

Supporting Information

Silica-Supported Isolated Molybdenum Di-oxo Species: Formation and Activation with Organosilicon Agent for Olefin Metathesis

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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 synthesis of grafted catalysts, reactions were carried out using glove-box techniques. High vacuum lines (10^{-5} mbar) were used to remove volatiles from the surface of silica materials. 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 according to a literature method.¹ SiO_{2-700} was obtained by calcination at 500°C under air for 4 h and treated under vacuum (10^{-5} mbar) at 500°C for 12 h, and then at 700°C for 20 h and contained 0.31 mmol of OH per gram as measured by titration with $\text{Mg}(\text{CH}_2\text{Ph})_2$.

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 Bruker spectrometer equipped with a 4 mm probe. Cross polarization magic angle spinning (CPMAS) was 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.

UV-Vis spectra of all materials were obtained using a Varian Cary UV-vis spectrophotometer equipped with a Praying Mantis integration sphere. The UV-vis spectra were processed with Microsoft Excel software. The edge energy (Eg) for allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of a plot of $h\nu$ vs $[\text{F}(\text{R}_\infty)h\nu]^2$.

Continuous Wave (CW) EPR spectra were measured at X band (9.5-GHz microwave frequency) on a Bruker EMX spectrometer at 110 K.

XAS measurements were carried out at the Mo K edge at the SuperXAS beamline at SLS (PSI, Villigen, Switzerland). The storage ring was operated at 2.4 GeV in top-up mode with a ring current of around 400 mA. The incident photon beam provided by a 2.9 T super bend magnet source was selected by a Si (311) quick-EXAFS monochromator and the rejection of higher harmonics and focusing were achieved by a rhodium-coated collimating mirror at 2.8 mrad and a rhodium-coated toroidal mirror at 2.5 mrad. The beam size on the sample was $100 \times 100 \mu\text{m}$. During the measurements the monochromator was rotating with 10 Hz frequency in 2 deg angular range and X-ray absorption spectra were collected in transmission mode using ionization chambers specially developed for quick data collection with 1 MHz frequency.² The spectra were collected for 2 minutes and averaged. The beamline energy was calibrated with Mo reference foil to the Mo K-edge position at 20000.0 eV. To avoid contact with air all samples were sealed in a glovebox. Each pellet of samples (with optimized thickness for transmission detection) was placed in two aluminized plastic bags (Polyaniline ($15 \mu\text{m}$), polyethylene ($15 \mu\text{m}$), Al ($12 \mu\text{m}$), polyethylene ($75 \mu\text{m}$) from Gruber-Folien GmbH & Co. KG, Straubing, Germany) using an impulse sealer inside a glovebox; one sealing layer was removed immediately before the measurements. Data were analyzed by standard procedures³ using Ifeffit program package.⁴

Molecular compounds, $\text{MoO}_2\text{Cl}_2(\text{dme})$,⁵ $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$,⁶ and 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (Me_4BTDP)⁷ were synthesized according to literature procedures. MoO_2Cl_2 was purchased from Aldrich and used without purification.

B) Syntheses

Synthesis of $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$

To a solution of $\text{MoO}_2\text{Cl}_2(\text{dme})$ (2.50 g, 8.65 mmol) in toluene (100 mL) and DME (2 mL) cooled to -78°C was added dropwise over 1 h a solution of $\text{Li}[\text{OSi}(\text{OtBu})_3]$ (4.68 g, 17.3 mmol) in toluene (50 mL). The reaction mixture was allowed to warm to room temperature, and then stirred for 3 h. All volatiles were removed under reduced pressure to give a white solid, which was extracted with pentane (4×20 mL). Concentration of solution and cooling to -30°C overnight afforded $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$ as colorless crystals (4.53 g, 6.91 mmol, 80% yield). ^1H NMR (300 MHz, C_6D_6 , rt): δ 1.39 (s, 54H, OCMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , rt): δ 74.0 (s, OCMe_3), 31.6 (s, OCMe_3).

Preparation of **1**: Grafting of $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$ on SiO_{2-700}

A solution of $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$ (853 mg, 1.30 mmol) in $\text{C}_6\text{H}_6/\text{DME}$ (15 mL/1.5 mL) was added to a suspension of SiO_{2-700} (4.00 g, SiOH of 1.24 mmol) in $\text{C}_6\text{H}_6/\text{DME}$ (5 mL/0.5 mL) at room temperature. The resulting suspension was stirred (100 rpm) at room temperature for 16 h. The supernatant was removed and the resulting solid was washed with C_6H_6 (7 mL \times 3). The solid was thoroughly dried under high vacuum (10^{-5} mbar) at room temperature for 5 hours to give $(\equiv\text{SiO})\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]$ (**1**) as a white powder. The supernatant and washing solutions were collected and analyzed by ^1H NMR spectroscopy in C_6D_6 using ferrocene as an internal standard, indicating the consumption of 0.54 equiv of $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$ and the release of 0.42 equiv. of $\text{HOSi}(\text{OtBu})_3$ upon grafting.

Elemental Analysis: Mo 1.52%

IR (cm^{-1}): 1367 (s), 1392 (m), 1464 (m), 2832 (m), 2879 (m), 2908 (m), 2939 (m), 2979 (s), 3745 (m).

IR spectrum of **1** is given in Figure S2.

Preparation of **2**: Thermal decomposition of $(\equiv\text{SiO})\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]$ (**1**) and calcination

$(\equiv\text{SiO})\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]$ (**1**) was loaded into a reactor and placed under high vacuum (10^{-5} mbar) at 200°C ($1^\circ\text{C}/\text{min}$) for 3 h, then heated at 400°C ($1^\circ\text{C}/\text{min}$) for 8 h. The reactor was cooled to ambient temperature under vacuum, and the resulting powder was loaded into a flow reactor, then calcined at 400°C ($1^\circ\text{C}/\text{min}$) for 3 h to give $(\equiv\text{SiO})_2\text{Mo}(\text{O})_2$ (**2**) as a white powder.

Elemental analysis: Mo 1.56 wt% (0.163 mmol/g)

IR (cm^{-1}): 3745 (s).

IR spectrum of **2** is given in Figure S2.

Preparation of 2-(Me₄BTDP)_x: Reduction of 2 with Me₄BTDP

In a 20 mL Schlenk tube, a solution of Me₄BTDP (18.4 mg, 0.0651 mmol, 1 equiv. to Mo) in C₆H₆ (1 mL) was added to a suspension of **2** (400 mg, 0.0652 mmol) in C₆H₆ (1 mL) at room temperature. The reaction suspension was slowly stirred at 70 °C for 4 h, resulting in colour change of the material from white to brown. After the supernatant was decanted, the residual solid was washed with C₆H₆ (1 mL × 3). The resulting solid was dried thoroughly under high vacuum (10⁻⁵ mbar) at room temperature for more than 3 h to afford **2-(Me₄BTDP)₁** as a brown powder. The supernatant and washing solutions were combined and analysed by ¹H NMR spectroscopy in C₆D₆ using ferrocene as an internal standard. Similarly, **2-(Me₄BTDP)₂**, which is a purple-brown powder, was prepared.

IR (cm⁻¹) of **2-(Me₄BTDP)₁**: 3741 (s), 3694 (br), 2960 (m), 2904 (m), 1448 (m), 1415 (m).

