

Supporting Information

Low Temperature Activation of Supported Metathesis Catalysts by Organosilicon Reducing Agents

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A) General procedures

All experiments were carried out under dry and oxygen free argon atmosphere using either standard Schlenk or glove-box techniques for organometallic synthesis. For the syntheses, reactions were carried out using high vacuum lines (10^{-5} mbar) and glove-box techniques. Pentane, toluene and diethyl ether were purified using double MBraun SPS alumina column, and were degassed using three freeze-pump-thaw cycles before being used. DME and THF were distilled from Na/Benzophenone. Silica (Aerosil Degussa, $200 \text{ m}^2 \cdot \text{g}^{-1}$) was compacted with distilled water, calcined at $500 \text{ }^\circ\text{C}$ under air for 4 h and treated under vacuum (10^{-5} mbar) at $500 \text{ }^\circ\text{C}$ for 6 h and then at $700 \text{ }^\circ\text{C}$ for 10 h (support referred to as SiO_{2-700}) and contained 0.26 mmol of OH per g as measured by titration with PhCH_2MgCl . All infrared (IR) spectra were recorded using a Bruker α -T spectrometer placed in an Ar glovebox, equipped with OPUS software. A typical experiment consisted in the measurement of transmission in 32 scans in the region from 4000 to 400 cm^{-1} . The ^1H and ^{13}C -NMR spectra were obtained on Bruker Avance III 400, 700, 850 and 1000 MHz Bruker spectrometers equipped with a 4 mm probe. Cross polarization magic angle spinning (CPMAS) and spin echo type experiments were used to measure ^{13}C and ^1H , respectively. The radio frequency (RF) field of proton was always set to 100 kHz while the ^1H decoupling was set to 80 kHz. The solution spectra were recorded in C_6D_6 at room temperature. The electronic structures of the catalysts were obtained with a Varian Cary UV-vis spectrophotometer employing a Praying Mantis integration sphere. The UV-vis spectra were processed with Microsoft Excel software, consisting of calculation of the Kubelka-Monk function, $F(R_\infty)$, which was extracted from the UV-vis DRS absorbance. The edge energy (E_g) for allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of a plot of $[F(R_\infty)hv]^2$.¹ Continuous Wave (CW) EPR spectra were measured at X band (9.5-GHz microwave frequency) on a Bruker EMX spectrometer at 110 K. Powder XRD experiments were performed on a STOE Padi Diffractometer in Debye-Scherrer Mode (2θ) with a Dectris Mythen 1K area detector using $\text{Cu K}\alpha 1$ radiation. The sample was prepared and measured in a sealed quartz capillary. X-ray absorption spectroscopy (XAS) at the W L_{III} -edge was measured at the SuperXAS beamline at the Swiss Light Source (SLS; Paul Scherrer Institute, Villigen, Switzerland). The SLS is a third-generation synchrotron operating at a 2.4-GeV electron energy and a current of 400 mA. The SuperXAS beamline is positioned at 2.9 T super-bent port. The incident beam was collimated by a Rh-coated mirror at 2.8 mrad, monochromatized using a channel-cut $\text{Si}(111)$ monochromator, and focused with an Rh-coated toroidal mirror (at 2.8 mrad) down to $500 \times 500 \text{ }\mu\text{m}$ with a beam intensity of $4\text{--}5 \times 10^{11}$ ph/s. Calibration of the beamline energy was performed using Pt reference foil (Pt L_{III} -edge position at 11564 eV). XAS spectra in transmission mode were measured at room temperature using ionization chambers filled with He-N₂ gas mixtures. To avoid contact with air, all samples were sealed in a Ar glovebox. Each pellet of samples (with optimized thickness for transmission detection) was placed in two aluminized plastic bags (Polyaniline (15 μm), polyethylene (15 μm), Al (12 μm), polyethylene (75 μm) from Gruber-Folien GmbH & Co. KG) using an impulse sealer inside a glovebox; one sealing layer was removed just before the measurements. Multiple extended X-ray absorption fine structure (EXAFS) scans (10207–11207 eV) were averaged using new spots for each scan, with a scan time of ca. 30 min. EXAFS data were analyzed using the Ifeffit program package. The EXAFS data were fitted in R-space (1–2.2 Å) after a Fourier transform ($k = 1.5\text{--}14.2 \text{ Å}^{-1}$) using a k -weight of 3.

Compounds $\text{WO}_2\text{Cl}_2(\text{DME})$,² $\text{WOCl}_3(\text{bipy})$,³ 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (**R1**),⁴ 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**R2**), 2,5-dimethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**R3**), 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene ($\text{Me}_4\text{-BTDP}$, **Red**),⁵ were synthesized according to literature procedures. Ammonium metatungstate and ammonium heptamolybdate hydrates were purchased from Fluka and used without purification. WO_3/SiO_2 and $\text{MoO}_3/\text{SiO}_2$ were synthesized by incipient wetness impregnation followed by calcination at $450 \text{ }^\circ\text{C}$.¹ It was determined by elemental analysis to contain 7.12% W in mass for WO_3/SiO_2 and 7% Mo in mass for $\text{MoO}_3/\text{SiO}_2$.

B) Syntheses

1) Synthesis of the molecular precursors:

Synthesis of [W(O)(OSi(OtBu)₃)₄]

[W(O)(OSi(OtBu)₃)₄] was synthesized following the procedure described by Tilley.⁶ XRD suitable crystals were obtained upon cooling at -40 °C a saturated toluene solution of the complex.

Synthesis of [W(O)₂(OSi(OtBu)₃)₂(DME)]

[W(O)₂(OSi(OtBu)₃)₂(DME)] was synthesized using a modification of the procedure described by Tilley.⁶ A solution of LiOSi(OtBu)₃ (2.87 g, 10.6 mmol, 2 eq.) in cold toluene (15 mL, -40 °C) was added dropwise to a suspension of WO₂Cl₂(DME) (2.00 g, 5.3 mmol, 1 eq.) in toluene (20 mL, -78 °C) containing 200 μL of DME under vigorous stirring. After 1 hour stirring at -78 °C and 2 h at room temperature, the solution was filtered through a short Celite® pad to afford a colorless solution. Crystallization of the product from this solution at -40 °C afforded 3.2 g (3.8 mmol, 72 %) of the title product as large colorless needle shaped crystals suitable for XRD (collected in two crops).

¹H-NMR (300 MHz, C₆D₆) δ 1.38 (s, 54H, (OtBu)₃), 3.15 (s, 6H, DME), 3.33 (s, 4H, DME).

IR (KBr, cm⁻¹): 703(m), 830(m), 858(m), 902(m), 948(m), 962(m), 1028(m), 1066(s), 1191(m), 1243(m), 1366(m), 1390(m), 1473(w), 2975(m).

2) Synthesis of the heterogeneous complexes:

Synthesis of [(≡SiO)W(O)₂(OSi(OtBu)₃)]

A solution of 1.00 g of WO₂[OSi(O^tBu)₃]₂(DME) (1.25 mmol, 1.05 equiv.) in benzene (6 mL) was added to a suspension of SiO₂₋₍₇₀₀₎ (4.61 g, 1.19 mmol, 1 equiv.) in benzene (3 mL) at room temperature. The suspension was slowly stirred at room temperature for 12 h. The white solid was collected by filtration, and was washed by five suspension/filtration cycles in benzene (5 x 2 mL). The resulting solid was dried thoroughly under high vacuum (10⁻⁵ mbar) at room temperature for 3 h to afford 4.55 g of the title compound. All the filtrate solutions were collected and analyzed by ¹H NMR spectroscopy in C₆D₆ using ferrocene as internal standard, indicating that 1.7 mmol of (tBuO)₃SiOH and 0.47 mmol of DME were released upon grafting (0.70 (tBuO)₃SiOH/W_{surf} and 0.40 DME/W_{surf}). Additional 0.65 mmol of DME were quantified in the volatiles collected upon high vacuum drying, indicating that >95% of DME was not retained on the silica surface.

Elemental Analysis: W 3.12%, H 0.64%, C 2.97% corresponding to 14.5 C/W (12 expected), 38 H/W 39 expected).

IR (KBr, cm^{-1}): 1369 (s), 1393 (m), 1474 (w), 2937 (m, sh), 2979 (s).

IR and solid state NMR spectra of the material are given in Fig. S3 and Fig. S8-Fig. S9, respectively.

Thermal decomposition of $[(\equiv\text{SiO})\text{WO}_2(\text{OSi}(\text{OtBu})_3)]$: preparation of **1**

$[(\equiv\text{SiO})\text{WO}_2(\text{OSi}(\text{OtBu})_3)]$ (3.0 g) was loaded into a reactor and placed under high vacuum (10^{-5} mbar) and heated to 200 °C (1 °C/min) and held at this temperature for 3 h then heated at 400 °C (1 °C/min) and held at this temperature for 6 h . The reactor was cooled to ambient temperature under vacuum, and **1** was stored in an Ar filled glovebox. The volatiles evolved during this process were quantified by ^1H NMR in C_6D_6 using ferrocene as an internal standard, indicating the release of 2.5 equiv. of isobutylene, 0.6 equiv. of water and 0.8 equiv. of tBuOH per surface W complex.

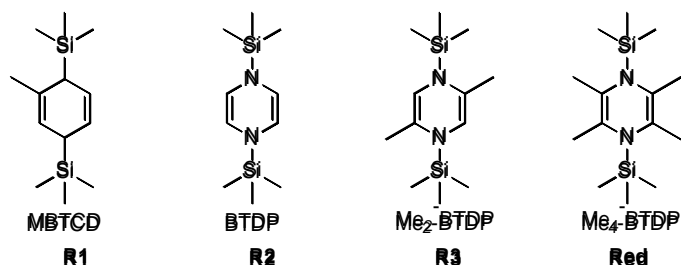
Elemental analysis: W 3.15 %.

IR (KBr, cm^{-1}): 3746 (s).

IR spectrum, UV-DRS and powder XRD pattern of the material are given in Fig. S3, Fig. S17 and Fig. S19, respectively.

3) Reductions of 1

Acronyms:



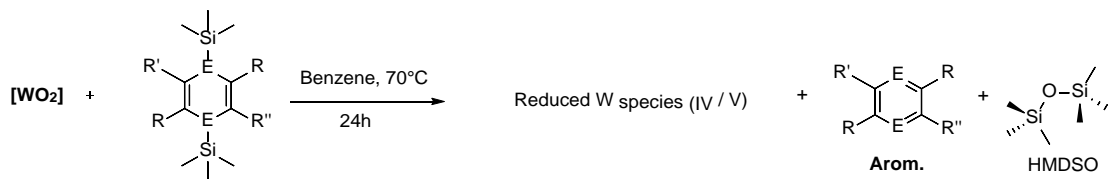
Representative procedure: Preparation of 1-(Red)₂

A solution of 5.4 mg of Me₄-BTDP (19.4 μmol, 1 equiv.) in benzene (0.5 mL) was added to a suspension of **1** (50 mg, 9.7 μmol) in benzene (0.5 mL) at room temperature. The suspension was slowly stirred at 70 °C for 12 h, resulting in color change of the material from colorless to dark violet. The solid was collected by filtration, and was washed by four suspension/filtration cycles in benzene (4 x 1 mL). The resulting dark violet solid was dried thoroughly under high vacuum (10⁻⁵ mbar) at room temperature for 3 h to afford 45 mg of the title compound. All the filtrate solutions were collected and analyzed by ¹H NMR spectroscopy in C₆D₆ using ferrocene as internal standard, indicating consumption of 13.1 μmol of Me₄-BTDP and that 9.7 μmol of 2,3,5,6-tetramethylpyrazine and 1.2 μmol of HMDSO were released upon reacting (0.18 equiv. 2,3,5,6-tetramethylpyrazine /W_{surf}). Elemental Analysis: W 2.93 %, C 2.57 %, H 0.54%, N 0.24 % corresponding to 13 C/W, 33 H/W and 1 N/W.

IR, UV-DRS and solid state NMR spectra of the material are given in Fig. S5, Fig. S18, and Fig. S10-Fig. S11, respectively.

Reduction of 1 with 1 equiv. of reductant R1, R2, R3 or Red

General reaction scheme:



Reductions were carried out following the procedure above on 100 mg of **1** with 1 equiv. of the four reductants represented above. Analyses of the filtrate by NMR are summarized in Table S1, and IR spectra of the materials are given in Fig. S4.

Table S1: Filtrate analysis by ¹H NMR after reduction.

Reductant	Consumption of reductant ^a	Aromatized Bp (Arom.) ^a	HMDSO ^a	Colour of the material	Material name
R1	10%	10%	1%	Blue	1-(R1)₁
R2	100%	1%	2%	Dark violet	1-(R2)₁
R3	100%	33%	4%	Dark violet	1-(R3)₁
Red	100%	55%	3%	Dark violet	1-(Red)₁

^a Values given in % with respect to the amount of reductant used in the reduction.

Reduction of **1** with 0.5-3 equiv. of reductant Me₄-BTDP:

Reductions were carried out following the procedure above on 100 mg of **1** with various amounts of reductant Me₄-BTDP. Analyses of the filtrate by NMR are summarized in Table S2 and IR spectra of the materials are given in Fig. S5.

Table S2: Filtrate analysis by ¹H NMR after reduction with various amount Me₄-BTDP.

Equiv. of Me ₄ -BTDP per W center	Consumption of Me ₄ -BTDP ^a	Aromatized Bp (Arom.) ^a	HMDSO ^a	Material name
0.5	100%	29%	3%	1-(Red)_{0.5}
1	100%	55%	3%	1-(Red)₁
2	68%	50%	6%	1-(Red)₂
3	62%	29%	4%	1-(Red)₃

^a Values given in % with respect to the amount of reductant used in the reduction.

Passivation of SiO₂₋₇₀₀ with Me₄-BTDP

A solution of 3.7 mg of Me₄-BTDP (13 μmol, 1 equiv.) in benzene (0.5 mL) was added to a suspension of SiO₂₋₇₀₀ (50 mg, 19 μmol) in benzene (0.5 mL) at room temperature. The suspension was slowly stirred at 70 °C for 12 h. The solid was collected by filtration, and was washed by four suspension/filtration cycles in benzene (4 x 1 mL). The resulting solid was dried thoroughly under high vacuum (10⁻⁵ mbar) at room temperature for 3 h. All the filtrate solutions were collected and analyzed by ¹H NMR spectroscopy in C₆D₆ using ferrocene as internal standard, indicating consumption of 0.8 equiv. of Me₄-BTDP and that 0.5 equiv. 2,3,5,6-tetramethylpyrazine was released upon reacting (together with other unidentified products). IR spectrum of the material is given in Fig. S6.

Reaction of **1** with HMDSO

Hexamethyldisiloxane (7.6 μL , 35 μmol , 4 equiv) was added to a suspension of **1** (55 mg, 9 μmol) in 1 mL C_6D_6 . The suspension was slowly stirred at 70 $^\circ\text{C}$ for 12 h. The solid was collected by filtration, and washed by three suspension/filtration cycles in C_6D_6 (3 x 0.5 mL). The resulting solid was dried thoroughly under high vacuum (10⁻⁵ mbar) at room temperature for 2 h. All the filtrate solutions were collected and analyzed by ^1H NMR spectroscopy in C_6D_6 using ferrocene as internal standard, indicating consumption of 41% (14 μmol) of HMDSO. The intensity of isolated SiOH in the IR decreased by 22% and a broad peak is observed ca. 3600 cm^{-1} . IR spectrum of the material is given in Fig. S7.

C) Single crystal XRD structures

CCDC 1479019 and 1479020 contains the supplementary crystallographic data

Fig. S1: Thermal ellipsoid plot at the 50% probability of $[\text{WO}_2(\text{OSi}(\text{OtBu})_3)_2(\text{DME})]$. Hydrogen atoms have been omitted and only one of the three independent molecules in the asymmetric unit have been represented for clarity.

