *ia* by Schrock's synthesis of W(NAr)(Np)₂(CH*t*Bu) from W(NAr)(Np)₃Cl and NpLi,¹⁰ we studied the reaction of **1-Cl** with several alkylating agents. Only unconventional NaNp afforded a tractable product (**1-Np**) as a colourless, light- and highly moisture-sensitive oil in a 35% yield. NMR features indicate the presence of equivalent neopentyl moieties, with the methylenic group giving rise to a singlet at 1.83 ppm and at 85.60 ppm (¹J_{W–C} = 48.1 Hz) on the ¹H and ¹³C NMR spectra, respectively. Alkylation results in significant shielding as the CH₂ signals in ¹H and ¹³C NMR are 2.46 and 100.9 ppm in **1-Cl**, respectively.‡ DFT calculations (B3PW91/SDDall) indicate that **1-Np** adopts a distorted trigonal bipyramidal geometry, with the oxo and two Np ligands in the equatorial positions, while the axial sites are occupied by alkyl moieties.‡ A similar distorted TBP structure was reported for **1-NR₂** complexes.¹¹ Moreover, like **1-Np**, these also feature Np ligands that are equivalent on the NMR time scale at room temperature.

In order to achieve the selective synthesis of species singly bound to the support, we selected a silica that solely bears isolated silanol surface groups, namely silica heated under vacuum at 700 °C (SiO₂-700). Grafting of **1-Np** was carried out in the absence of light at room temperature (Scheme 1). The

^a Université Lyon 1, Institut de Chimie Lyon, CPE Lyon, CNRS, UMR 5265 C2P2, LCOMS, Bât. 308 F, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne Cedex, France. E-mail: taoufik@cpe.fr; Fax: +33 (0)472 431 798; Tel: +33 (0)472 431 795

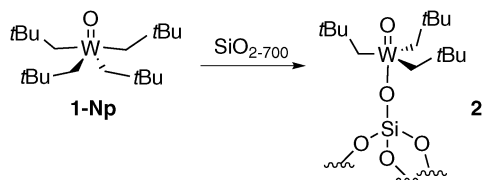
^b KAUST Catalysis Center (KCC), Thuwal, Kingdom of Saudi Arabia. E-mail: jeanmarie.basset@kaust.edu.sa

^c Université Lille Nord de France, CNRS UMR8181, Unité de Catalyse et de Chimie du Solide, UCCS USTL, F-59655 Villeneuve d'Ascq, France. E-mail: regis.gauvin@ensc-lille.fr; Fax: +33 (0)320 436 585; Tel: +33 (0)320 436 754

^d Exploratory Catalysis Research, UOP LLC, a Honeywell Company, 25 East Algonquin Rd., Des Plaines, IL, USA

† We dedicate this article to the memory of John A. Osborn and J. Kress, mentors and friends.

‡ Electronic supplementary information (ESI) available: General procedures, experimental details and additional characterization data for **1-Np** and **2**. See DOI: 10.1039/c0cc02507k



Scheme 1 Grafting of 1-Np.

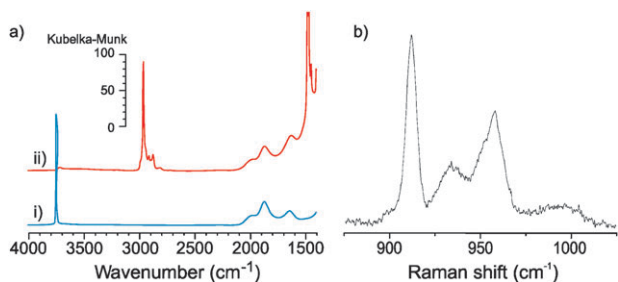


Fig. 1 (a) DRIFT spectra of (i) SiO₂-700 and (ii) **2**; (b) selected region of Raman spectrum of **2**.

resulting material (**2**) was stable to light exposure, and contained 4.1 wt% of tungsten and 4.2 wt% of carbon ($C/W = 14.9 \pm 0.1$, theory = 15). Gas phase analysis indicates evolution of 0.9 equivalent of NpH per metal center. Thus mass balance analysis is fully in line with the $[(\equiv SiO)(WO)Np_3]$ formulation. Infrared studies revealed the disappearance of the isolated silanol peak, and minor quantities of interacting SiOH (3700 cm^{-1}), as observed in related materials.¹² Other main spectral features are $\nu(C-H)$ and $\delta(C-H)$ ($2990\text{--}2800$ and $1460\text{--}1480\text{ cm}^{-1}$, respectively; Fig. 1a). In order to gain information on the $W=O$ bond, the vibration band of which is hidden by the silica network's absorption in the infrared spectrum, we applied Raman spectroscopy (Fig. 1b). A characteristic broad line of medium intensity is observed in **2** at around 958 cm^{-1} . The lines at about 910 , 935 and 990 cm^{-1} result from neopentyl-related modes.