IR (cm⁻¹) of **2-(Me₄BTDP)₂**: 3694 (br), 2959 (s), 2902 (m), 1445 (m), 1415 (m).

IR of the material are given in Figure S3.

Table S1. Summary of the results of the reduction.

Equiv. of Me ₄ BTDP to Mo	Consumption of Me ₄ BTDP	Released Me ₄ -pyrazine	Released HMDSO	Name of the material
1 equiv.	0.065 mmol	0.015 mmol	0.013 mmol	2-(Me₄BTDP)₁
2 equiv.	0.110 mmol	0.057 mmol	0.013 mmol	2-(Me₄BTDP)₂

C) Single Crystals XRD

a)

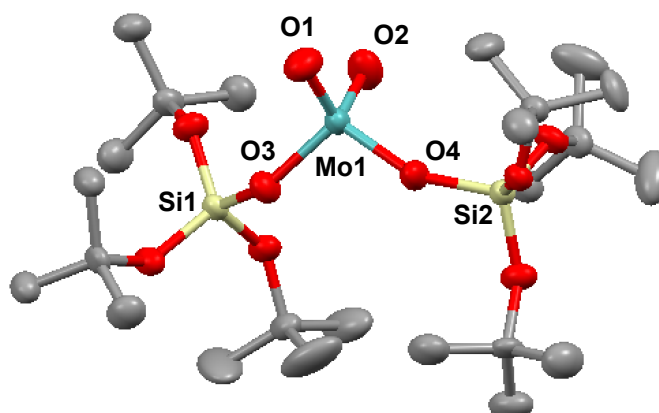


Figure S1. Thermal ellipsoid plot at the 50% probability of $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$. Hydrogen atoms were omitted and only one of the two independent molecules in the asymmetric unit have been represented for clarity.

Table S2. Selected bonds and angles for $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$ (distances are given in Å).

Mo1–O1	1.689(4)
Mo1–O2	1.665(4)
Mo1–O3	1.845(4)
Mo1–O4	1.840(4)

Table S3. Crystallographic data for $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]$.

formula	$\text{MoSi}_2\text{O}_{10}\text{C}_{24}\text{H}_{54}$
crystal size (nm)	$0.42 \times 0.08 \times 0.08$
crystal system	monoclinic
space group	$P2_1/c$ (#14)
volume (Å ³)	7006(3)
a (Å)	16.151(5)
b (Å)	27.037(8)
c (Å)	16.893(5)
α (°)	—
β (°)	108.232(5)
γ (°)	—
Z	8
formula weight (g/mol)	654.79
density (g cm ⁻³)	1.242
F(000)	2784.0
temp (K)	100(2)
total no. reflections	36518
unique reflections [R(int)]	12370 ($R_{\text{int}} = 0.0993$)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0710$, $wR_2 = 0.1184$
GOF	1.049

D) Infrared (IR) spectra

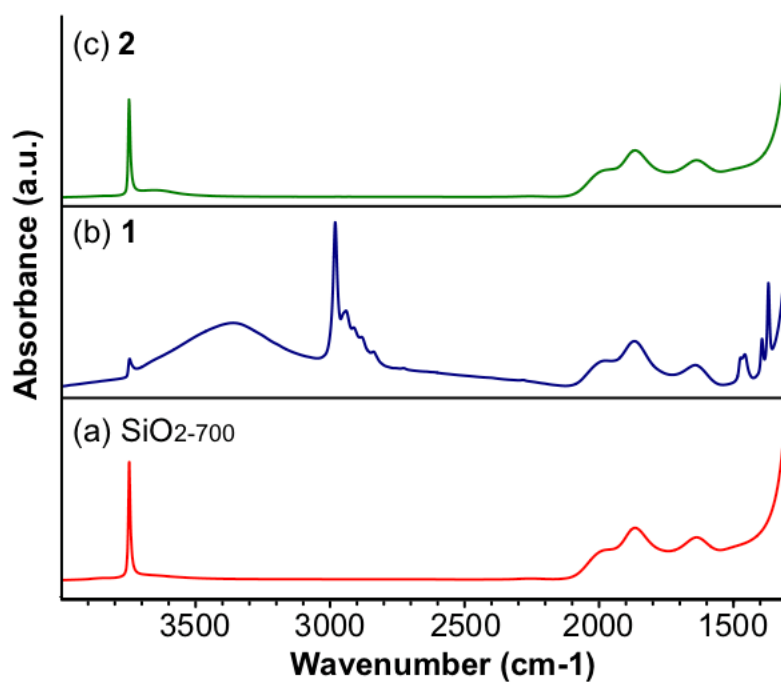


Figure S2. IR spectra of SiO₂₋₇₀₀, 1, and 2.

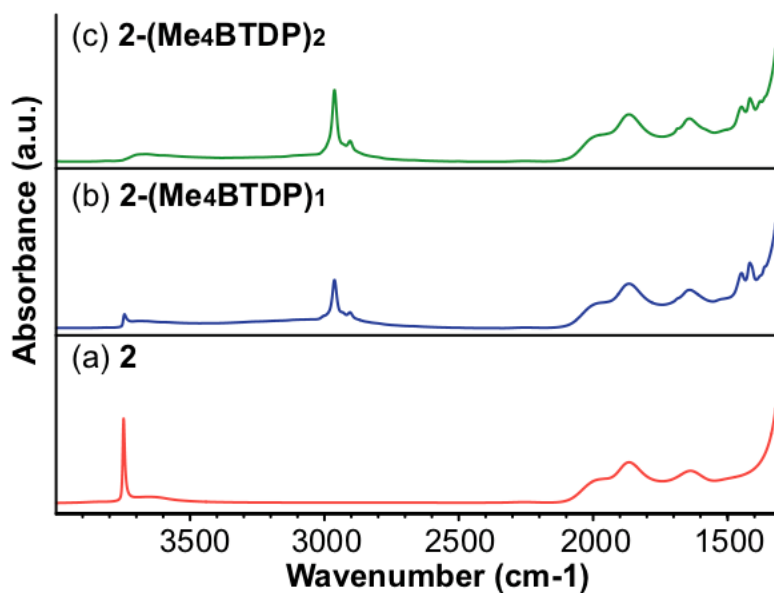


Figure S3. IR spectra of 2, 2-(Me₄BTDP)₁, 2-(Me₄BTDP)₂.