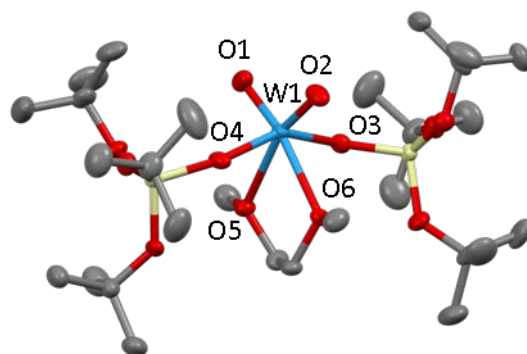


Table S3: Selected bonds for $[\text{WO}_2(\text{OSi}(\text{OtBu})_3)_2(\text{DME})]$ (distances are given in Å)

Structural parameters	$[\text{WO}_2(\text{OSi}(\text{OtBu})_3)_2(\text{DME})]$
W1 – O1	1.719(5)
W1 – O2	1.716(5)
W1 – O3	1.924(4)
W1 – O4	1.928(4)
W1 – O5	2.332(4)
W1 – O6	2.344(4)

Table S4: Crystallographic data for $[\text{WO}_2(\text{OSi}(\text{OtBu})_3)_2(\text{DME})]$

Formula	$\text{C}_{119}\text{H}_{264}\text{O}_{48}\text{Si}_8\text{W}_4$
Crystal size (mm)	$0.7 \times 0.2 \times 0.2$
cryst syst	Tetragonal
space group	$I41$
volume (Å ³)	16779.5(4)
a (Å)	23.6586(3)

b (Å)	23.6586(3)
c (Å)	29.9778(5)
α (deg)	90
β (deg)	90
γ (deg)	90
Z	4
formula weight (g/mol)	3423.44
density (g cm ⁻³)	1.355
F(000)	7075.3
temp (K)	150.0(3)
total no. reflections	30830
unique reflections [R(int)]	23689 [0.1046]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0641$, $wR_2 = 0.1208$
Largest diff. peak and hole (e.Å ⁻³)	2.62/-3.91
GOF	1.050

Fig. S2: Thermal ellipsoid plot at the 50% probability of [WO(OSi(OtBu)₃)₄]. Hydrogen atoms have been omitted for clarity.

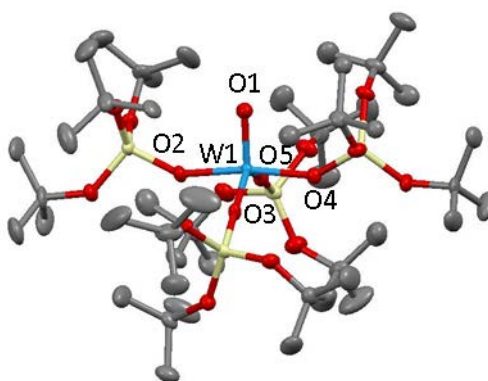


Table S5: Selected bonds for [WO(OSi(OtBu)₃)₄] (distances are given in Å)

Structural parameters	[WO(OSi(OtBu) ₃) ₄]
W1 – O1	1.682(4)
W1 – O2	1.897(4)
W1 – O3	1.857(5)

W1 – O4	1.905(4)
W1 – O5	1.856(4)

Table S6: Crystallographic data for [WO(OSi(OtBu)₃)₄]

Formula	C ₄₈ H ₁₀₈ O ₁₇ Si ₄ W
Crystal size (mm)	0.4 × 0.33 × 0.21
cryst syst	Monoclinic
space group	<i>C2/c</i>
volume (Å ³)	16779.5(4)
<i>a</i> (Å)	26.1638(10)
<i>b</i> (Å)	13.7832(5)
<i>c</i> (Å)	36.0594(14)
<i>α</i> (deg)	90
<i>β</i> (deg)	91.306(4)
<i>γ</i> (deg)	90
Z	8
formula weight (g/mol)	1253.55
density (g cm ⁻³)	1.281
F(000)	5296.0
temp (K)	150.0(3)
total no. reflections	88239
unique reflections [R(int)]	13807[R(int) = 0.1303]
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0766, <i>wR</i> ₂ = 0.1187
Largest diff. peak and hole (e.Å ⁻³)	3.10/-2.92
GOF	1.273

D) IR

Fig. S3: FTIR transmission spectra of **1** (red line) compared with the parent $[(\equiv\text{SiO})\text{WO}_2(\text{OSi}(\text{OtBu})_3)]$ complex (pink line) and SiO_{2-700} (blue line).

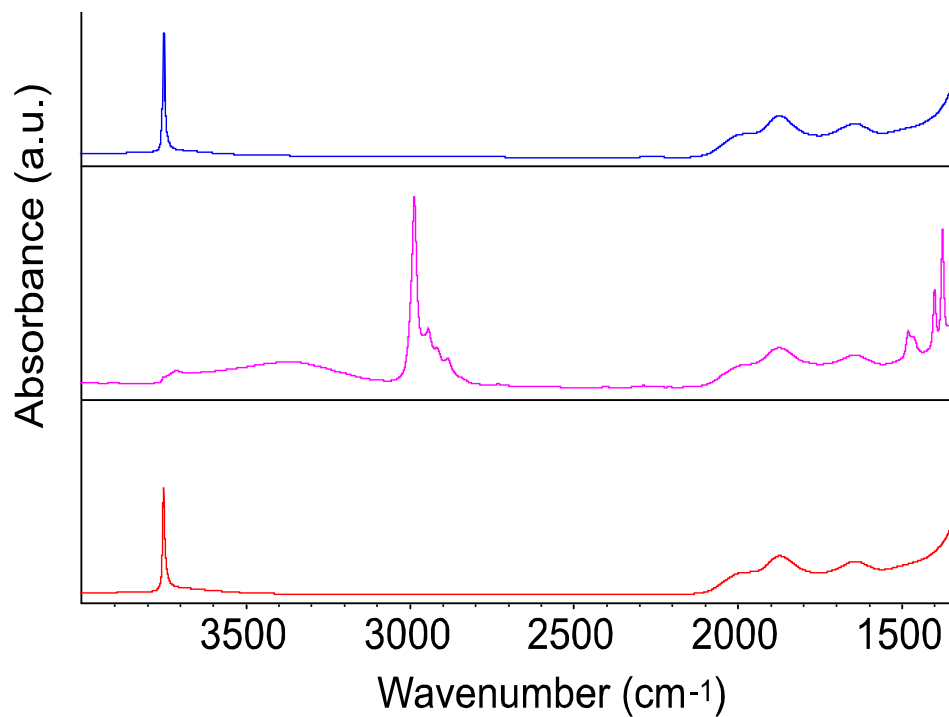


Fig. S4: FTIR of the materials **1-(R1)₁**, (red line), **1-(R2)₁**, (blue line), **1-(R3)₁**, (green line), and **1-(Red)₁**, (purple line).

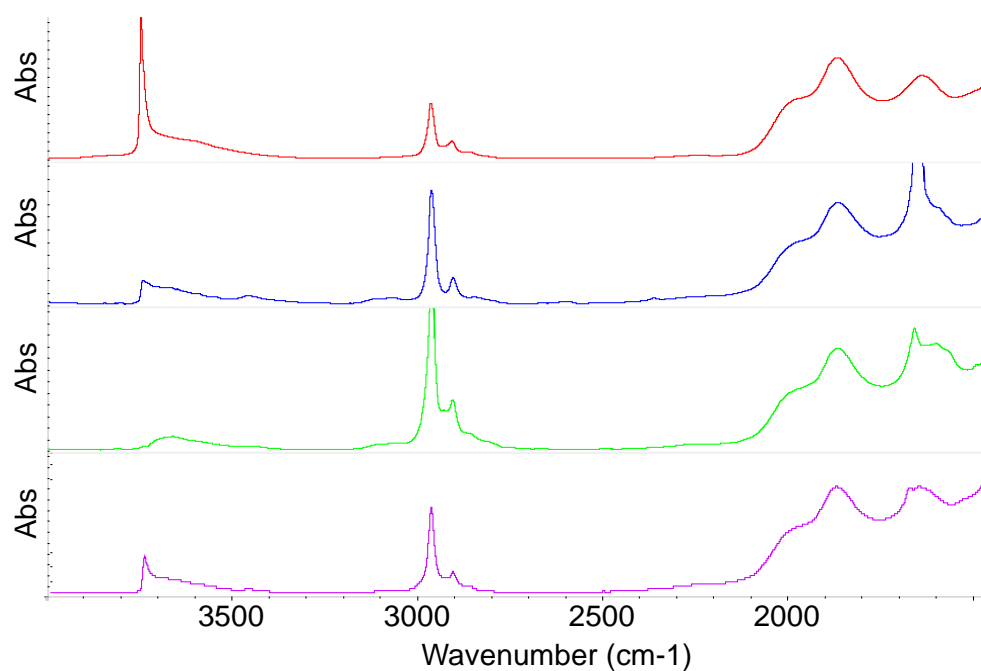


Fig. S5: FTIR of the materials **1-(Red)_{0.5}**, (blue line), **1-(Red)₁**, (light green line), **1-(Red)₂**, (red line), and **1-(Red)₃**, (dark green line).

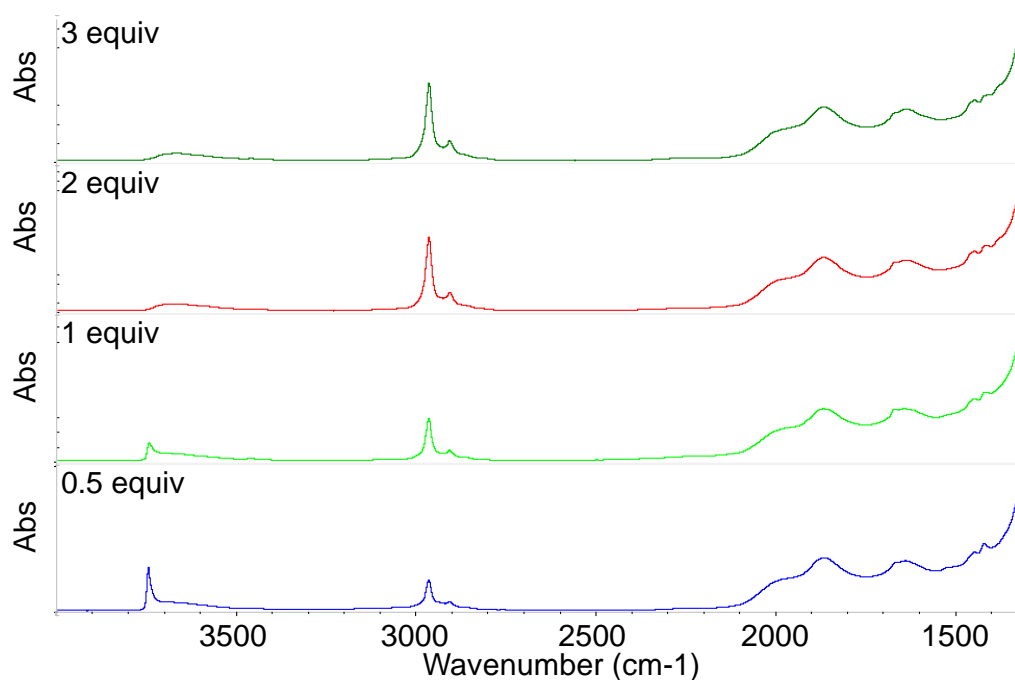


Fig. S6: FTIR of the SiO₂₋₇₀₀ before (red line) and after (blue line) passivation with one equiv. of Me₄-BTDP (procedure described above).

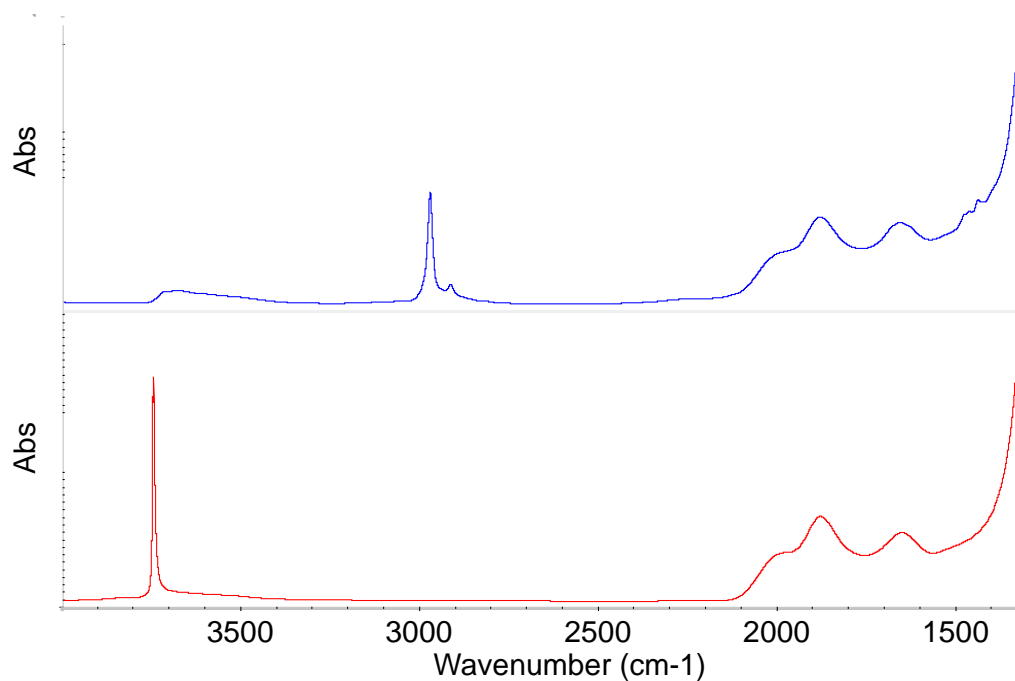
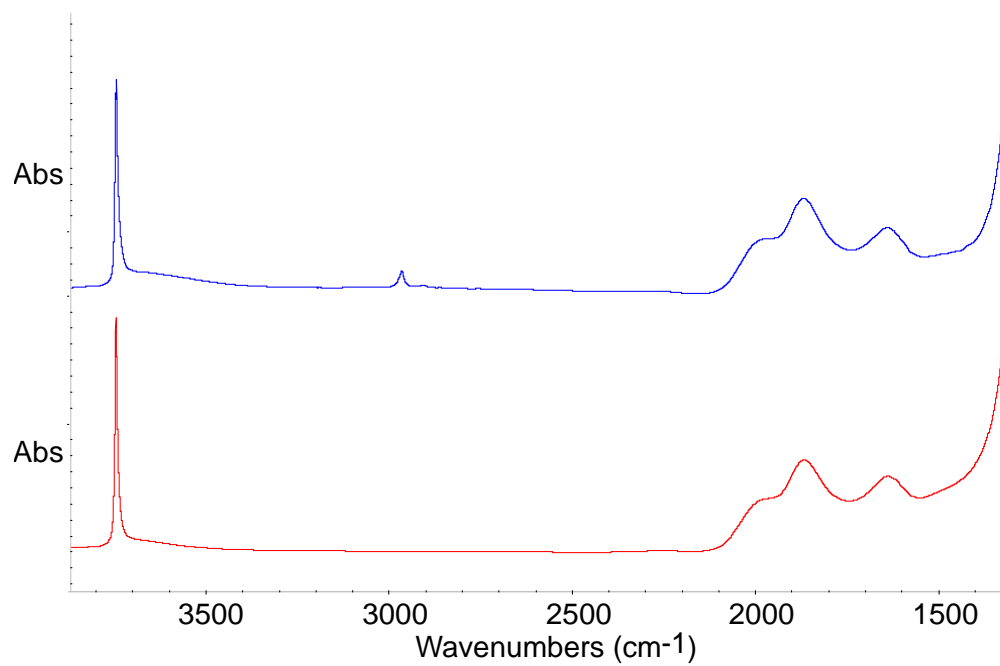


Fig. S7: FTIR of **1** before (red line) and after (blue line) reaction with 4 equiv. HMDSO (procedure described above).



E) Solid State NMR

Fig. S8: ^1H NMR spectrum (400 MHz, spinning rate 10 kHz, 4 mm rotor) of $[(\equiv\text{SiO})\text{WO}_2(\text{OSi}(\text{OtBu})_3)]$.

