

Supporting Information

Isostructural Molecular and Surface Mimics of the Active Sites of the Industrial WO₃/SiO₂ Metathesis catalysts.

Victor Mougel^a, Christophe Copéret^{a*}

^a Department of Chemistry and Applied Biosciences, Vladimir Prelog Weg 1-5, ETH Zürich, 8093 Zürich, Switzerland
E-mail: ccoperet@ethz.ch

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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. Silica (Aerosil Degussa, $200\text{ m}^2\text{g}^{-1}$) was compacted with distilled water, calcined 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 12 h (support referred to as $\text{SiO}_{2-(700)}$) and contained 0.26 mmol of OH per g as measured by titration with MeMgCl . All infrared (IR) spectra were recorded using a Bruker spectrometer placed in the 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 solutions ^1H and ^{13}C -NMR spectra were obtained on Bruker DRX 300, DRX 250 or DRX 500 spectrometers. The solution spectra were recorded in C_6D_6 at room temperature. The ^1H and ^{13}C chemical shifts are referenced relative to the residual solvent peak. Solid-state NMR spectra were recorded under MAS on Bruker Advance III 400, 600 and 700 MHz spectrometers with a conventional triple resonance 4 or 3.2 mm CP-MAS probe. The MAS frequency was set to 10 kHz for all of the experiments reported here, unless otherwise specified. The samples were introduced in a zirconia rotor in the glovebox and tightly closed. Compounds $[\text{W}(\text{O})\text{Cl}_2(\text{PPhMe}_2)_2(\text{CHtBu})]^1$, $[\text{W}(\text{O})\text{Cl}_2(\text{PPhMe}_2)_2(^{13}\text{CHtBu})]^2$ and $\text{WO}_3/\text{SiO}_2^3$ were synthesized according to literature procedures. $\text{KOSi}(\text{OtBu})_3$ was obtained by deprotonation of $\text{HOSi}(\text{OtBu})_3$ with KH in toluene followed by recrystallization in cold toluene. Vinylanisole was fractionally distilled, degassed and stored over $4\text{\AA}$ molecular sieves prior to use.

B) Syntheses

Synthesis of the molecular precursors:

Synthesis of [W(O)(CHtBu)(OSi(OtBu)₃)₂(PPhMe₂)], 1-PPhMe₂.

A cold (-95 °C) solution of [W(O)Cl₂(PPhMe₂)₂(CHtBu)] (200 mg, 0.32 mmol, 1 equiv.) in diethyl ether (2 mL) was added to a suspension of 196 mg of KOSi(OtBu)₃ (0.65 mmol, 2 equiv.) in cold diethyl ether (2 mL, -95 °C) while stirring. The yellow solution was stirred for 3h at room temperature, resulting in the formation of a off white precipitate. The suspension was filtered on Celite® to afford a clear yellow solution. The filtrate was taken to dryness *in vacuo*, affording a yellow oil. Extraction in pentane followed by filtration on Celite® and high vacuum drying (10⁻⁵ mBar, 5h) afforded [W(O)(CHtBu)(OSi(OtBu)₃)₂(PPhMe₂)] as a yellow waxy solid (240 mg, 0.026 mmol, 80%). ¹H NMR (200 MHz, C₆D₆) δ (ppm) *cis* (88%): 9.87 (s, 1H, CHCMe₃), 7.60 (t, 2H, Ar), 7.12-7.03 (m, 3H, Ar), 1.60 (br s, 6H, PPhMe₂), 1.52 (br s, 54H, OSi(OCMe₃)₃), 1.21 (s, 9H, CHCMe₃). *trans* (12%): 11.14 (s, 1H, CHCMe₃), 7.60 (t, 2H, Ar), 7.12-7.03 (m, 3H, Ar), 1.60 (br s, 6H, PPhMe₂), 1.52 (br s, 54H, OSi(OCMe₃)₃), 1.32 (s, 9H, CHCMe₃). ¹³C NMR (75.432 MHz, C₆D₆) δ (ppm) *cis* (88%): 270.6 (CHCMe₃), 131.5 (Ar), 129.6 (Ar), 128.6 (Ar), 72.2 (OSi(OCMe₃)₃), 43.1 (CHCMe₃), 34.1 (CHCMe₃), 32.1 (OSi(OCMe₃)₃), 15.0-14.7 (PPhMe₂); *anti* (12%): 278.5 (CHCMe₃), 131.5 (Ar), 129.6 (Ar), 128.6 (Ar), 72.2 (OSi(OCMe₃)₃), 42.3 (CHCMe₃), 34.3 (CHCMe₃), 32.7 (OSi(OCMe₃)₃), 15.0-14.7 (PPhMe₂). ³¹P NMR (121.442 MHz, C₆D₆) : *cis* (88%) 8.9; *anti* (12%) 11.1 ppm. Elemental Analysis: C 47.60 % (expected 47.53 %), H 7.98 % (exp. 8.09 %), P 3.16 % (exp. 3.31 %). ¹³C labeled compound at the alkylidene position was synthesized following the procedures described above using ¹³C labeled [W(O)Cl₂(PPhMe₂)₂(CHtBu)].