Solid-state NMR data are fully in line with the proposed structure (Fig. S3, ESI[†]). The ¹H NMR spectrum comprises signals at 1.93 (CH_2) and 1.01 ($C(CH_3)_3$) ppm. On the ¹³C NMR spectrum of **2**, Np groups resonate at 91 (CH_2), 34 ($C(CH_3)_3$) and 31 ppm ($C(CH_3)_3$). This compares favourably with NMR features of the model alkoxide species **1-ONp** (1.93 and 87.3 ppm for WCH_2 groups in ¹H and ¹³C NMR, respectively).⁶ No resonances originating from carbenic species were detected. Assignments have been confirmed by ¹H-¹³C HETCOR 2D NMR, indicating the expected correlation between the 1.93 (¹H) and 91 (¹³C) ppm methylenic fragments' signals (Fig. 2).

The structure of the supported tungsten complex **2** was further confirmed by analysis of the W L_{III}-edge extended X-ray

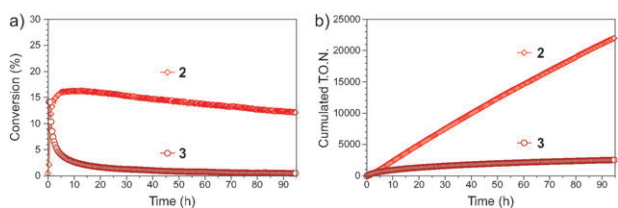


Fig. 2 Catalytic performances of **2** and **3** in propene metathesis ($80\text{ }^\circ\text{C}$, 20 mL min^{-1}): (a) conversion vs. time and (b) cumulated TON vs. time.

absorption fine structure (EXAFS) data (Table 1).[†] The results are consistent with a W coordination sphere comprising one oxygen atom at $1.71(1)\text{ \AA}$, one oxygen at $1.97(3)\text{ \AA}$ and three carbons at $2.12(3)\text{ \AA}$, assigned to an oxo ligand, a siloxide's σ -bonded oxygen, and methylenic carbons from neopentyl ligands, respectively. This is consistent with the bond distances found in $W_2O_3Np_6$ where the $W=O_{\text{terminal}}$ ($1.676\text{--}1.736\text{ \AA}$), $W-O_{\text{bridging}}$ ($1.913\text{--}1.987\text{ \AA}$) and $W-C$ ($2.113\text{--}2.150\text{ \AA}$) bond lengths are in the same range.^{9b,†} $W-O$ distances for σ -bonded siloxide ligands are usually shorter, e.g. ($1.876\text{--}1.882\text{ \AA}$) in the case of $(t\text{Bu}_3\text{SiO})_2(C_2H_5)_2W=O$.¹³ The rather long $\equiv SiO-W$ bond distance found here pleads for a *trans* mutual arrangement of the oxo and siloxy ligands, following from the strong *trans* influence of terminal $M=O$.¹⁴ Moreover, the fit was improved when considering further layers of backscatterers: (i) three C atoms at $3.24(4)\text{ \AA}$, assigned to the Np 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 $W_2O_3Np_6$;^{9b} (ii) *ca.* one silicon at $3.60(4)\text{ \AA}$, corresponding to a $171 \pm 9^\circ$ $W-O-Si$ angle: combined with the *trans* arrangement of the oxo and siloxy ligands, this indicates a quasi-linear $O=W-O-Si$ framework; and (iii) *ca.* one oxygen atom at $2.98(8)\text{ \AA}$, assigned to siloxane bridges of the silica surface.^{7b} These structural propositions have been corroborated by DFT calculations. Of the two possible structures,[†] the most stable one ($\Delta E = 65\text{ kJ}$) consists of a distorted trigonal bipyramid with mutually *trans* oxo and siloxide as axial ligands, and with equatorial positions occupied by alkyl moieties. The calculated bond lengths and angles are in very good agreement with the EXAFS data, giving a clear picture of the surface organometallic fragment (Table 1).

Exposure of 40 equivalent of propene to **2** at $80\text{ }^\circ\text{C}$ in a batch reactor led to the formation of equilibrated mixture of metathesis products: propene, ethene and 2-butene (*trans/cis* ratio of 2.3), along with 0.9 equivalent of neopentane per tungsten, in agreement with the formation of the expected carbenic catalytic active species $[(\equiv SiO)(WO)Np(=CH_2tBu)]$. Accordingly, *neohexene* was also detected (0.7 equivalent). Attempts to observe alkylidene species by heating ($80\text{ }^\circ\text{C}$) prior to substrate addition were not successful. DFT calculations indicated that generation of this species from alkyl compound **2** is an exothermic process ($\Delta E = -29\text{ kJ mol}^{-1}$ for the corresponding species with H-substituted POSS as surface surrogate[†]) and is thermodynamically favored by the formation of a gaseous byproduct.