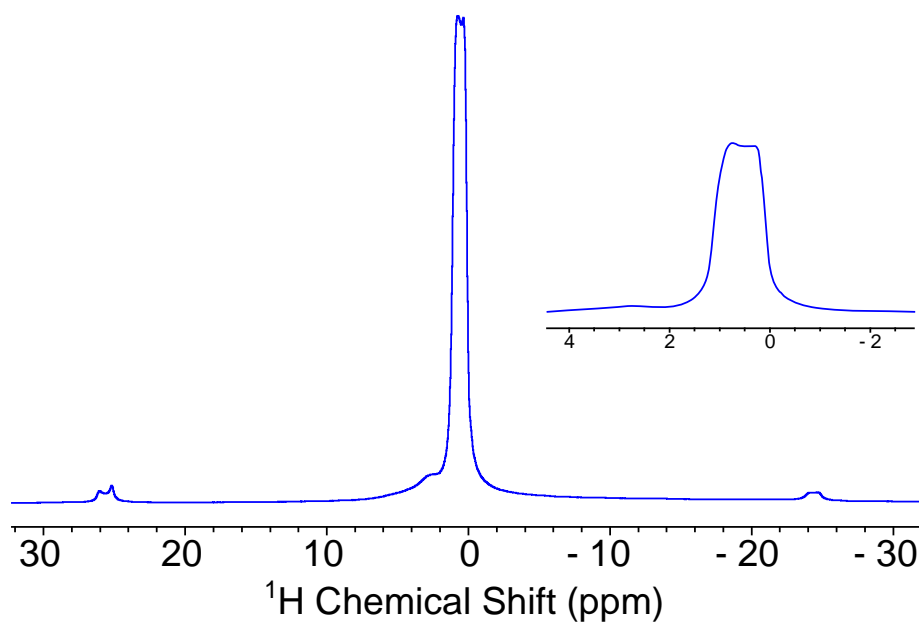


Fig. S9: ^{13}C CP-MAS NMR spectrum (400 MHz, spinning rate 10 kHz, 4 mm rotor) of $[(\equiv\text{SiO})\text{WO}_2(\text{OSi}(\text{OtBu})_3)]$ ($d_1 = 2$ s, contact time = 2 ms).

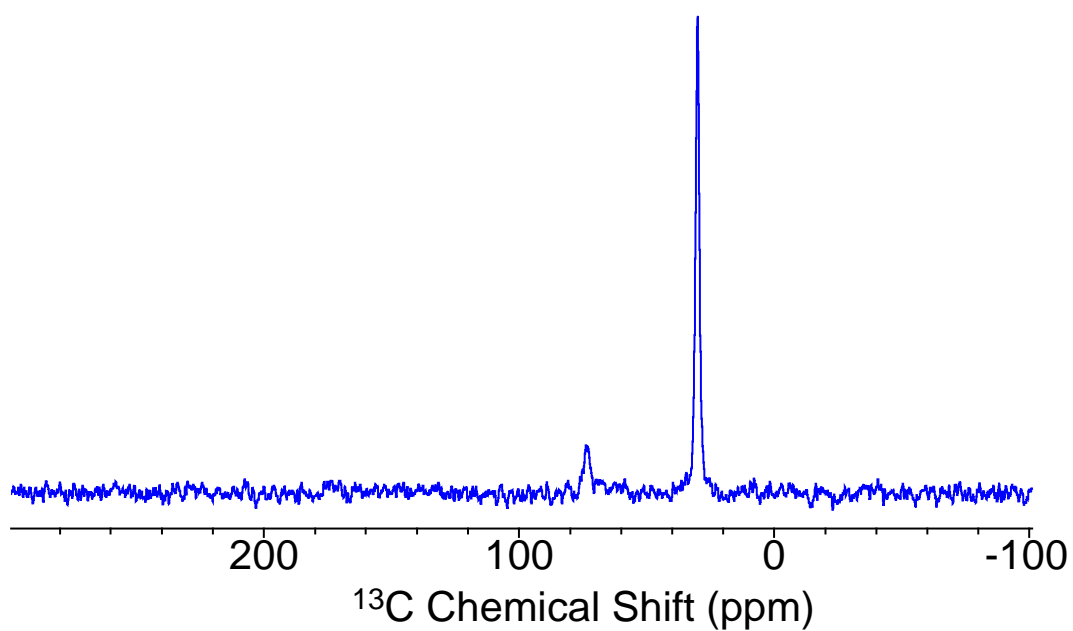


Fig. S10: ^1H NMR spectrum (400 MHz, spinning rate 10 kHz, 4 mm rotor) of **1-(Red)₂**.

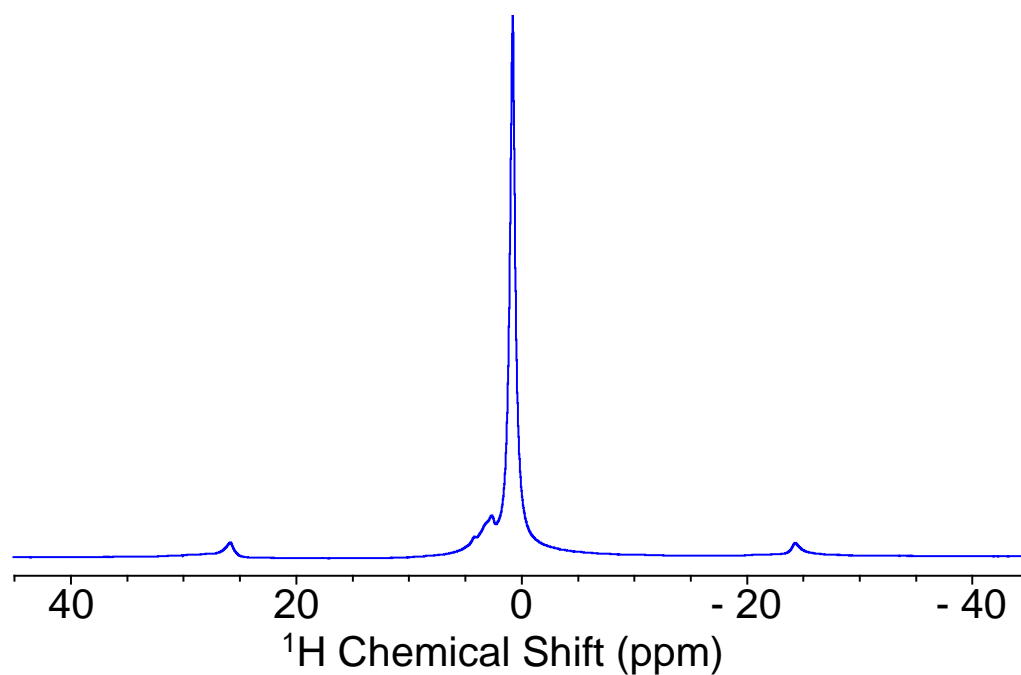


Fig. S11: ^{13}C CP-MAS NMR spectrum (400 MHz, spinning rate 10 kHz, 4 mm rotor) of **1-(Red)₂** (d1 = 2 s, contact time = 2 ms).

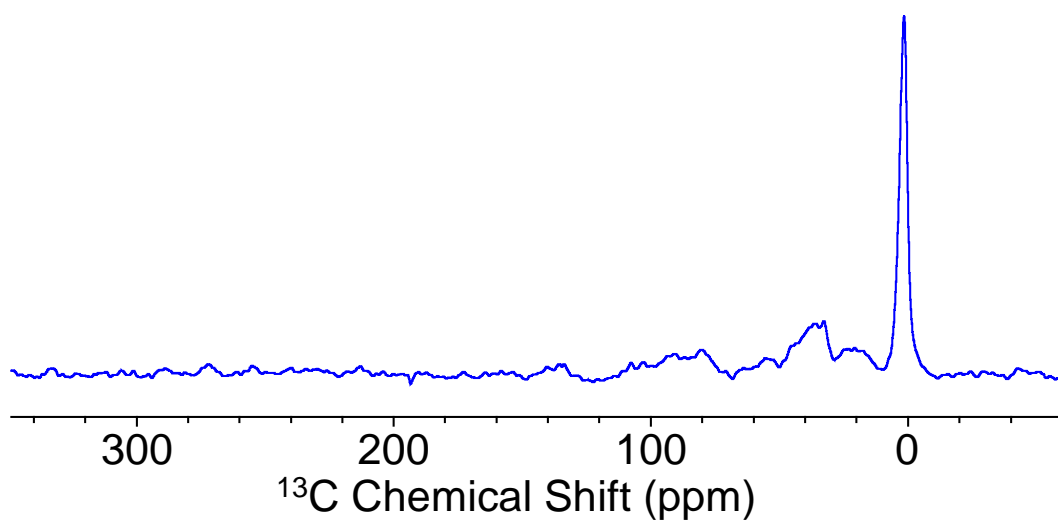


Fig. S12: ^1H NMR spectrum (400 MHz, spinning rate 10 kHz, 4 mm rotor) of **1-(Red)₂** after exposure to ^{13}C dilabeled ethylene (see details in part “N”).

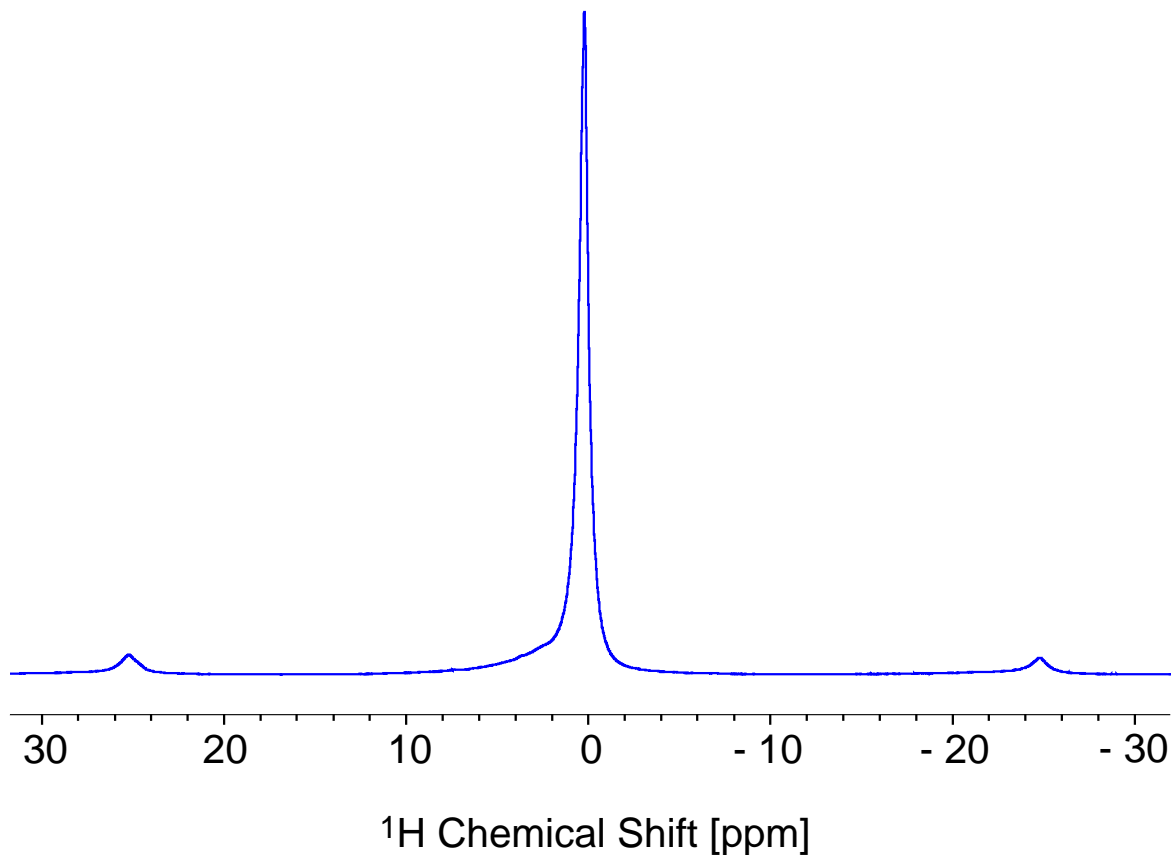


Fig. S13: ^{13}C CP-MAS NMR spectrum (400 MHz, spinning rate 10 kHz, 4 mm rotor) of **1-(Red)₂** after exposure to ^{13}C dilabeled ethylene (d1 = 2 s, contact time = 2 ms).

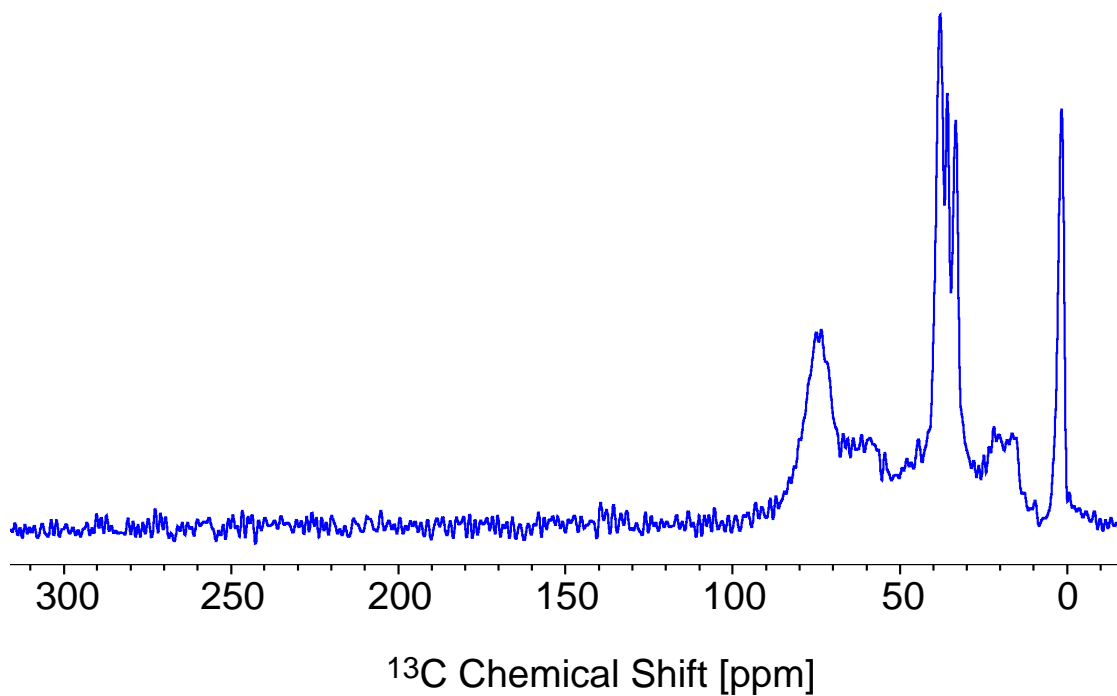


Fig. S14: HETCOR spectrum (400 MHz, spinning rate 10 kHz, 4 mm rotor) of **1-(Red)₂** of **1-(Red)₂** after exposure to ¹³C dilabeled ethylene.