Synthesis of [W(O)(CHtBu)(OSi(OtBu)₃)₂], 1.

A cold (-95 °C) solution of [W(O)Cl₂(PPhMe₂)₂(CHtBu)] (100 mg, 0.16 mmol, 1 equiv.) in diethyl ether (1 mL) was added to a suspension of 98 mg of KOSi(OtBu)₃ (0.32 mmol, 2 equiv.) in cold diethyl ether (2 mL, -95 °C) while stirring. The yellow solution was stirred for 3h at room temperature, resulting in the formation of a off white precipitate. The suspension was filtered on Celite® to afford a clear yellow solution. The filtrate was taken to dryness *in vacuo*, affording yellow oil. This oil was dissolved in pentane and cooled to -95°C. A cold solution of tris(pentafluorophenyl)borane in pentane (-95°C, 2 mL) was added to the yellow solution, resulting in the immediate formation of a white precipitate. The suspension was stirred at -95°C for 30 min and filtered cold on Celite® to afford after

drying cold under high vacuum (10^{-5} mBar, 30 min, -30°C) the title compound as a dark yellow oil (99 mg, 0.124 mmol, 77%). The compound is very temperature sensitive and decomposes in within 1h at 25°C . ^1H NMR (200 MHz, C_6D_6) δ (ppm) *syn* (96%): 8.47 (s, 1H, CHCMe_3), 1.44 (s, 9H, CHCMe_3), 1.39 (br s, 54H, $\text{OSi}(\text{OCMe}_3)_3$). *anti* (4%): 11.45 (s, 1H, CHCMe_3), 1.44 (s, 9H, CHCMe_3), 1.39 (br s, 54H, $\text{OSi}(\text{OCMe}_3)_3$). ^{13}C NMR (75.432 MHz, C_6D_6) δ (ppm) *syn* (96%): 245.5 (CHCMe_3), 73.17 ($\text{OSi}(\text{OCMe}_3)_3$), 41.4 (CHCMe_3), 34.2 (CHCMe_3), 31.5 ($\text{OSi}(\text{OCMe}_3)_3$); *anti* (4%): 256.0 (CHCMe_3), 73.17 ($\text{OSi}(\text{OCMe}_3)_3$), 41.4 (CHCMe_3), 34.2 (CHCMe_3), 31.5 ($\text{OSi}(\text{OCMe}_3)_3$). Elemental Analysis: The compound is very temperature sensitive and decomposes in within hours at 25°C , no elemental analysis could thus be carried out. ^{13}C labeled compound at the alkylidene position was synthesized following the procedures described above using ^{13}C labeled $[\text{W}(\text{O})\text{Cl}_2(\text{PPhMe}_2)_2(\text{CHtBu})]$.

Synthesis of $[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-o-OMe})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)]$, 2-PPhMe₂.