E) Solid State NMR

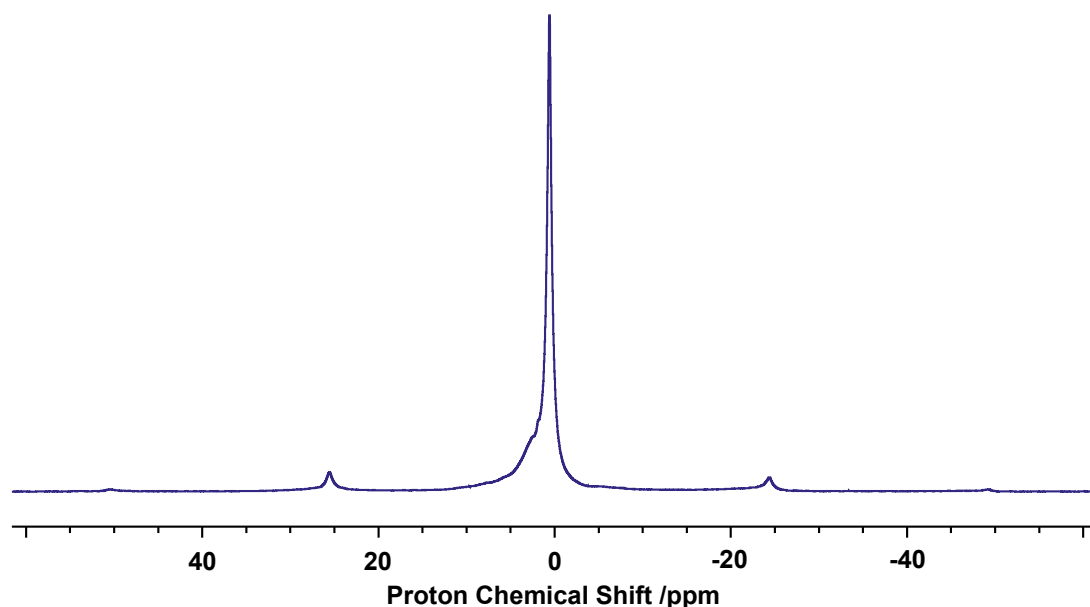


Figure S4. ^1H NMR spectrum (400 MHz, spinning rate 10 kHz, 4 mm rotor) of the material after the reaction of **2-(Me₄BTDP)₁** with ethylene at 70 °C for 2 h, followed by ^{13}C dilabeled ethylene.

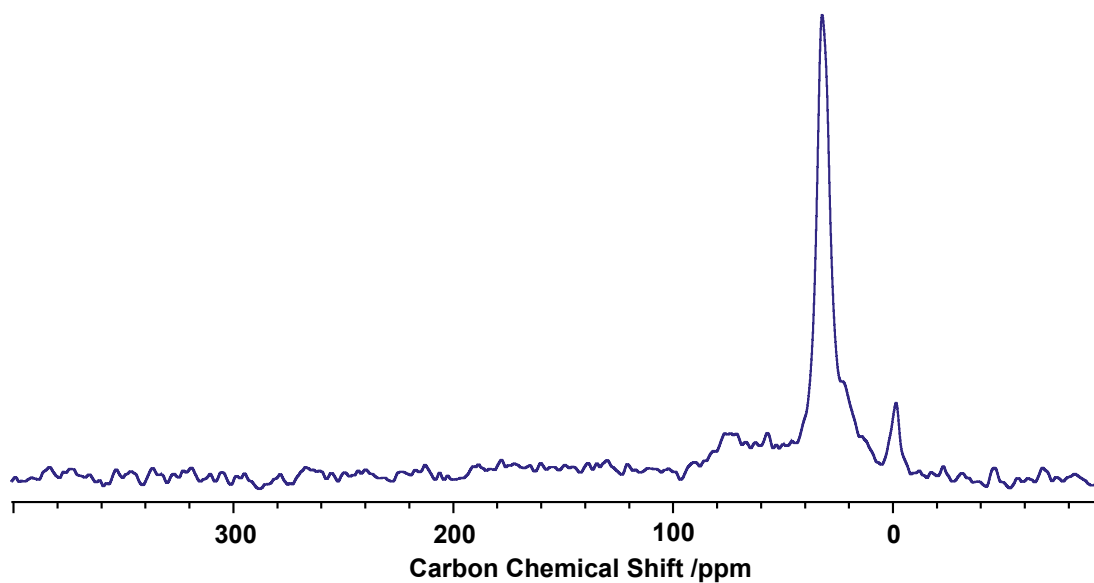


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, spinning rate 10 kHz, 4 mm rotor) of the material after the reaction of **2-(Me₄BTDP)₁** with ethylene at 70 °C for 2 h, followed by ^{13}C dilabeled ethylene. The contact time for CP was 2 ms, and the recycle delay was 1 s.

F) UV-Vis DRS spectra

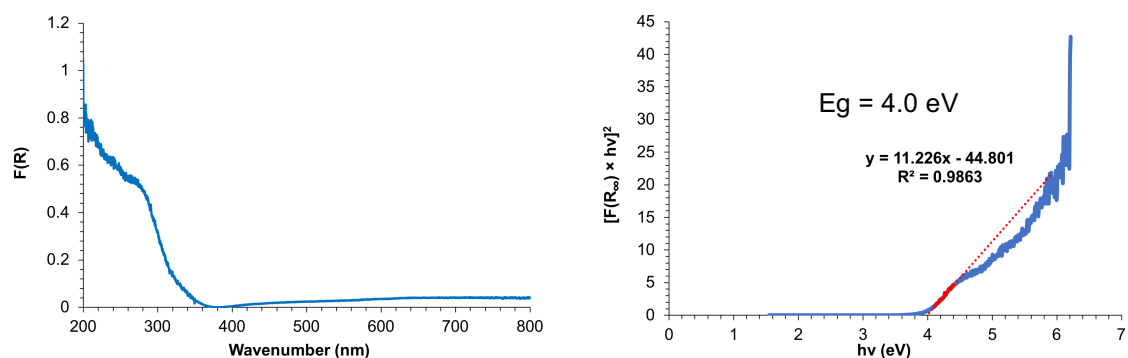


Figure S6. UV-vis diffuse reflectance spectrum and the E_g value of $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$.

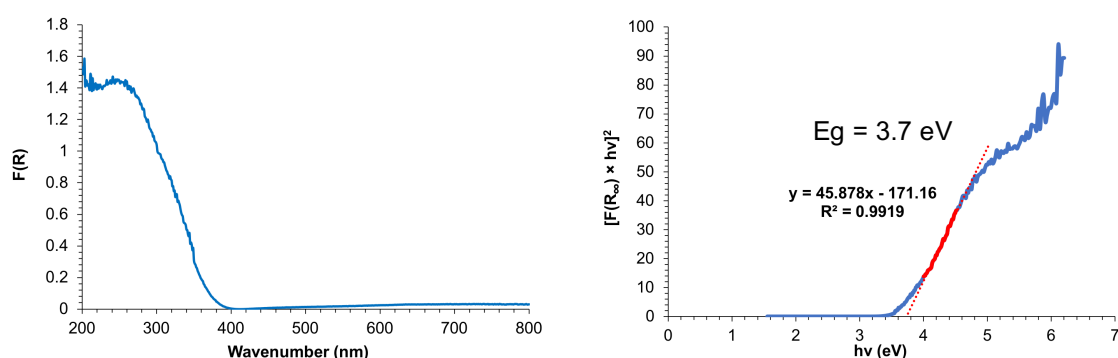


Figure S7. UV-vis diffuse reflectance spectrum and the E_g value of 1.