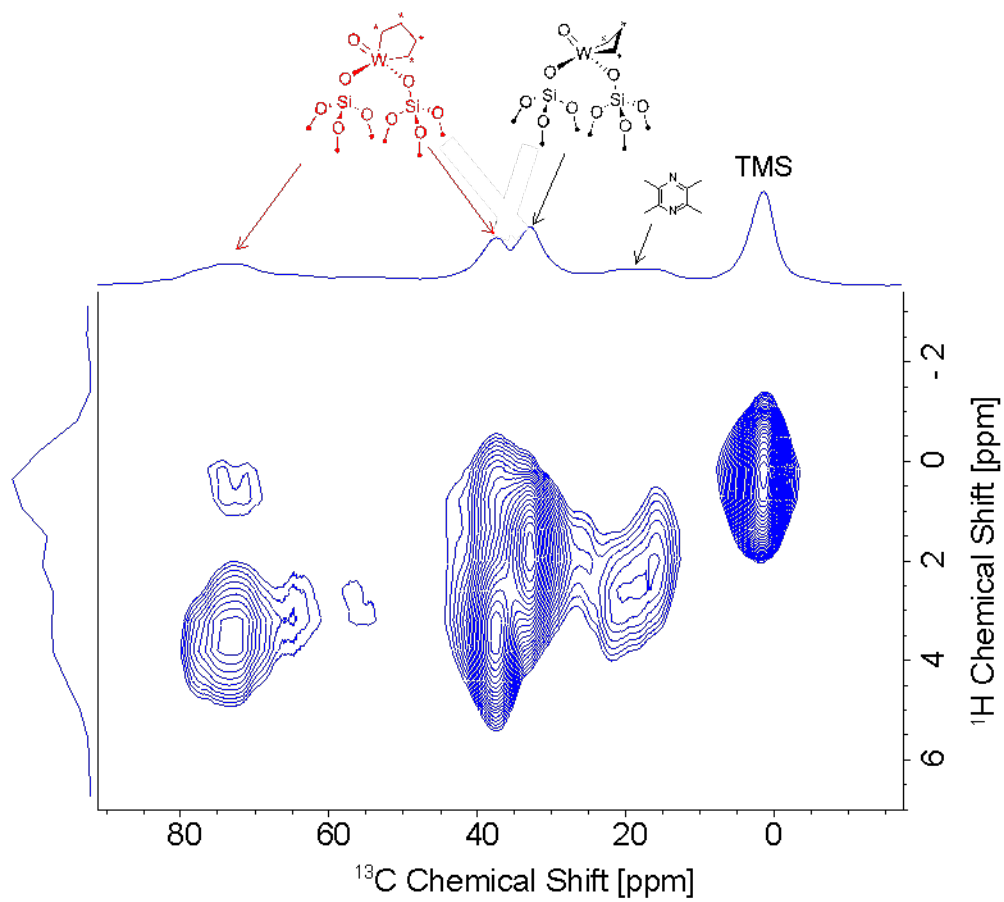


Fig. S15: ^1H NMR spectrum (400 MHz, spinning rate 10 kHz, 4 mm rotor) of **1-(Red)₂** after isotopic exchange (see details in part “N4”)

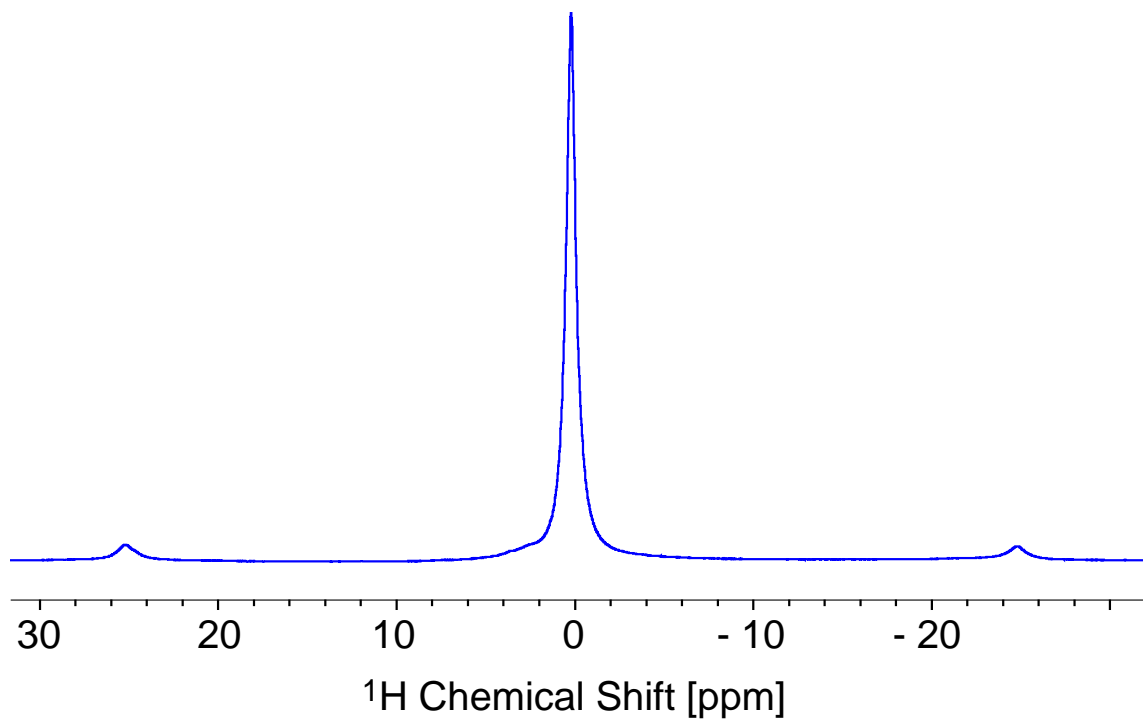
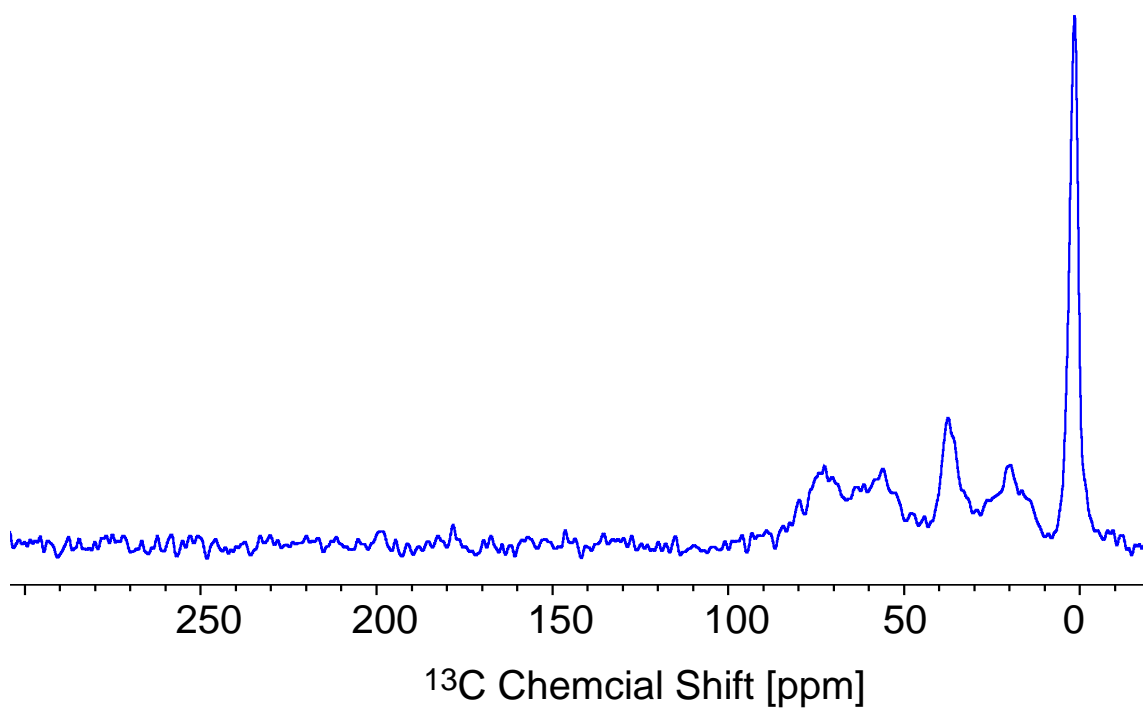


Fig. S16: ^{13}C CP-MAS NMR spectrum (400 MHz, spinning rate 10 kHz, 4 mm rotor) of **1-(Red)₂** after isotopic exchange (see details in part “N4” (d1 = 2 s, contact time = 2 ms)).



F) UV-Vis DRS

Fig. S17: UV-vis DRS spectra and E_g values of **1**

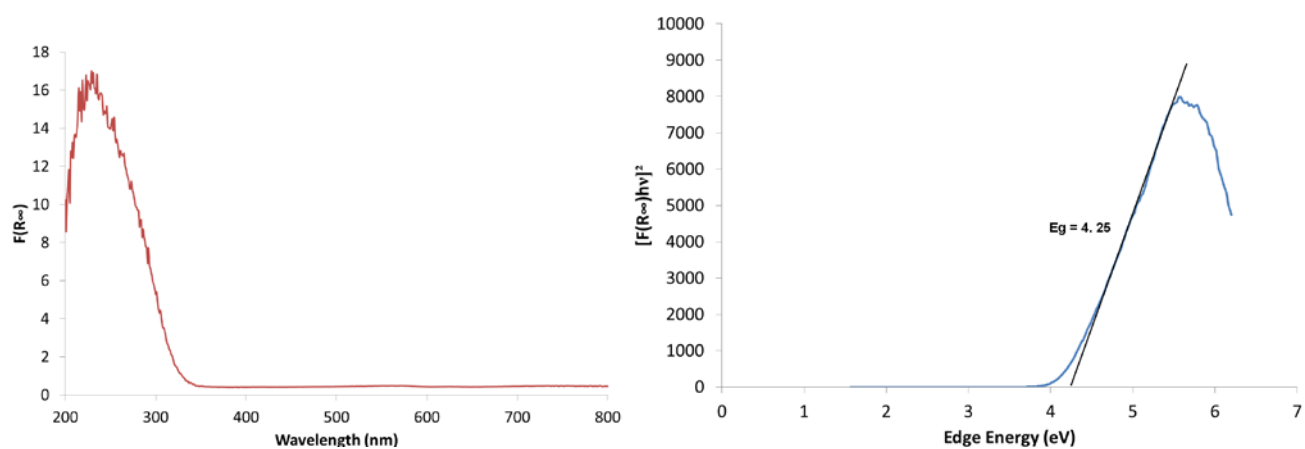
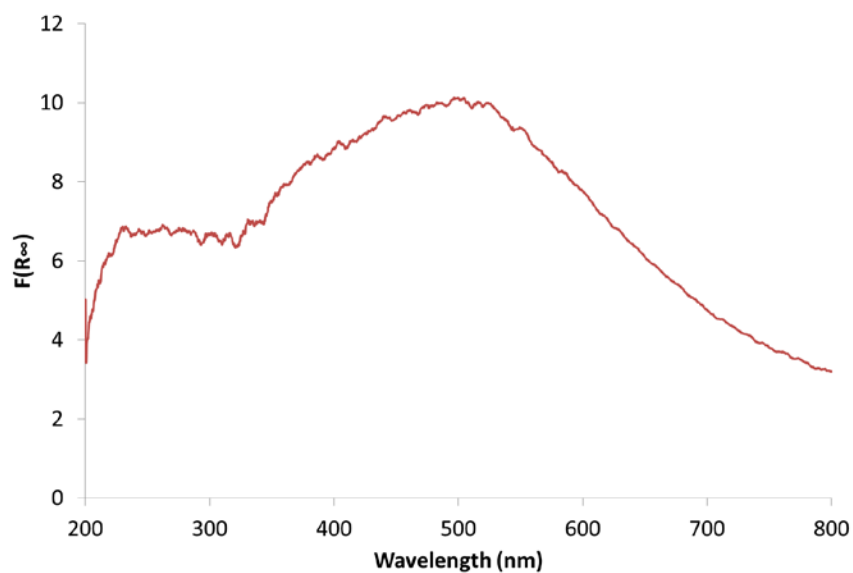
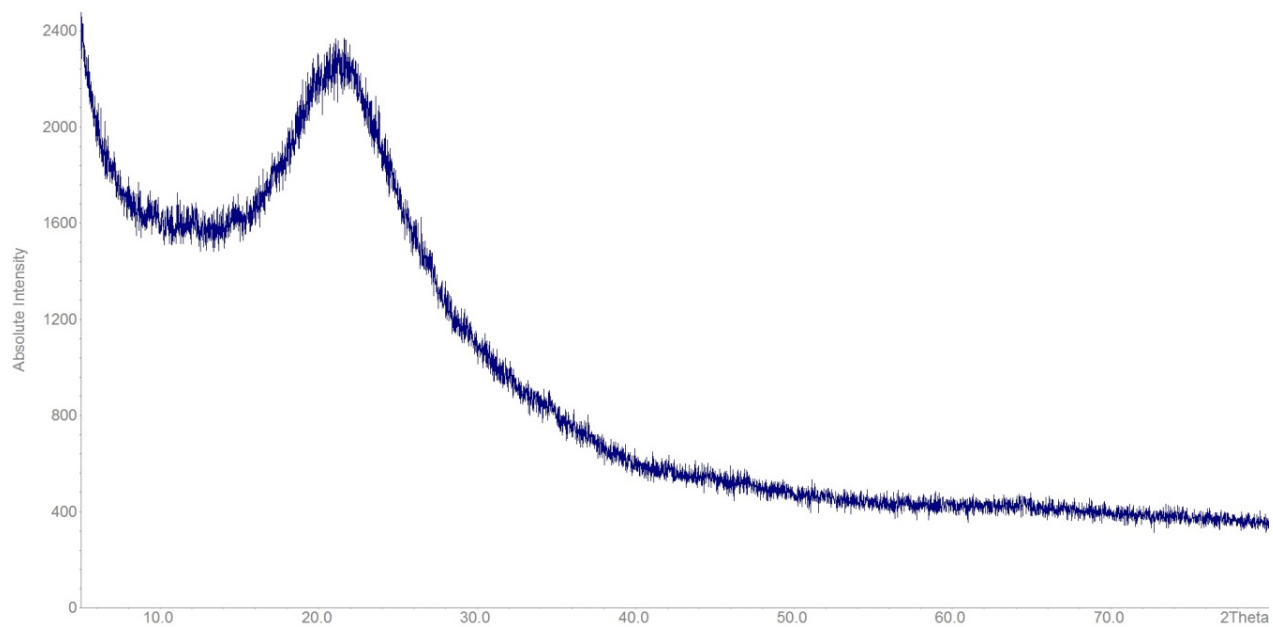


Fig. S18: UV-vis DRS spectrum of **1-(Red)₂**



G) Powder XRD

Fig. S19: Powder XRD pattern of **1**.



H) XAS

XAS characterisation of **1**

Fig. S20: Fit of **1** in k-space (top plot) and R-space (bottom plot).