In a further step, catalytic performances of **2** were probed in a flow reactor ($20\text{ mL C}_3\text{H}_6\text{ min}^{-1}$; $30\text{ mol C}_3\text{H}_6\text{ mol W}^{-1}\text{ min}^{-1}$). An initial conversion rate of $4.9\text{ mol C}_3\text{H}_6\text{ mol W}^{-1}\text{ min}^{-1}$ (*ca.* 16% conversion) was reached (Fig. 2a), and 22 000 cumulated turnover

Table 1 EXAFS parameters for **2**^a

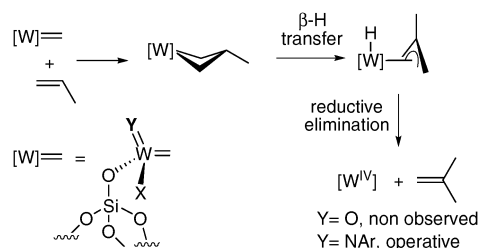
Type of neighbor	Number of neighbor	Distance/ \AA	DFT calculated distance/ \AA	$\sigma^2/\text{\AA}^2$
$W=O$	1.1(3)	1.71(1)	1.755	0.0018(9)
$W-O\text{Si}\equiv$	1.2(6)	1.97(3)	1.990	0.002(2)
$W-CH_2CMe_3$	3.1(15)	2.12(3)	2.150–2.153	0.003(2)
$W-CH_2CMe_3$	3.1	3.24(4)	3.321–3.324	0.004(3)
$W-O\text{Si}\equiv$	0.8(4)	3.60(4)	3.637	0.004(4)
$W-O(\text{Si}\equiv)_2$	0.8(7)	2.98(7)	—	0.007(8)

^a Errors in parentheses; fit residue: $\rho = 3.4\%.[†]$

numbers (TON) were achieved after 95 hours (Fig. 2b). The selectivity remained constant with time on stream, with equimolar quantities of ethene 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), in agreement with that observed in the literature for other d⁰ systems; that is, terminal alkenes typically give the *trans*-alkene as the major kinetic product, due to the easier formation of the least sterically hindered metallacyclobutane by an *anti* approach.¹⁵ In order to compare the impact of isoelectronic oxo and imido ligands on catalytic performances, we studied the behavior of parent species [(≡SiO)W(=NAr)(=CH*t*Bu)Np] (**3**)^{7b} under identical conditions. Sharp differences are to be emphasized: (i) although a comparable initial rate is observed for **3** (4.5 mol_{C₃H₆} mol_W⁻¹ min⁻¹, ca. 15% conversion), fast deactivation quickly followed (Fig. 2a): conversion dropped to about 4% after 5 hours, and slower but steady deactivation led to 2500 cumulated TONs after 95 hours; (ii) regarding selectivity, along with the expected formation of ethylene (49.3%) and 2-butenes (48.5%), other products were formed, namely isobutene (0.05%), C₅ olefins (0.6%) and C₆ olefins (1.3%) (*vide infra*); the *trans/cis* 2-butene ratio is 0.9, twice lower than for **2**: this can be explained by the difference of electronic properties and steric hindrance between oxo and imido ligand that impacts on the relative stabilities of the tungstacyclobutanes; (iii) whereas the above mentioned higher alkenes (C₅ and C₆) are secondary cross-metathesis products, formation of isobutene can only be tracked back to a well-established olefin metathesis catalyst decomposition pathway, namely rearrangement of metallacyclobutanes by β-H transfer.¹⁶ Indeed, a 2-methyltungstacyclobutane thus affords a 2-methyltungsten hydride that further reductively eliminates isobutene and generates reduced, inactive tungsten species (Scheme 2). As the profile of isobutene formation closely follows that of deactivation of **3**, one can assume that this mechanism plays a significant role in the imido species deactivation. Importantly, such a pathway does not seem to operate in the case of **2**. This emphasizes the importance of the oxo ligand in enforcing catalyst stability.

In conclusion, we have prepared and fully characterized the first example of a well-defined tungsten surface species that solely combines oxo and alkyl ligands. Under mild conditions and without need of a co-catalyst, this material demonstrates high, sustained activity in propene metathesis, in contrast to the parent imido-derived material. This represents a significant step toward the understanding of the WO₃/SiO₂ system, as we have shown here that isolated organometallic metal oxide fragments give rise to high performance in propene metathesis.

This was accomplished by using the surface organometallic chemistry approach that allows for rational design



Scheme 2 Catalyst deactivation by β-H elimination in the metallacyclobutane.

of heterogeneous catalysts and thus can significantly contribute to the preparation of more efficient catalytic materials. Ongoing efforts are now targeted at the design and characterization of related carbene species of W and Mo, as the latter is expected to display higher activity at lower temperature.

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