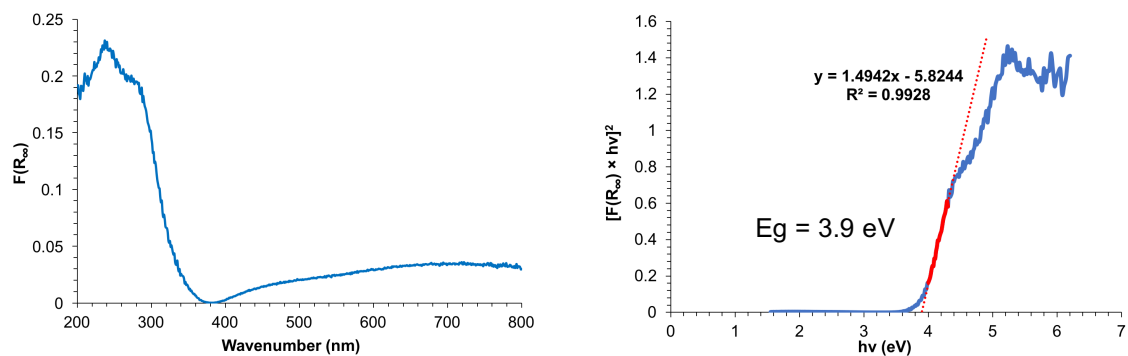


Figure S8. UV-vis diffuse reflectance spectrum and the E_g value of 2.

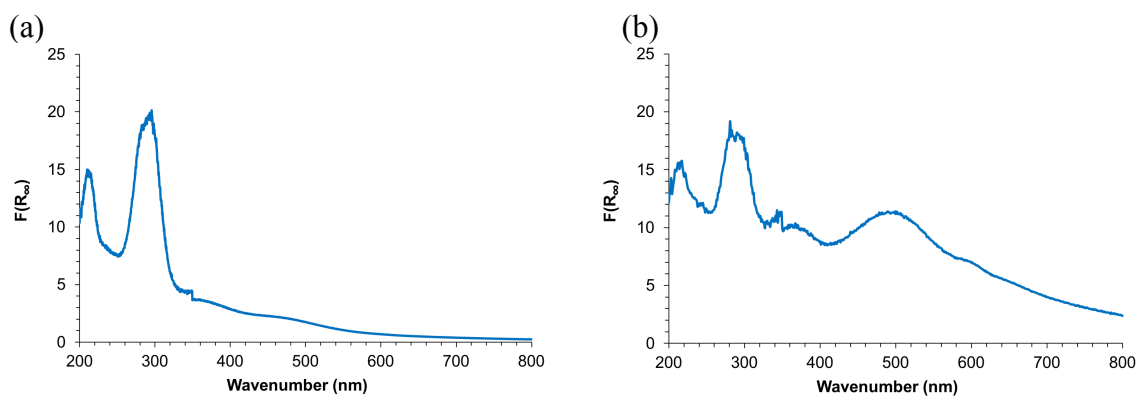


Figure S9. UV-vis diffuse reflectance spectra of (a) $2-(\text{Me}_4\text{BTDP})_1$ and (b) $2-(\text{Me}_4\text{BTDP})_2$.

G) XAS

XAS characterization of $(\equiv\text{SiO})\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]$ (**1**)

Table S4. EXAFS fit parameters for **1**. $S_0^2 = 1.039$; ΔE_0 (eV) = 1 (2); k range 3-13 \AA^{-1} ; R range 1-3.7 \AA . Values without errors were fixed in the EXAFS fits.

Atoms	No. of neighbor	σ^2 (\AA^2)	R (\AA)
O	2	0.0030 (3)	1.723 (5)
O	2	0.0035 (5)	1.952 (7)
O	1	0.006 (2)	2.39 (2)
Si	1	0.005 (2)	3.31 (2)
Si	1	0.005 (2)	3.43 (2)

XAS characterization of $(\equiv\text{SiO})_2\text{Mo}(\text{O})_2$ (**2**)

Table S5. EXAFS fit parameters for **2**. $S_0^2 = 1.039$; ΔE_0 (eV) = 0 (2); k range 3-13 \AA^{-1} ; R range 1-3.7 \AA . Values without errors were fixed in the EXAFS fits.

Atoms	No. of neighbor	σ^2 (\AA^2)	R (\AA)
O	2	0.0021 (3)	1.699 (5)
O	2	0.0026 (4)	1.921 (6)
Si	1	0.011 (7)	3.39 (5)
Si	1	0.011 (7)	3.52 (5)

XANES white line energy

Table S6. XANES edge energies of $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$, **1**, **2**, **2-(Me₄BTDP)₁**, **2-(Me₄BTDP)₂**.

Sample	Edge energy (eV)
$\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$	20014.9
1	20014.9
2	20014.9
2-(Me₄BTDP)₁	20014.5
2-(Me₄BTDP)₂	20013.2

H) EPR spectroscopy

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

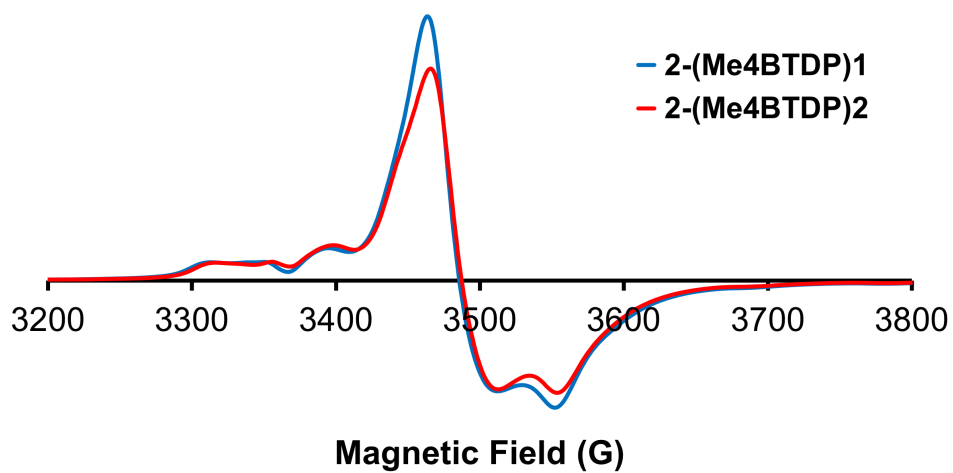
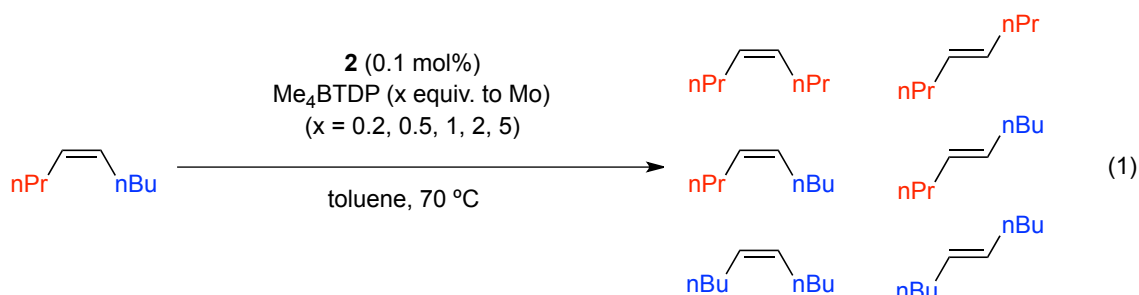


Figure S10. EPR spectra of 2-(Me₄BTDP)₁ and 2-(Me₄BTDP)₂.