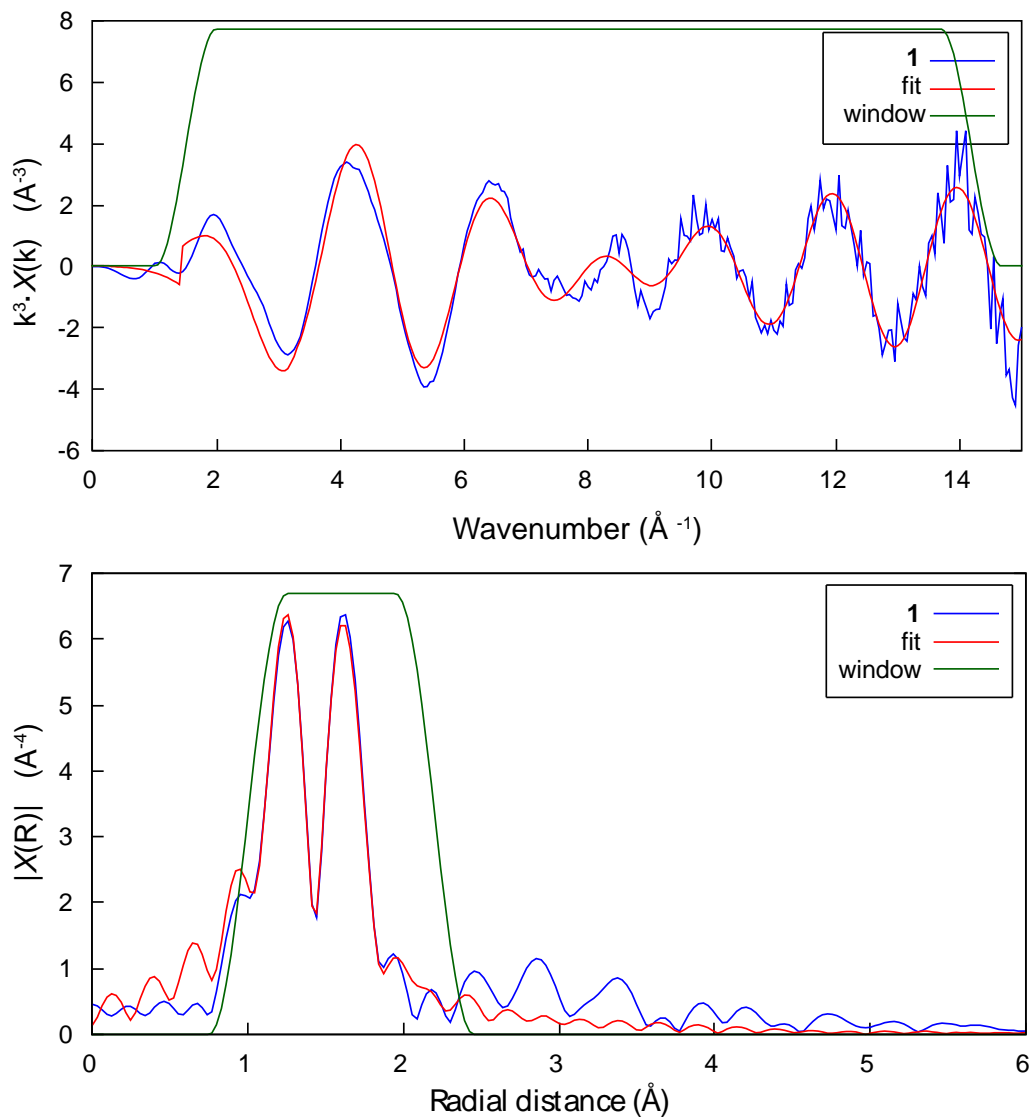


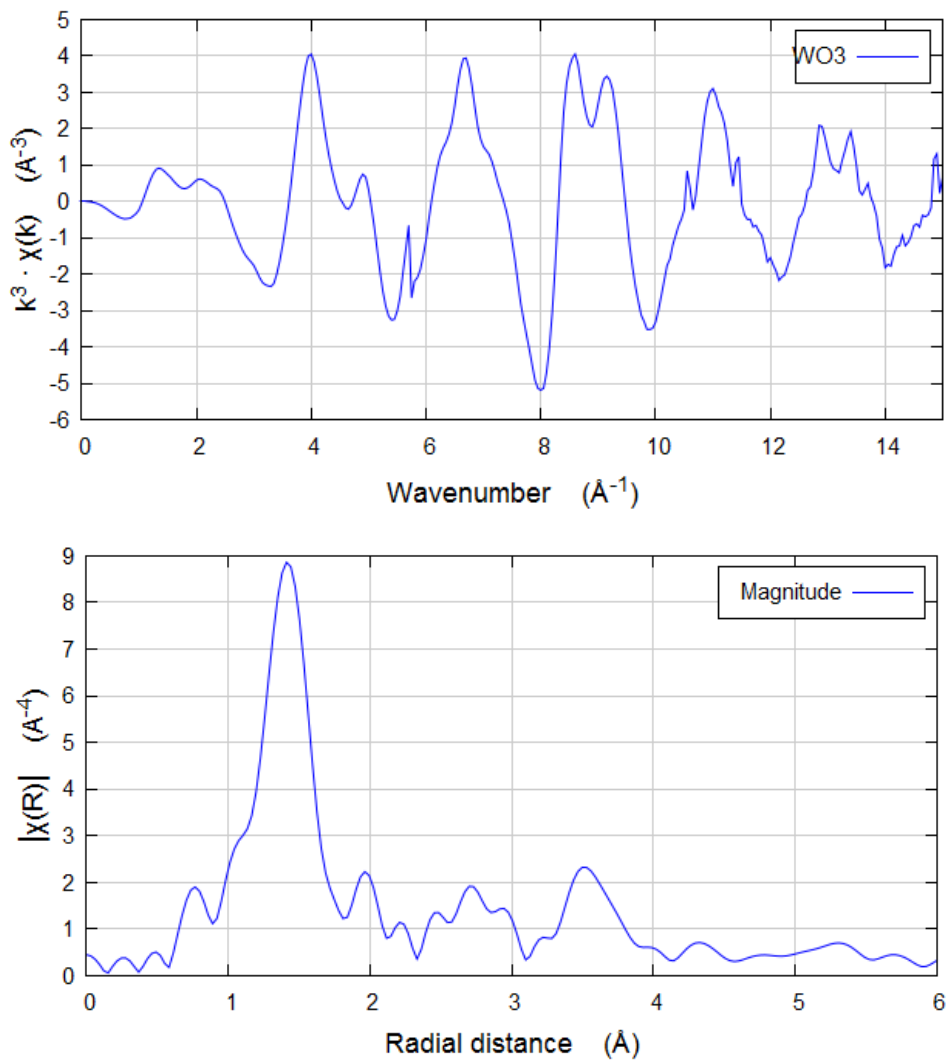
Table S7: Scattering paths for **1.**

Scatterer	N	S02	σ^2 (Å ²)	ΔE_0 (eV)	Delr	Reff (Å)	R (Å)
O (W=O)	1.52 +/- 0.09	0.94*	0.00153*	7.598	-0.013 +/- 0.002	1.71730	1.704 +/- 0.002
O (W—O)	2.9 +/- 0.1	0.94*	0.00355*	7.598	-0.034 +/- 0.002	1.92630	1.892 +/- 0.002

*Values fixed in the fit.

XAS characterisation of WO_3

Fig. S21: L_{III} -edge EXAFS k-space (top plot) and R-space (bottom plot) of WO_3 .



XANES whteline energy**Table S8:** XANES whteline energy of reference samples and **1**, before and after reduction with various amount Me₄-BTDP.

Sample	Whiteline energy (eV)	Reference (synthesis)
1	10210,93	This paper
1-(Red)_{0,5}	10209,61	This paper
1-(Red)₁	10209,15	This paper
1-(Red)₂	10209,13	This paper
1-(Red)₃	10209,13	This paper
[WO(OSi(OtBu)₃)₄]	10210.97	6
[WO₂(OSi(OtBu)₃)₂(DME)]	10210.87	This paper
[(≡SiO)WO₂(OSi(OtBu)₃)]	10210.90	This paper
W(OEt)₅/SiO₂	10209.53	7

EXAFS of the reduced species

Fig. S22: Fit of 1-(Red)₂ in k-space (top plot) and R-space (bottom plot).

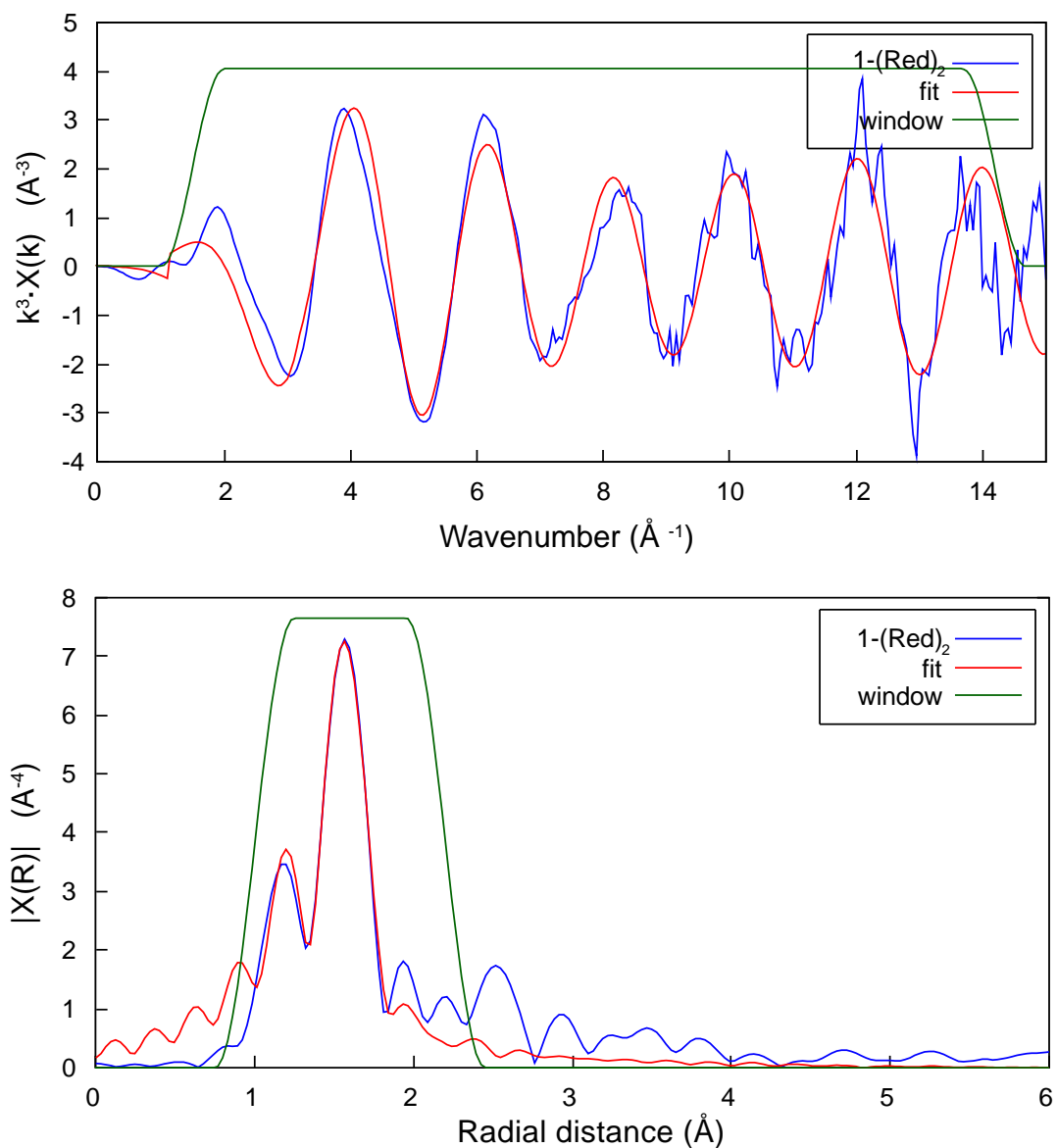


Table S9: Scattering paths for 1-(Red)₂.

Scatterer	N	S02	σ^2 (\AA^2)	ΔE_0 (eV)	Delr	Reff (\AA)	R (\AA)
O (W=O)	0.8 +/- 0.2	0.94*	0.00153*	4.708	-0.021 +/- 0.009	1.71730	1.696 +/- 0.009
O (W—O)	3.1 +/- 0.2	0.94*	0.00355*	4.708	-0.029 +/- 0.008	1.92630	1.898 +/- 0.008

*Values fixed in the fit.

XANES spectra

Fig. S23: W L₃ XANES spectra of **1** (blue line), [WO(OSi(OtBu)₃)₃]₄ (red line) and [WO₂(OSi(OtBu)₃)₂(DME)] (green line) reference materials

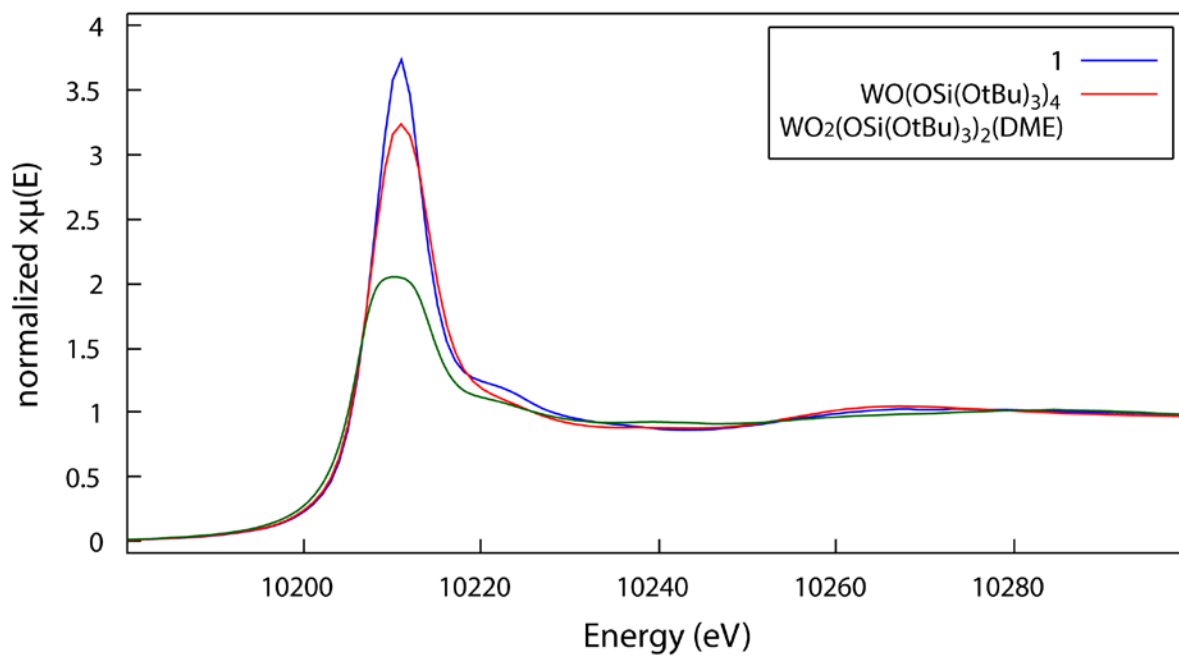
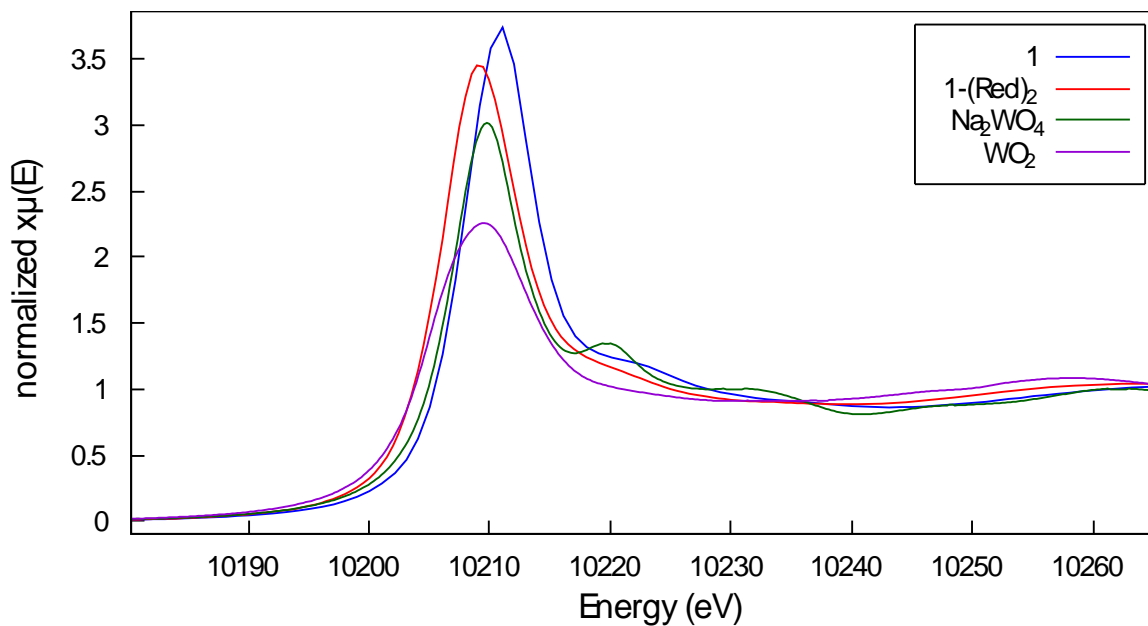


Fig. S24: W L₃ XANES spectra of **1** (blue line), **1-(Red)₂** (red line), Na₂WO₄ (green line), and WO₂ (purple line) reference materials



I) EPR spectroscopy

All measurements were conducted at X band (9.5-GHz electron paramagnetic resonance (EPR) frequency) at 110 K. Attenuation was varied between 14-20 dB such that no saturation was observed.

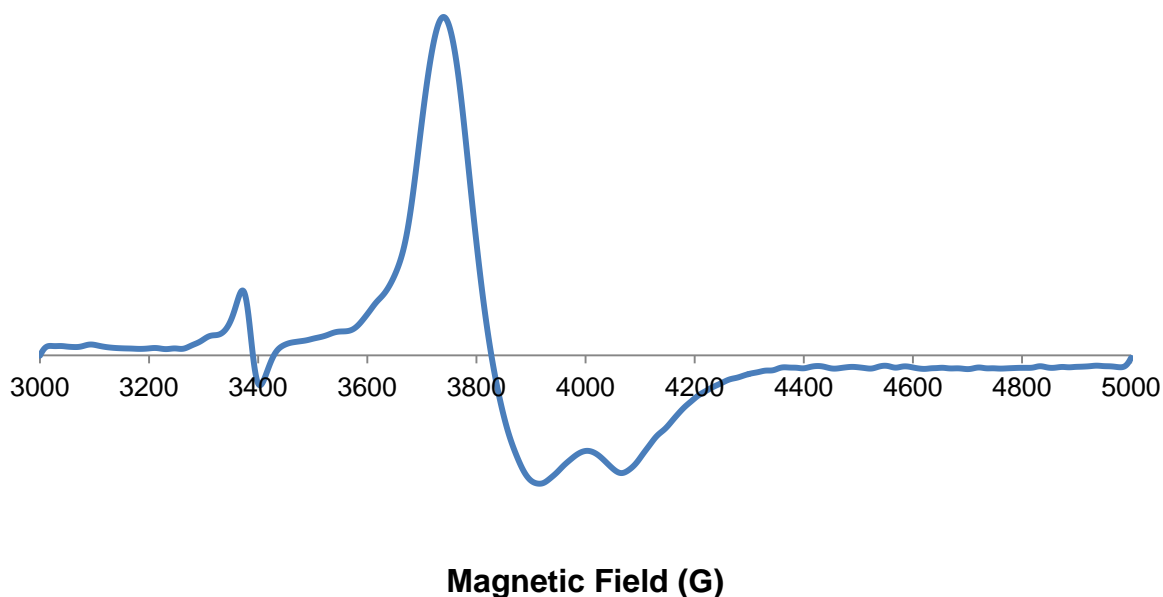
EPR of **1-(Red)₂**

Spin counting

12.1 mg of the material **1-(Red)₂** was introduced in a Suprasil Quartz EPR tube fitted with a J. Young valve under argon. This amount was chosen to ensure that the total sample height is about 1 cm. The amount of W(V) in the material was determined by double integration of the continuous wave EPR spectrum between 3451 and 4282 Gauss and referencing to a calibration curve of obtained using the W(V) standard $\text{WOCl}_3(\text{bpy})$ (concentration range used for the calibration curve between 0.72 and 4.32 mM, in acetonitrile/ 2-methyltetrahydrofuran = 4:1). Additional correction of the difference in the incident microwave power was taken into account. Using this method, 0.33 μmol of W(V) centers were determined to be present in the sample, indicating the presence of ca 15% of W(V) sites among all W centers in **1-(Red)₂** (determined by elemental analysis).

This value was found constant among 2 measurements with different samples of **1-(Red)₂**.

Fig. S25: EPR spectra of **1-(Red)₂**



EPR of 1-(Red)₂ before and after exposure to 10 equiv. of *cis*-4-nonene

12.1 mg of 1-(Red)₂ was loaded into a Suprasil quartz EPR tube fitted with a J. Young valve. EPR spectrum was initially measured, followed by the addition of 22 μ L of a 0.97 M solution of *cis*-4-nonene in toluene. The reaction mixture was heated at 70 °C for 6 h. The volatiles were removed under vacuum after reaction and EPR spectrum was measured again in same conditions (See Fig. S26).

Fig. S26: EPR spectra of 1-(Red)₂ before and after exposure to 10 equiv. of *cis*-4-nonene (Procedure described above) Note: Similar small sharp peak with g value 2.01 was reported to be O₂⁻ radical in the WO₃/Al₂O₃ system)

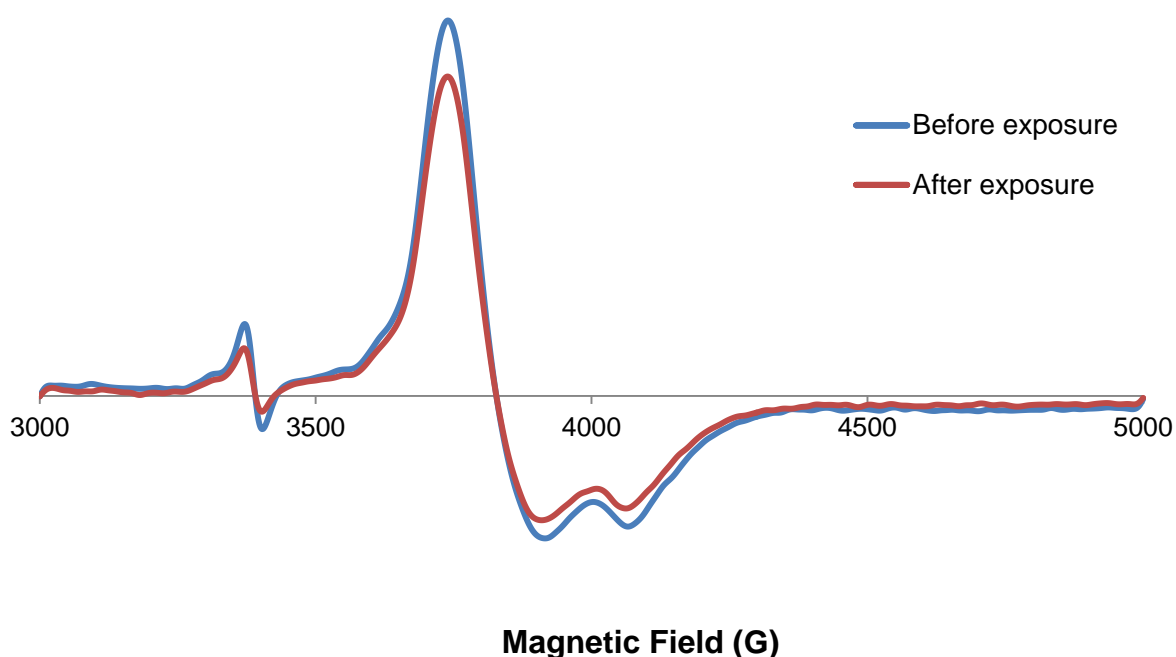


Table S10: g-values of the material before and after exposure to 10 equiv. of *cis*-4-nonene.

	g1	g2	g3
Before exposure	2.014	1.777	1.674
After exposure	2.012	1.777	1.681

J) Titration of surface OH sites:

In an Ar filled glovebox, 30 mg of the supported catalyst were weighed into a Schlenk tube. A stock solution containing both ferrocene (internal standard, 0.075 mmol, 14 mg) and benzyl magnesium bromide (190 μ l, 0.19 mmol, 1 M solution in Et₂O) in 3 ml of d₆-benzene was prepared. 1 mL of this stock solution (0.063 mmol PhCH₂MgBr) was added dropwise into the Schlenk tube containing the catalyst. The reaction mixture was stirred at 200 rpm for 2 h at room temperature. After transferring the supernatant to a J. Young NMR tube, the amount of toluene formed was evaluated by ¹H NMR (d1=30 s). The results are shown in **Table S11**.

Table S11: OH content of 1 and 1-(Red)₂.

Catalyst	Amount of OH sites (mmol/g)	No. of OH site per W (OH/W)
1	0.4	2.33
1-(Red)₂	0.15	0.94

K) Redox titration of surface W sites

A solution of ferrocenium hexafluorophosphate (2.3 mg, 0.0063 mmol, 2.5 equiv) in d_8 -THF (0.5 mL) was added at room temperature to 13 mg of **1-(Red)₂** and the reaction mixture was stirred at 70 °C for 12 h. The filtrate was then separated and analyzed by ¹H NMR using DME (10 μl, 0.080 mmol) as internal standard for quantification. Results of the titration are given in **Table S12**.

Table S12: Amount of different products observed by ¹H-NMR after reaction of 1-(Red)₂ with FcPF₆.

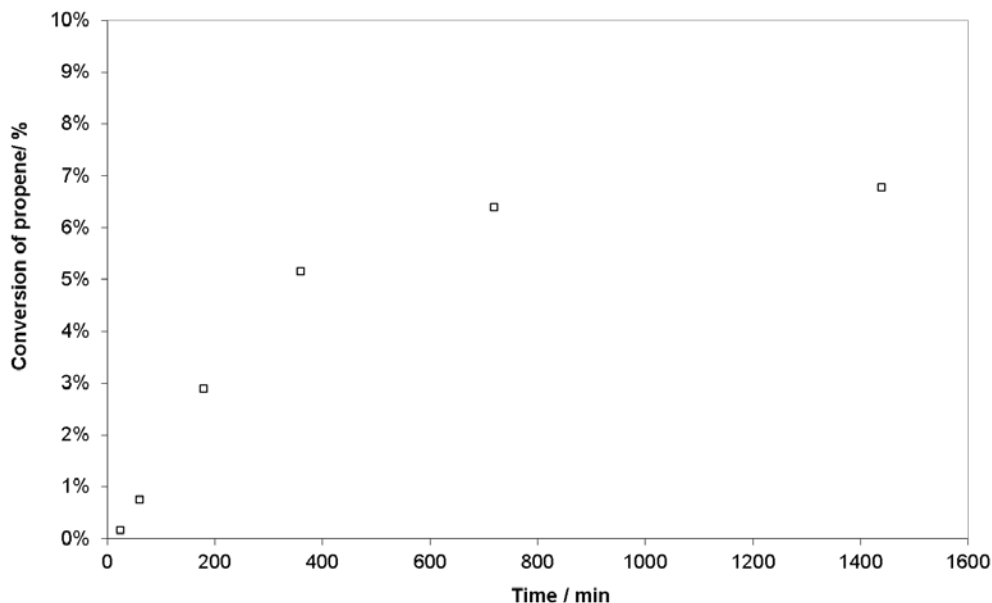
Products observed	Amount (equiv/ W)
Ferrocene	1.66
Tetramethylpyrazine	0.1
TMS moieties	0.8

L) Catalytic activity

Propene metathesis with **1** at 500 °C

Catalyst **1** (10 mg, 1.9 μmol) was loaded in a 400 mL reactor flask at 25 °C. The reactor was evacuated under high vacuum (10^{-5} mbar), and warmed to 500 °C (10 °C/min). Propene (305 mbar, 1.9 mmol, 1000 equiv.) was added. 250 μL aliquots were analysed by GC over time to follow the conversion and the product selectivities.

Fig. S27: Conversion vs time, propene metathesis, 0.1 mol% W, 500 °C for **1**



Metathesis of *cis*-4-nonene in presence of 2 equiv. of Me₄-BTDP.

At $t=0$ a 0.97 M solution of *cis*-4-nonene in toluene containing heptane as internal standard (0.11 M) and 2 equiv. of Me₄-BTDP (with respect to W centers) was added to the catalyst introduced in a conical base vial containing a wing shaped magnetic stirring bar. The reaction mixture was stirred at 600 rpm and kept at 70 °C using an aluminum heating block. 5 μL aliquots of the solution were sampled, diluted with pure toluene (100 μL) and quenched by the addition of 1 μL of wet ethyl acetate. The resulting solution was analyzed by GC/FID (Agilent Technologies 7890 A) equipped with an HP-5 (Agilent Technologies) column. Conversion is shown by eq.1. Equilibrium conversion is reached at ca. 50%.

$$\text{Product conversion}_t = \frac{\Sigma[\text{products}]_t}{[\text{substrate}]_{\text{ini}}} \quad (1)$$

Molecular precursors

Catalytic activity of toluene solution of molecular precursors in presence of 2 equiv. of Me₄-BTDP was investigated. For all these precursors, no activity was observed in the absence of reductant. Conversion, TON and TOF at 70 °C are given in **Table S13**.

Table S13: Catalytic activity of the molecular precursors (*cis*-4-nonene, 1 mol% W, 2 mol% Me₄-BTDP, 70 °C).

Catalyst (0.1 mol % W)	TOF _{3min} (min ⁻¹)	TOF _{max} (min ⁻¹) ^a	Conversion at 24 h
WO(OSi(OtBu) ₃) ₄	<0.1	<0.1	< 1 %
WO ₂ (OSi(OtBu) ₃) ₂ (DME)	<0.1	<0.1	< 1 %

^a Maximum TOF determined during the test.

Heterogeneous catalysts

Catalytic activity of heterogeneous precursors in presence of 2 equiv. of Me₄-BTDP was investigated. For all these precursors, no activity was observed in absence of reductant. Conversion, TON and TOF at 70 °C are given in **Table S14**.

Table S14: Catalytic activity of the heterogeneous catalysts (*cis*-4-nonene, 1 mol% W, 2 mol% Me₄-BTDP, 70 °C).

Catalyst (0.1 mol % W)	TOF _{3min} (min ⁻¹)	TOF _{max} (min ⁻¹) ^a	Time conversion	to
[(≡SiO)W(O)(OSi(OtBu) ₃) ₃]	<0.1	<0.1	< 1 % after 24h	
[(≡SiO)W(O) ₂ (OSi(OtBu) ₃) ₃]	<0.1	<0.1	< 1 % after 24h	
1	3	8 (10 min)	3 h	
WO ₃ /SiO ₂	1	2 (320 min)	24 h	
MoO ₃ /SiO ₂	0.5	0.6 (60 min)	24 h	

^a Maximum TOF determined during the test.

Metathesis of *cis*-4-nonene by pre-reduced materials 1-(Red)x

At t=0 a 0.97 M solution of *cis*-4-nonene in toluene containing heptane as internal standard (0.11 M) was added to the catalysts introduced in a conical base vial containing a wing shaped magnetic stirring bar. The reaction mixture was stirred at 600 rpm and kept at 70 °C using an aluminum heating block. 5 μL aliquots of the solution were sampled, diluted with pure toluene (100 μL) and quenched by the addition of 1 μL of wet ethyl acetate. The resulting solution was analyzed by GC/FID (Agilent Technologies 7890 A) equipped with an HP-5 (Agilent Technologies) column. Conversion, TON and TOF are given in **Table S15**.

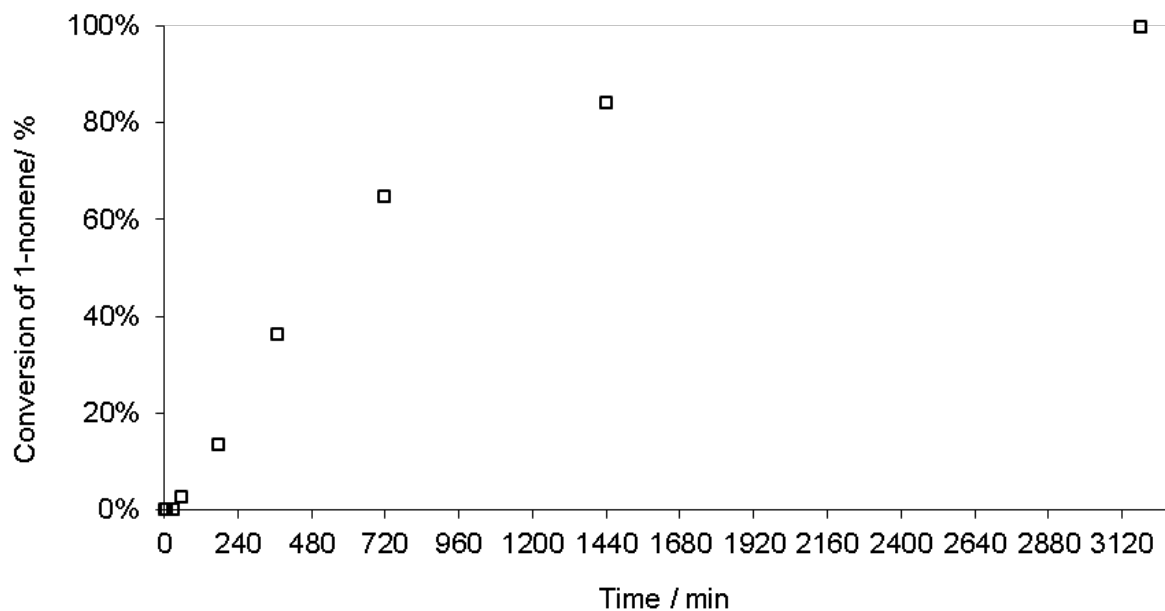
Table S15: Catalytic activity of the heterogeneous catalysts (*cis*-4-nonene, 1 mol% W, 70 °C).