I) Catalytic Activity

Metathesis reaction of *cis*-4-nonene at 70 °C catalyzed by **2** in the presence of M₄BTDP

The catalyst **2** (3.0 mg, 0.49 μmol of Mo) was loaded in a conical base vial with a wing shaped magnetic stirring bar. A solution of *cis*-4-nonene (0.9832 M) in toluene containing heptane as an internal standard (0.1069 M) and Me₄BTDP (0.2, 0.5, 1, 2, 5 equiv.) were added to the vial (eq. 1). The reaction mixture was stirred at 600 rpm and kept at 70 °C using an aluminum heating block. 5 μL of aliquots of the solution were drawn, and then diluted with pure toluene (100 μL). The resulting solution was analyzed by GC/FID (Agilent Technologies 7890 A) equipped with an HP-5 (Agilent Technologies) column. Conversion is given by eq. 2, that is without taking into account *cis*/*trans* isomerization of 4-nonene. Equilibrium conversion is reached at ca. 51%.



$$\text{Product conversion (t)} = \frac{[\text{cis/trans-4-octene}]_t + [\text{cis/trans-5-decene}]_t}{[\text{cis-4-nonene}]_{\text{int}}} \quad (2)$$

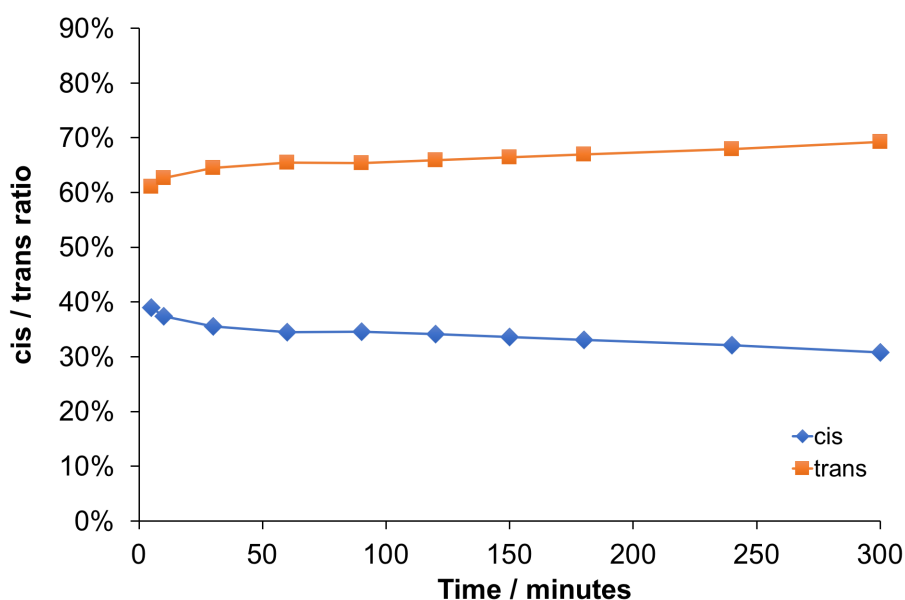


Figure S11. The *cis*-*trans* ratio of the 4-octene vs time, *cis*-4-nonene self-metathesis catalyzed by **2** and 0.2 equiv. of Me₄BTDP.

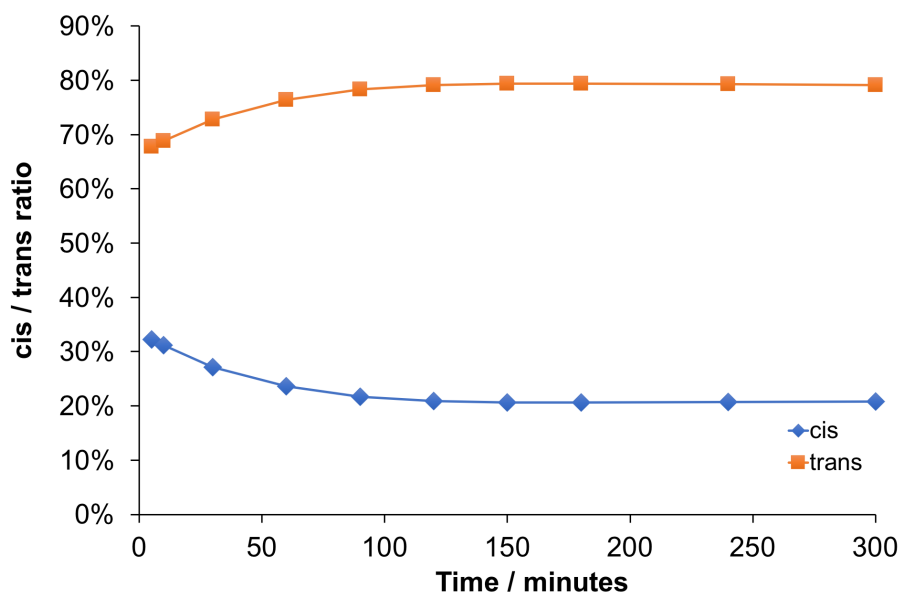


Figure S12. The cis-trans ratio of 4-octene vs time, *cis*-4-nonene self-metathesis catalyzed by **2** and 0.5 equiv. of Me₄BTDP.

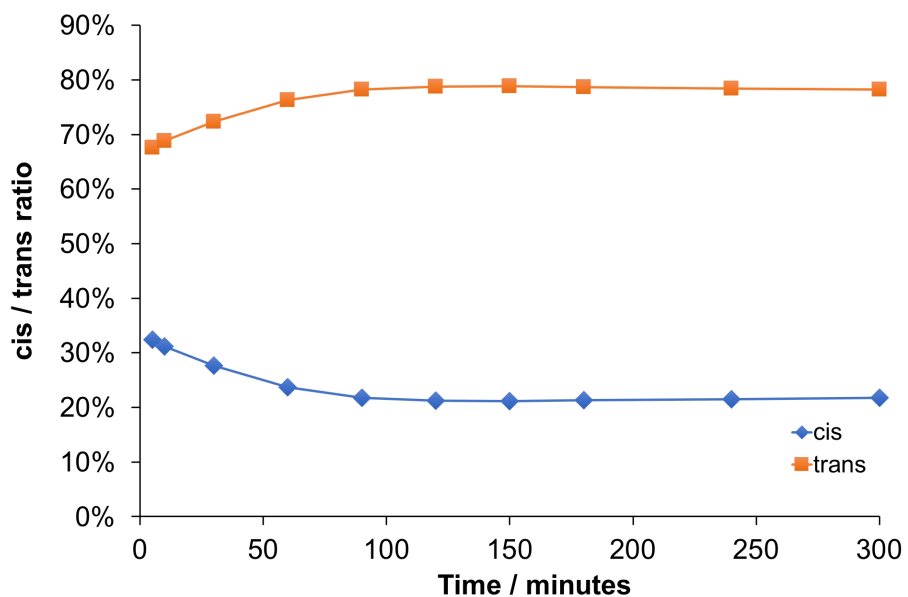


Figure S13. The cis-trans ratio of 4-octene vs time, *cis*-4-nonene self-metathesis catalyzed by **2** and 1 equiv. of Me₄BTDP.

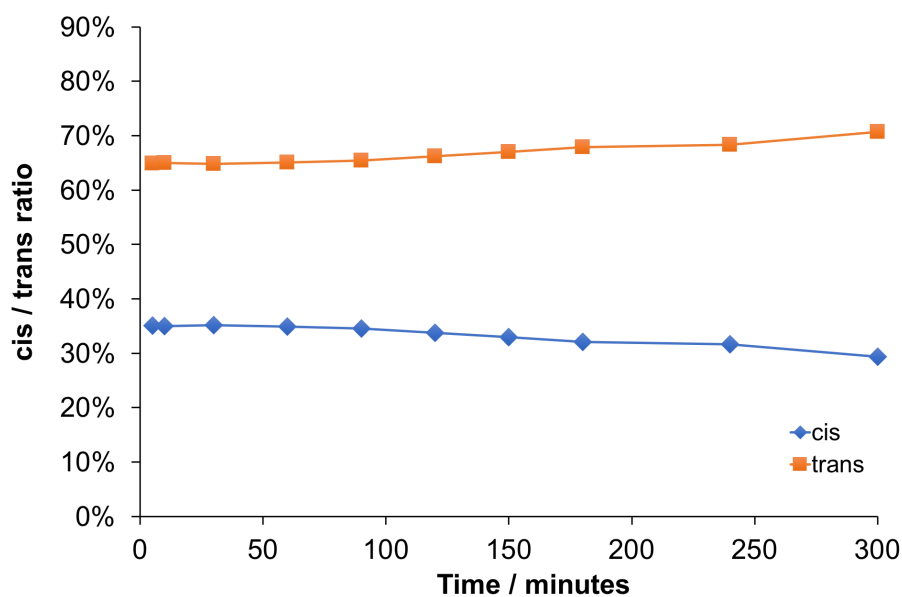


Figure S14. The cis-trans ratio of 4-octene vs time, *cis*-4-nonene self-metathesis catalyzed by **2** and 2 equiv. of Me₄BTDP.

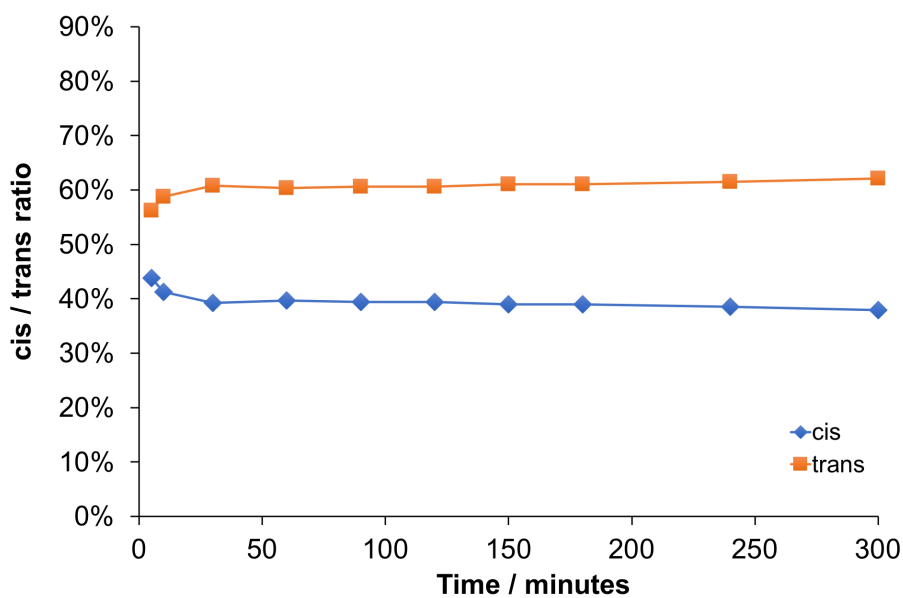


Figure S15. The cis-trans ratio of 4-octene vs time, *cis*-4-nonene self-metathesis catalyzed by **2** and 5 equiv. of Me₄BTDP.

Metathesis reaction of *cis*-4-nonene at 30 °C catalyzed by **2** in the presence of Me₄BTDP

The catalyst **2** (3.0 mg, 0.49 μ mol of Mo) was loaded in a conical base vial with a wing shaped magnetic stirring bar. A solution of *cis*-4-nonene (0.9832 M) in toluene containing heptane as an internal standard (0.1069 M) and Me₄BTDP (1 equiv.) was added to the vial. The reaction mixture was stirred at 600 rpm and kept at 30 °C using an aluminum heating block. 5 μ L of aliquots of the solution were drawn, and then diluted with pure toluene (100 μ L). The resulting solution was analyzed by GC/FID (Agilent Technologies 7890 A) equipped with an HP-5 (Agilent Technologies) column. Conversion is given by eq.2. Equilibrium conversion is reached at ca. 51%.

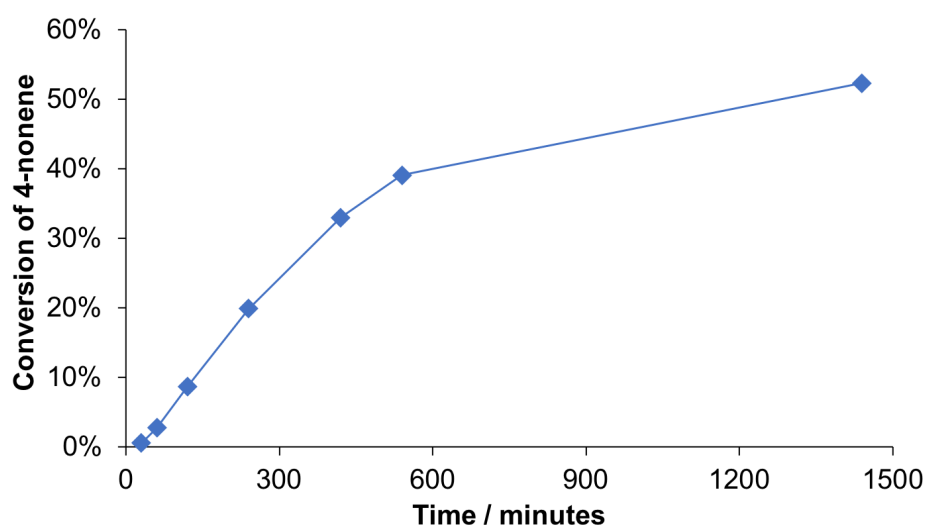


Figure S16. Conversion vs time, *cis*-4-nonene self-metathesis catalyzed by **2**/Me₄BTDP at 30 °C.

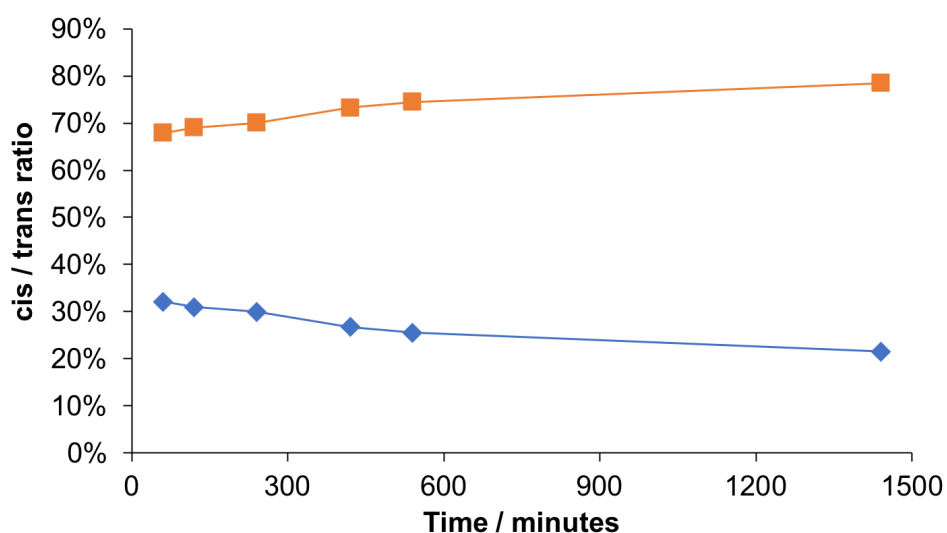


Figure S17. The *cis*-*trans* ratio of 4-octene vs time, *cis*-4-nonene self-metathesis catalyzed by **2**/Me₄BTDP at 30 °C.