Catalyst (0.1 mol % W)	TOF _{3min} (min ⁻¹)	TOF _{max} (min ⁻¹) ^a	Time to final conversion
1-(Red) _{0.5}	5	8 (10 min)	3 h
1-(Red) ₁	2	3 (10 min)	6 h
1-(Red) ₂	<1	2 (540 min)	12 h

^a Maximum TOF determined during the test. Values in bracket the time for which maximum TOF was observed.

Metathesis of 1-nonene by 1 in presence of 2 equiv. of Me₄-BTDP.

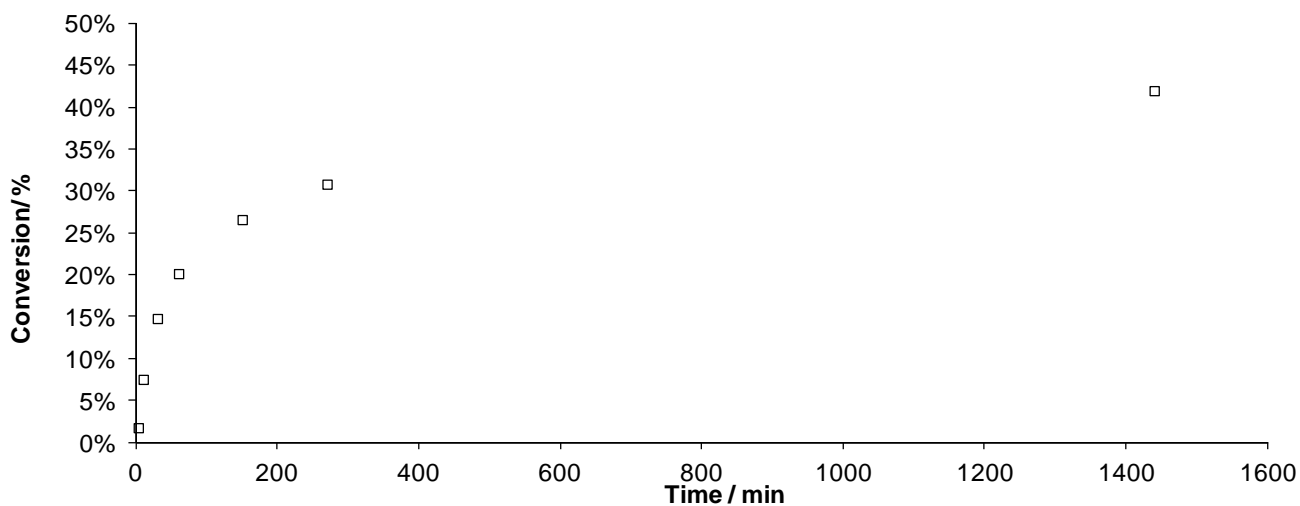
At t=0 a 0.79 M solution of 1-nonene in toluene containing heptane as internal standard (0.08 M) and 2 equiv. of Me₄-BTDP (with respect to W centers) was added to the catalyst introduced in a conical base vial containing a wing shaped magnetic stirring bar. The reaction mixture was stirred at 600 rpm and kept at 70 °C using an aluminum heating block. 5 μL aliquots of the solution were sampled (by opening the vial), diluted with pure toluene (100 μL) and quenched by the addition of 1 μL of wet ethyl acetate. The resulting solution was analyzed by GC/FID (Agilent Technologies 7890 A) equipped with an HP-5 (Agilent Technologies) column.

Fig. S28: Conversion vs time, 1-nonene homometathesis, 1 mol% W, 2 mol% Me₄-BTDP, 70 °C.

Metathesis of ethyl oleate by 1 in presence of 2 equiv. of Me₄-BTDP.

At t=0, a 0.53 M solution of ethyl oleate in toluene containing octadecane as internal standard (0.10 M) and 2 equiv. of Me₄-BTDP (with respect to W centers) was added to the catalyst introduced in a conical base vial containing a wing shaped magnetic stirring bar. The reaction mixture was stirred at 600 rpm and kept at 70 °C using an aluminum heating block. 5 μL aliquots of the solution were sampled (by opening the vial), diluted with pure toluene (100 μL) and quenched by the addition of 1 μL of wet ethyl acetate. The resulting solution was analyzed by GC/FID (Agilent Technologies 7890 A) equipped with an HP-88 (Agilent Technologies) column. Conversion is shown by eq.1. Equilibrium conversion is reached at ca. 50%.

Fig. S29: Conversion vs time, ethyl oleate homometathesis, 1 mol% W, 2 mol% Me₄-BTDP, 70 °C.



Propene metathesis with WO₃/SiO₂ at 100 °C

100 mg (38 μmol) of the selected catalyst (WO₃/SiO₂ or WO₃/SiO₂ reduced with 1 equiv. of Me₄-BTDP) mixed with 2.5 g SiC was loaded into the flow reactor in the glove box. The reactor was then connected to a PID Microactivity reactor, and the connections were flushed with argon:propene 2:1 mixture (in volume) for 2 h. The flow rate of the argon:propene 2:1 mixture was then set to 6 mL·min⁻¹, 1.5 bar (3.24 mol propene/ mol W/min⁻¹) and the temperature was set to 100 °C. The opening of the valve connecting the reactor to the gas line corresponds to the beginning of the catalytic test. The reaction was monitored by GC using an auto-sampler. Conversion and TONs are presented in Fig. S30 and in Fig. S31 respectively.

Fig. S30: Conversion of propene by 7.1 %_{wt} WO₃/SiO₂ (Red squares) and WO₃/SiO₂ reduced* (blue diamonds) at 100 °C in flow conditions (see details above). * ie. after reduction with one equiv. of Me₄-BTDP.

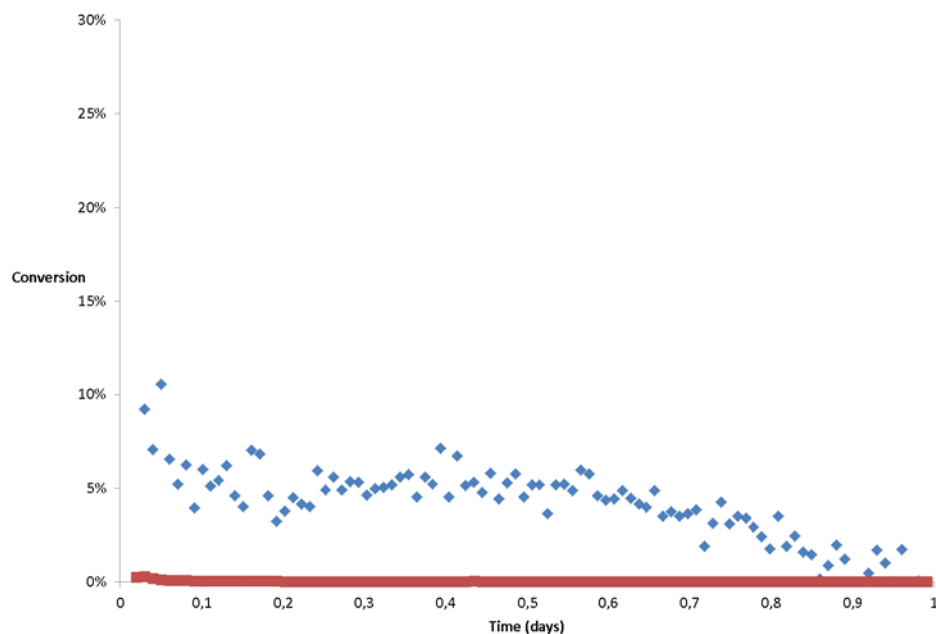
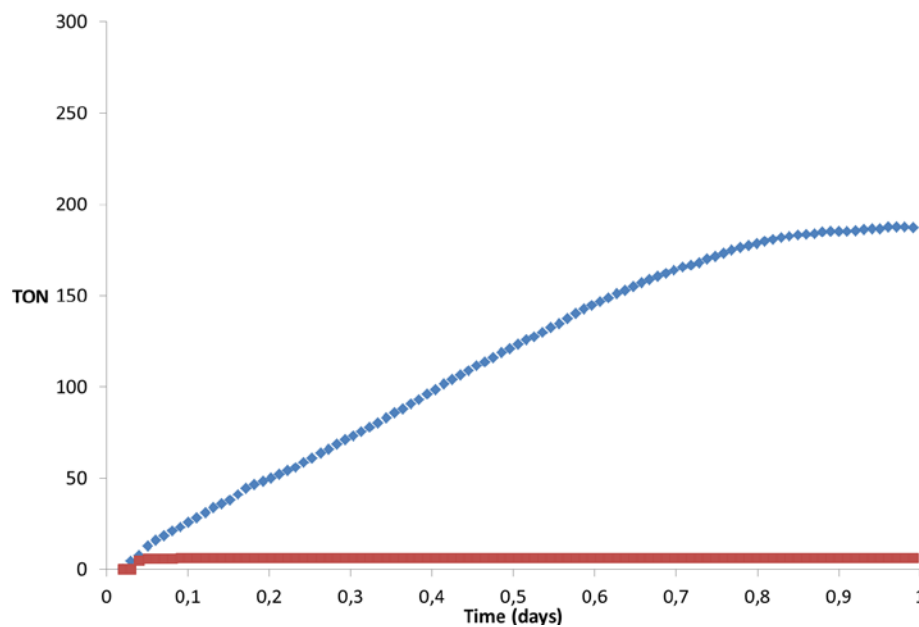


Fig. S31: TONs of propene metathesis by 7.1 %_{wt} WO₃/SiO₂ (Red squares) and WO₃/SiO₂ reduced* (blue diamonds) at 100 °C in flow conditions (see details above). * ie. after reduction with one equiv. of Me₄-BTDP.



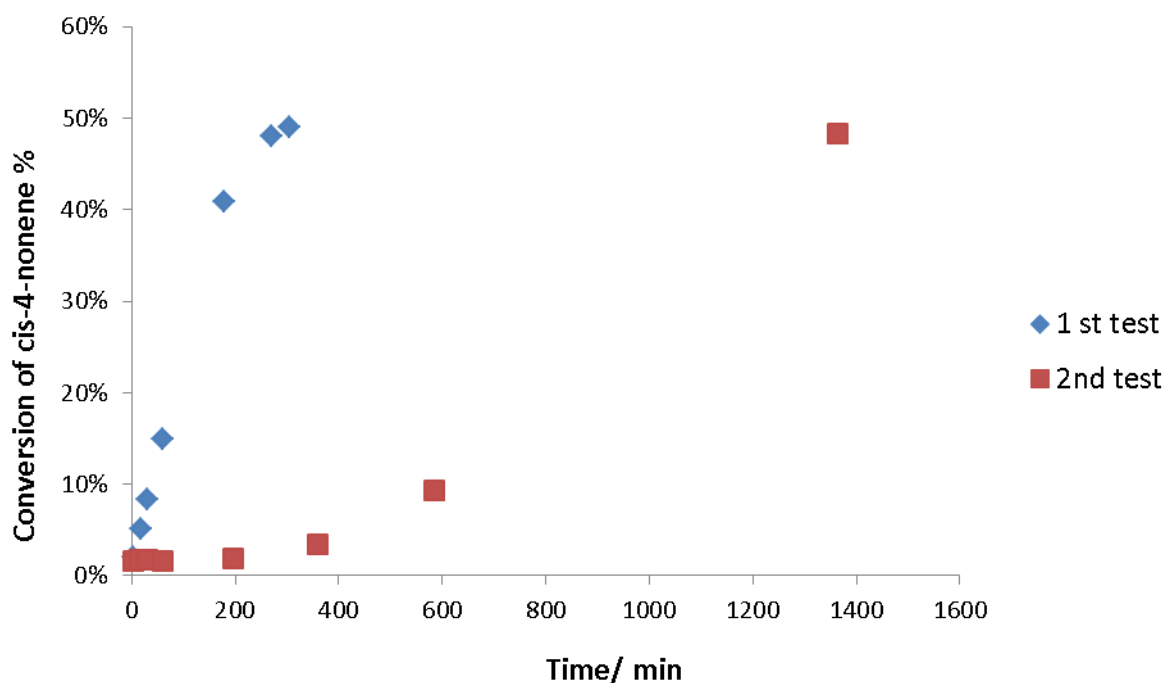
M) Recycling and poisoning studies

Recycling

Experimental procedure for recycling test: second addition of pure *cis*-4-nonene

At $t=0$ a 0.97 M solution of *cis*-4-nonene (1000 equiv.) in toluene containing heptane as internal standard (0.11 M) and 2 equiv. of $\text{Me}_4\text{-BTDP}$ (with respect to W centers) was added to the catalyst introduced in a conical base vial containing a wing shaped magnetic stirring bar. The reaction mixture was stirred at 600 rpm and kept at 70 °C using an aluminum heating block. 5 μL aliquots of the solution were sampled, diluted with pure toluene (100 μL) and quenched by the addition of 1 μL of wet ethyl acetate. The resulting solution was analyzed by GC/FID (Agilent Technologies 7890 A) equipped with an HP-5 (Agilent Technologies) column. After reaching equilibrium conversion, the liquid phase of the reaction mixture was removed, and a fresh aliquot of *cis*-4-nonene (1000 equiv.) was added to the catalyst, following catalytic activity as described before.

Fig. S32: Conversion vs time, *cis*-4-nonene homometathesis, 70 °C, 1000 equiv. of *cis*-4-nonene, 2 equiv. of $\text{Me}_4\text{-BTDP}$ (Blue diamonds) and after removal of solution and addition of a fresh aliquot of 1000 equiv. of *cis*-4-nonene in absence of $\text{Me}_4\text{-BTDP}$ (red squares, see procedure above for details).

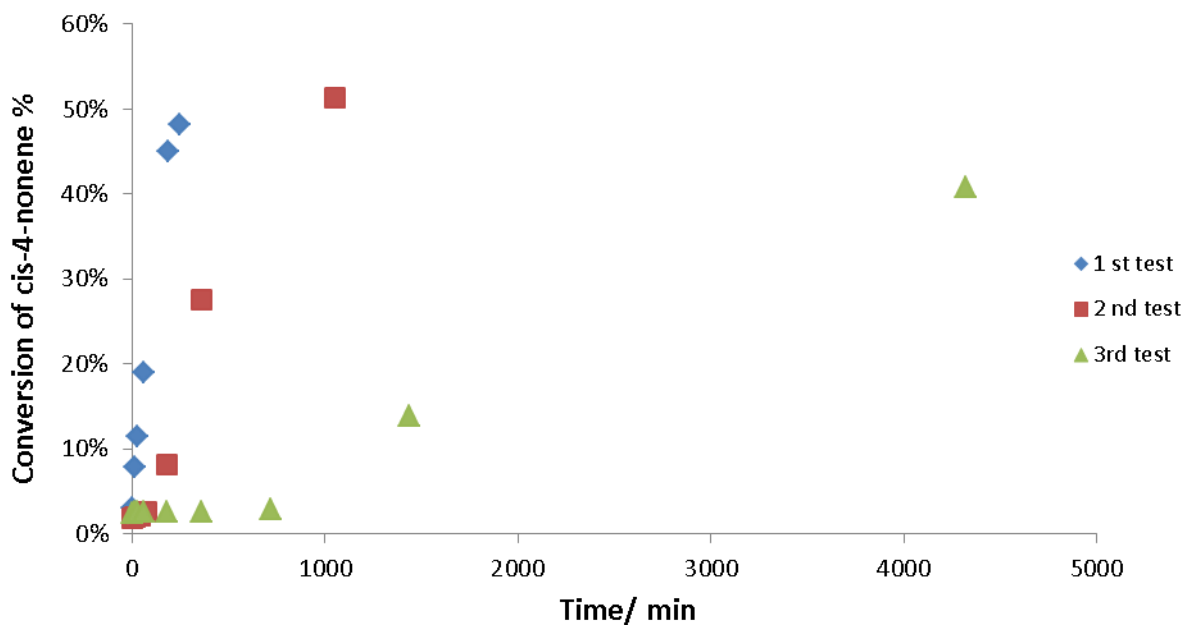


Experimental procedure for recycling test: recycling in presence of $\text{Me}_4\text{-BTDP}$

At $t=0$ a 0.97 M solution of *cis*-4-nonene (1000 equiv.) in toluene containing heptane as internal standard (0.11 M) and 2 equiv. of $\text{Me}_4\text{-BTDP}$ (with respect to W centers) was added to the catalyst introduced in a conical base vial containing a wing shaped magnetic stirring bar. The reaction mixture

was stirred at 600 rpm and kept at 70 °C using an aluminum heating block. 5 μL aliquots of the solution were sampled, diluted with pure toluene (100 μL) and quenched by the addition of 1 μL of wet ethyl acetate. The resulting solution was analyzed by GC/FID (Agilent Technologies 7890 A) equipped with an HP-5 (Agilent Technologies) column. After reaching equilibrium conversion, the liquid phase of the reaction mixture was removed, and a fresh aliquot of *cis*-4-nonene (1000 equiv.) and $\text{Me}_4\text{-BTDP}$ (1 equiv.) was added to the catalyst for the 2nd and 3rd test, following catalytic activity as before.