Metathesis reaction of *cis*-4-nonene at 70 °C catalyzed by 2-(Me₄BTDP)₁, 2-(Me₄BTDP)₂

Each catalyst, **2-(Me₄BTDP)₁**, **2-(Me₄BTDP)₂** (3.0 mg, 0.49 μmol of Mo), was loaded in a conical base vial with a wing shaped magnetic stirring bar. A solution of *cis*-4-nonene (0.1069 M) in toluene containing heptane as an internal standard (0.9832 M) was added to the vial. The reaction mixture was stirred at 600 rpm and kept at 70 °C using an aluminum heating block. 5 μL of aliquots of the solution were sampled, and then diluted with pure toluene (100 μL). The resulting solution was analyzed by GC/FID (Agilent Technologies 7890 A) equipped with an HP-5 (Agilent Technologies) column. Conversion is given by eq. 2, that is without taking into account *cis*/*trans* isomerization of 4-nonene. Equilibrium conversion is reached at ca. 51%.

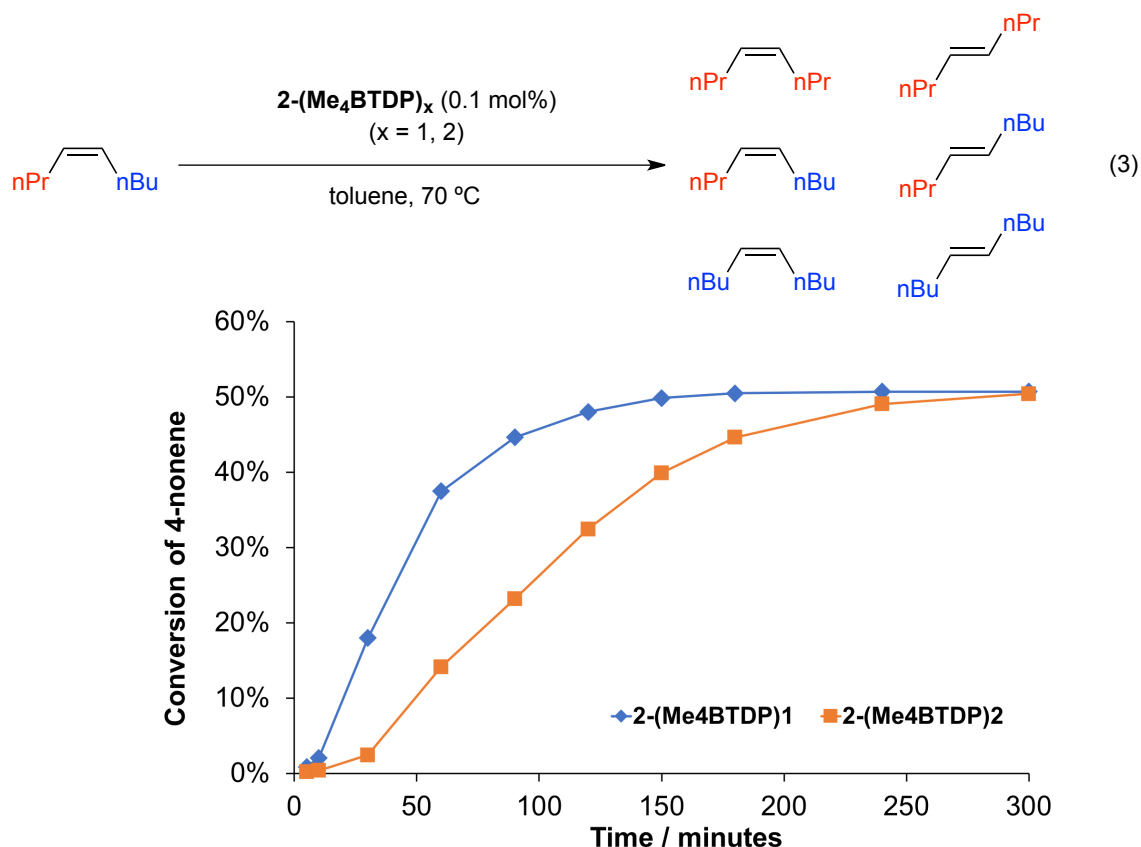


Figure S18. Conversion vs time, *cis*-4-nonene self-metathesis catalyzed by **2-(Me₄BTDP)₁** and **2-(Me₄BTDP)₂** at 70 °C.

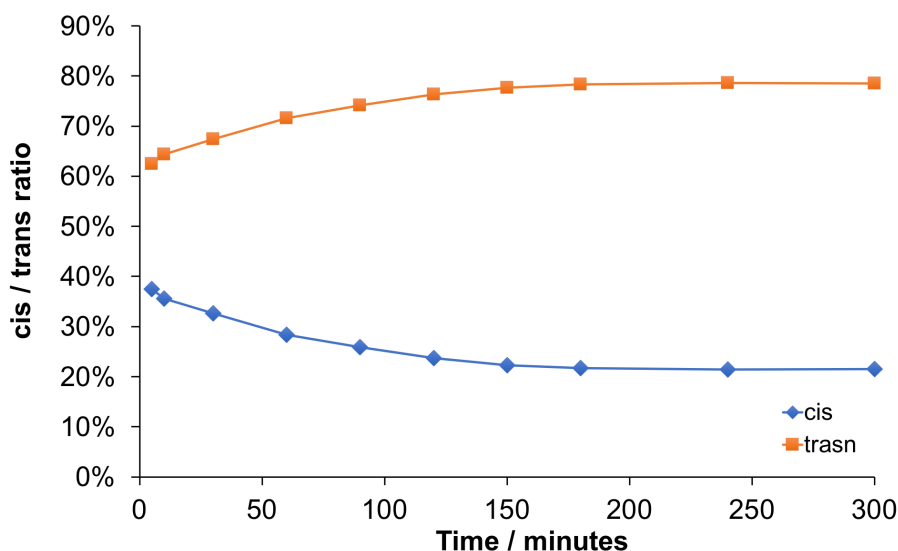


Figure S19. The cis-trans ratio of 4-octene vs time, *cis*-4-nonene self-metathesis catalyzed by **2-(Me₄BTDP)₁** at 70 °C.

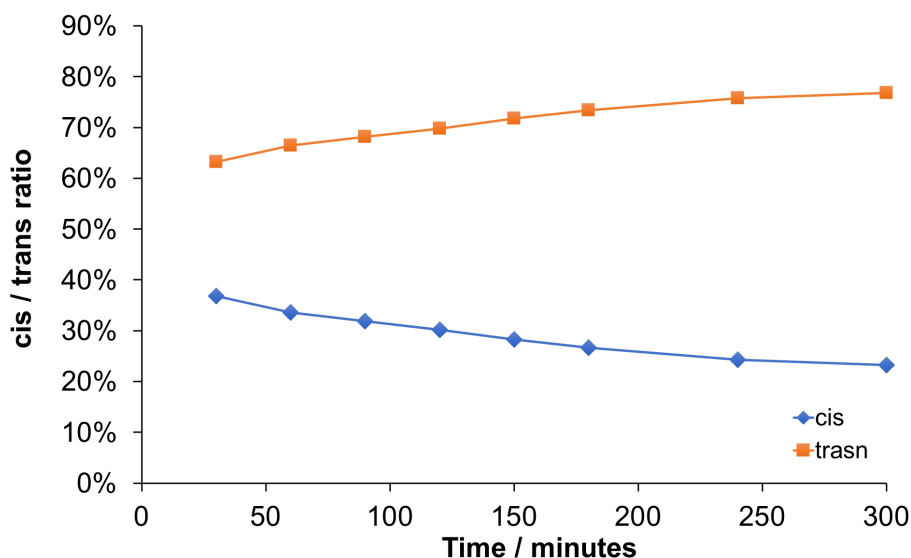
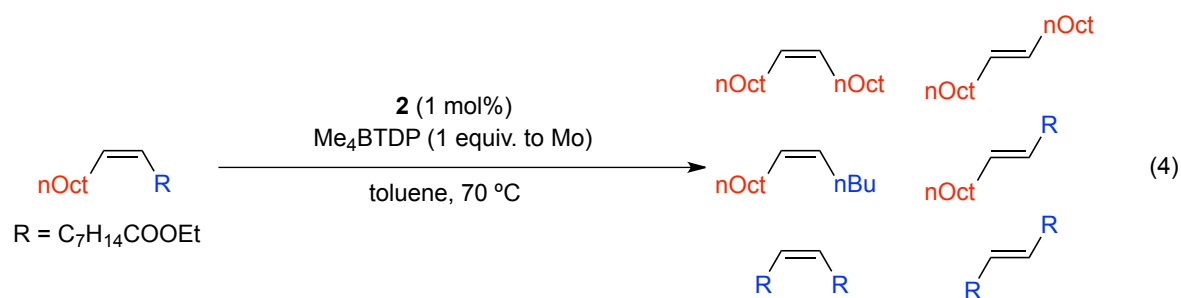


Figure S20. The cis-trans ratio of 4-octene vs time, *cis*-4-nonene self-metathesis catalyzed by **2-(Me₄BTDP)₂** at 70 °C.

Metathesis reaction of ethyl oleate at 70 °C by **2** in the presence of Me₄BTDP

The catalyst **2** (15 mg, 2.5 μmol) was loaded in a conical base vial with a wing shaped magnetic stirring bar. A solution of ethyl oleate (0.5056 M) in toluene containing heptane as an internal standard (0.0513 M) and Me₄BTDP (1 equiv. to Mo) were added to the vial. The reaction mixture was stirred at 600 rpm and kept at 70 °C using an aluminum heating block. 5 μL of aliquots of the solution were drawn, and then diluted with pure toluene (100 μL). The resulting solution was analyzed by GC/FID (Agilent Technologies 7890 A) equipped with an HP-88 (Agilent Technologies) column. Conversion is given by eq. 5, that is without taking into account cis/trans isomerization.



$$\text{Product conversion (t)} = \frac{[\text{cis/trans-9-octadecene}]_t + [\text{cis/trans-9-diethyl octadecenedioate}]_t}{[\text{ethyl oleate}]_{\text{int}}} \quad (5)$$

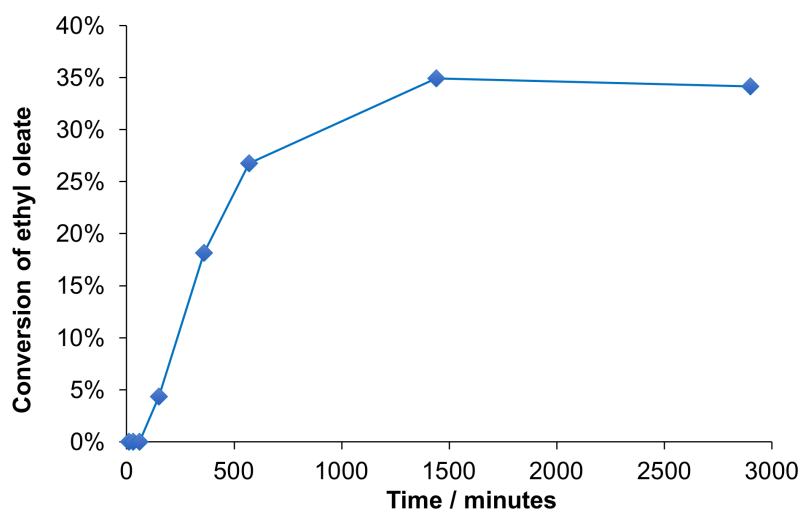


Figure S21. Conversion vs time, ethyl oleate self-metathesis catalyzed by **2**/Me₄BTDP at 70 °C.

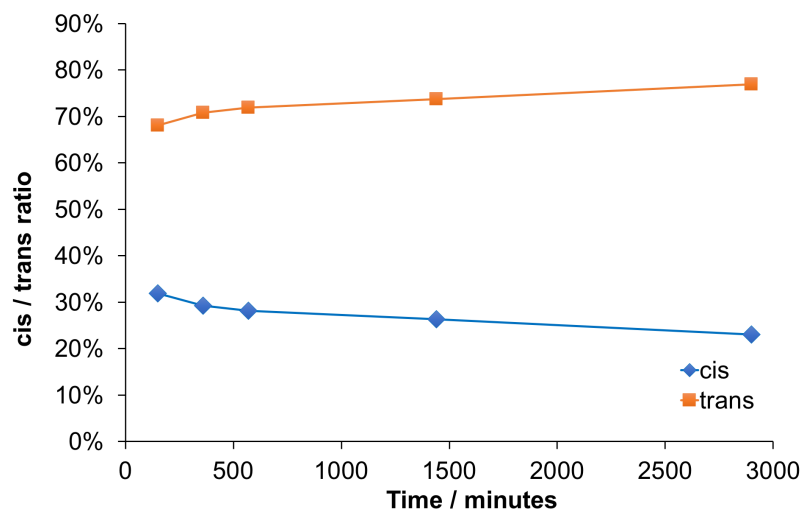


Figure S22. The cis-trans ratio of 9-diethyl octadecenedioate vs time, ethyl oleate self-metathesis catalyzed by **2**/Me₄BTDP at 70 °C.

J) Titration of Active Site Using Ethylene

Exposure of 2-(Me₄BTDP)₁ to ethylene

2-(Me₄BTDP)₁ (100 mg) was loaded in a 30 mL glass reactor and contacted with ethylene (10 equiv to Mo). After heating the reactor at 70 °C for 2 h, the gas phase was analyzed by GC-FID, showing the presence of unreacted ethylene and 0.08 equiv of propylene.

K) References

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