Fig. S33: Conversion vs time, *cis*-4-nonene homometathesis, 70 °C, 1000 equiv. of *cis*-4-nonene, 2 equiv. of $\text{Me}_4\text{-BTDP}$ (Blue diamonds) and after removal of solution and addition of a fresh aliquot of 1000 equiv. of *cis*-4-nonene and 1 equiv. of $\text{Me}_4\text{-BTDP}$ (red squares. Conversion for the same process repeated a second time is given in green triangles (see procedure above for details). The 2nd test has similar induction period than $[\text{WO}_2(\text{Red})_2]$.



Poisoning and reactivation

General procedure:

A 0.97 M solution of *cis*-4-nonene (1000 equiv.) in toluene containing heptane as internal standard (0.11 M) was added to the catalysts introduced in a conical base vial containing a wing shaped magnetic stirring bar. The reaction mixture was stirred at 600 rpm and kept at 70 °C using an aluminum heating block for 1.5 h. Catalytic activity of the material was ensured by following activity by GC (5 μ L aliquots, procedure described above). The catalyst was then contacted with H₂O (1 equiv., in toluene), O₂ (excess) or EtOH (1 equiv., in toluene) and stirred for 1.5 h. No further conversion was observed with respect to the conversion measured at the introduction of the H₂O, O₂ or EtOH respectively. The solution was then removed by filtration and a new batch of *cis*-4-nonene solution (1000 equiv.) was added. No catalytic activity at 24 h was observed in all cases confirming the complete deactivation of the catalyst after poisoning. At t=0, 2 equivalents of Me₄-BTDP (with respect to W centers) were added to the reaction mixture. Conversion vs. time after H₂O, O₂ and EtOH poisoning and addition of 2 equiv. of Me₄-BTDP are shown in Fig. S34, Fig. S35 and Fig. S36 respectively.

Fig. S34: Conversion vs time, *cis*-4-nonene (1000 equiv.) homometathesis at 70 °C after reactivation by additional 2 equiv. of Me₄-BTDP after H₂O poisoning

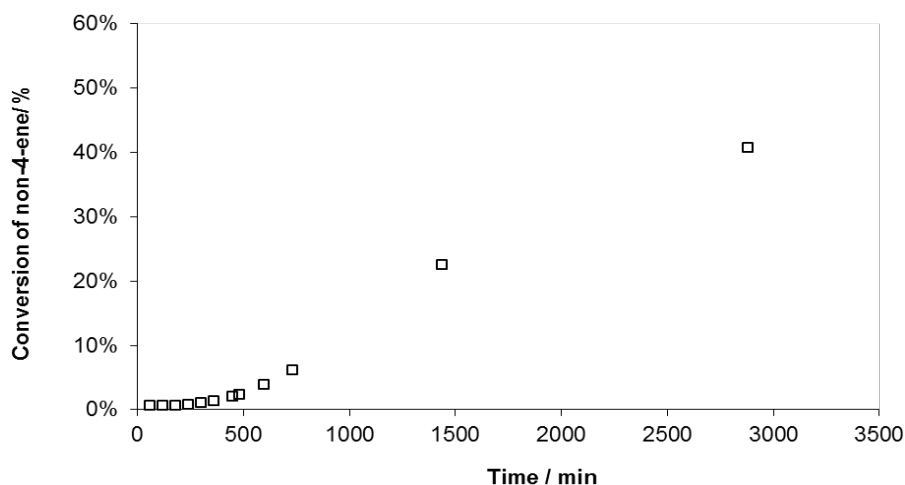


Fig. S35: Conversion vs time, *cis*-4-nonene (1000 equiv) homometathesis at 70 °C after reactivation by additional 2 equiv. of Me₄-BTDP after O₂ poisoning

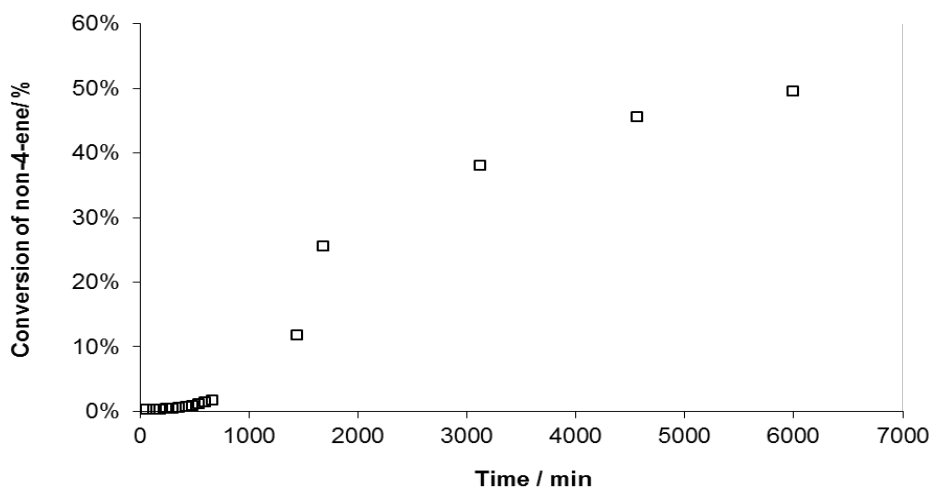
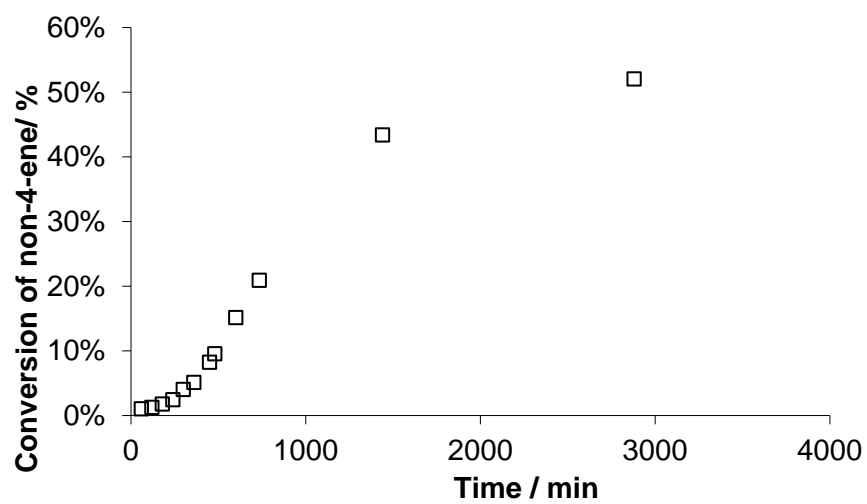
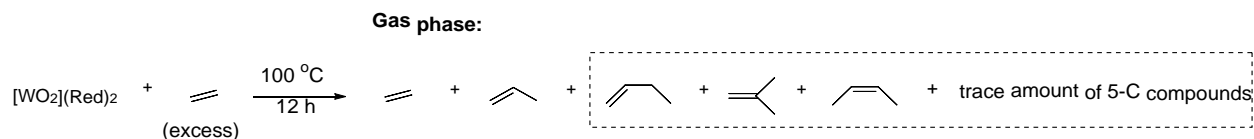


Fig. S36: Conversion vs time, *cis*-4-nonene (1000 equiv) homometathesis at 70 °C after reactivation by additional 2 equiv. of Me₄-BTDP after EtOH poisoning



N) Characterization of the active sites and mechanism

1) Exposure of 1-(Red)₂ to ethylene



1-(Red)₂ (62.1 mg) was loaded in a 26 mL glass reactor and contacted with ethylene (9.4 equiv. per W metal center). After 12 h at 100 °C, the gas phase was analyzed by GC-FID and GC-MS showing the presence of unreacted ethylene, propylene (0.5 equiv.) and a mixture of four-carbon containing hydrocarbons (1-butene, *cis*-2-butene, *trans*-2-butene and *iso*-butene; in total 0.03 equiv.).

Good reproducibility in the amount of propylene released was confirmed while reproducing twice this experiment on different samples of **1-(Red)₂**.

Table S16: Analysis of the gas phase after exposing reduced **1-(Red)₂** to ethylene (12 h, 100 °C).

ethylene added (equiv.)	propene released (equiv.)	C4 products released (equiv.)
9.4	0.50	0.03

2) Exposure of 1-(Red)₂ to ¹³C dilabeled ethylene

1-(Red)₂ (36 mg) was loaded in a 26 mL glass reactor and contacted with ¹³C dilabeled ethylene (32 equiv. per W metal center). After 12 h at 100 °C, the gas phase was evacuated under high vacuum (10⁻⁵ mbar, 1 h). ¹H, ¹³C solid state NMR and HETCOR spectrum of this material are given in Fig. S12, Fig. S13 and Fig. S14, respectively.

3) Br₂ exposure

1-(Red)₂ was first exposed to ethylene with the procedure described in experiment N)1). The sample was then evacuated under high vacuum (10⁻⁵ mbar) for 1 h followed by the addition of a bromine solution (4 equiv., 0.19 M) in dibromomethane at -78 °C. The reaction mixture was stirred at room temperature for 2 h and quenched with a concentrated sodium thiosulphate solution. The organic layer was extracted by ethyl acetate (1 mL x 3) and dried over anhydrous magnesium sulfate. The organic layer was then analyzed by GC-MS showing the presence of 1,4-dibromobutane.

Fig. S37: GC-MS chromatogram of the reaction mixture after Br₂ exposure (procedure described above).

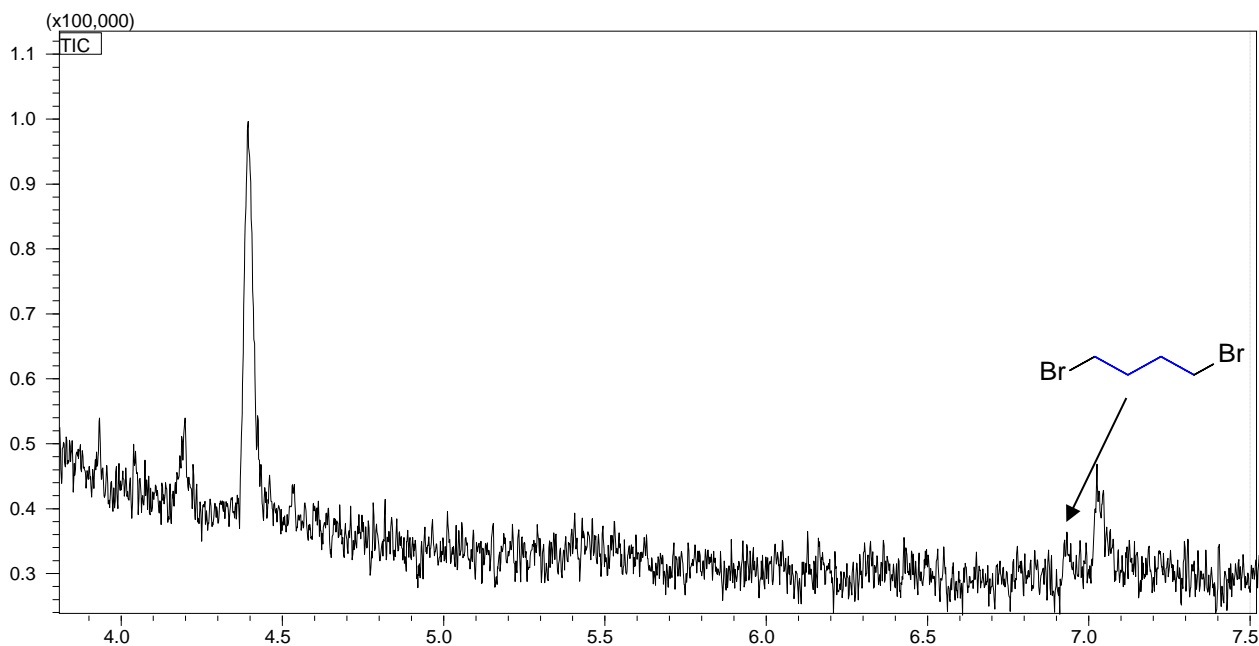


Fig. S38: Experimental MS spectrum of 1,4-dibromobutane (peak from 6.9 to 7 min retention time).

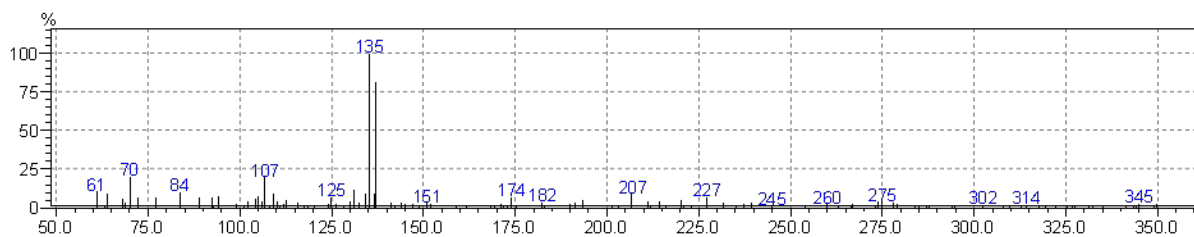
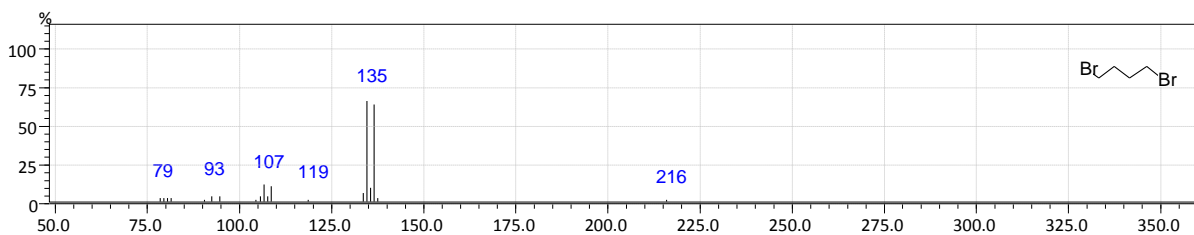


Fig. S39: Reference MS spectrum of 1,4-dibromobutane from NIST database



4) Isotopic exchange

The sample collected in experiment N)1) was evacuated under high vacuum (10^{-5} mbar) for 1 h and was then contacted with ¹³C dilabelled ethylene (6.9 equiv.). After 12 h at 100 °C, the gas phase was analyzed by GC-FID and GC-MS showing the presence of unreacted dilabeled

ethylene, but also of mono- (0.6 equiv.) and non-labelled (0.15 equiv.) ethylene. No C3, C4 or C5 products were observed in the gas phase.

The amount of mono-labelled ethylene determined in this titration and the amount of propylene formed in the initiation step (experiment N)1)) are ca. 1:1.

O) References

1. Ross-Medgaarden, E. I.; Wachs, I. E., Structural Determination of Bulk and Surface Tungsten Oxides with UV-vis Diffuse Reflectance Spectroscopy and Raman Spectroscopy. *J. Phys. Chem C* **2007**, *111*, 15089-15099.
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