A cold (-95°C) solution of $[\text{W}(\text{O})\text{Cl}_2(\text{PPhMe}_2)_2(\text{CHtBu})]$ (114 mg, 0.18 mmol, 1 equiv.) in diethyl ether (1 mL) was added to a suspension of 100 mg of $\text{LiOSi}(\text{OtBu})_3$ (0.37 mmol, 2 equiv.) in cold diethyl ether (2 mL, -95°C) while stirring. The yellow solution was stirred for 3h at room temperature, resulting in the formation of a off white precipitate. To this suspension was added a solution of vinylanisole (27.2 μL , 0.20 mmol, 1.1 equiv.) in diethyl ether (1 mL), resulting in a colour change to dark brown. The suspension was stirred at room temperature for 3h and filtered on Celite® to afford a clear brown solution. The filtrate was taken to dryness *in vacuo*, affording a brown oil. High vacuum drying (10^{-5} mBar, 8h) of the oil afforded an orange waxy solid that was recrystallized from cold pentane to afford the title compound as light brown crystals (130 mg, 0.13 mmol, 73%). X-Ray suitable crystals were obtained by slow diffusion of hexane in a concentrated benzene solution of **3**. ^1H NMR (200 MHz, C_6D_6) δ (ppm) *main* (94%): 11.04 (br s, 1H, $\text{CHC}_6\text{H}_4\text{-o-OMe}$), 7.26 (br t, 2H, PPhMe_2), 7.08-6.95 (br m, 3H, PPhMe_2), 6.86 (td, 1H, $\text{CHC}_6\text{H}_4\text{-o-OMe}$), 6.55-6.30 (br m, 2H, $\text{CHC}_6\text{H}_4\text{-o-OMe}$), 6.23-6.07 (br m, 1H, $\text{CHC}_6\text{H}_4\text{-o-OMe}$), 4.00 (s, 3H, $\text{CHC}_6\text{H}_4\text{-o-OMe}$), 1.52 (br s, 6H, PPhMe_2), 1.44 (br s, 54H, $\text{OSi}(\text{OCMe}_3)_3$). *minor* (6%): 11.35 (s, 1H, $\text{CHC}_6\text{H}_4\text{-o-OMe}$), 7.26 (br t, 2H, PPhMe_2), 6.86 (td, 1H, $\text{CHC}_6\text{H}_4\text{-o-OMe}$), 6.55-6.30 (br m, 2H, $\text{CHC}_6\text{H}_4\text{-o-OMe}$), 6.23-6.07 (br m, 1H, $\text{CHC}_6\text{H}_4\text{-o-OMe}$), 3.28 (s, 3H, $\text{CHC}_6\text{H}_4\text{-o-OMe}$), 1.52 (br s, 6H, PPhMe_2), 1.44 (br s, 54H, $\text{OSi}(\text{OCMe}_3)_3$). ^{13}C NMR (75.432 MHz, C_6D_6) δ (ppm) 265.5 (CHCAr), 159.9 (COMe); 136.2 (Ar) 132.3 (Ar); 130.0 (Ar); 125.3 (Ar); 120.4 (Ar); 107.1 (Ar); 71.95 ($\text{OSi}(\text{OCMe}_3)_3$); 56.3 (OMe); 31.8 ($\text{OSi}(\text{OCMe}_3)_3$) 15.6-14.5 (PPhMe_2). ^{31}P NMR (121.442 MHz, C_6D_6) : 14.6 (66%, coordinated); -46.1 (33%, free phosphine). Elemental Analysis ($\text{C}_{40}\text{H}_{73}\text{O}_{10}\text{PSi}_2\text{W}$): C 49.04 % (expected 48.78 %), H 7.62 % (exp. 7.47 %), P 3.03 % (exp. 3.14 %).

Synthesis of $[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-}o\text{-OMe})(\text{OSi}(\text{OtBu})_3)_2], \mathbf{2}$.

A solution of $[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-}o\text{-OMe})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)]$ (70 mg, 0.07 mmol, 1 equiv.) in benzene (1 mL) was added to a suspension of 7.7 mg of CuCl (0.08 mmol, 1.1 equiv.) in benzene (0.5 mL) while stirring, resulting in the formation of a white precipitate and a colour change of the solution to dark red. The red solution was stirred for 1h at room temperature. Solvent was removed *in vacuo* and the dark pink solid was extracted in pentane (2 x 1 mL) and filtered on Celite®. This solution was cooled and kept to -40°C for four hours, resulting in precipitation of a second crop of a white solid identified as CuCl(PPhMe₂). The solution was filtered cold on Celite®, concentrated to ca. 1 mL and stored at -40°C over 12h, resulting in the formation of large dark pink crystals of $[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-}o\text{-OMe})(\text{OSi}(\text{OtBu})_3)_2]$ (52 mg, 0.06 mmol, 85%). ¹H NMR (200 MHz, C₆D₆) δ (ppm) 10.85 (s, 1H, CHC₆H₄-*o*-OMe), 6.89 (td, 1H, CHC₆H₄-*o*-OMe), 6.65 (br d, 1H, CHC₆H₄-*o*-OMe), 6.47 (td, 1H, CHC₆H₄-*o*-OMe), 6.28 (dd, 1H, CHC₆H₄-*o*-OMe), 4.12 (s, 3H, CHC₆H₄-*o*-OMe), 1.34 (br s, 54H, OSi(OCMe₃)₃). ¹³C NMR (75.432 MHz, C₆D₆) δ (ppm) 219.9 (CHAr), 157.6 (COMe); 132.8 (Ar) 125.5 (Ar); 123.3 (Ar); 120.9 (Ar); 106.7 (Ar); 72.7 (OSi(OCMe₃)₃); 56.6 (OMe); 31.2 (OSi(OCMe₃)₃). Elemental Analysis (C₃₂H₆₂O₁₀Si₂W): C 45.02 % (expected 45.39 %), H 7.23 % (exp. 7.38 %).

Synthesis of the grafted catalysts

Synthesis of $[(\equiv\text{SiO})\text{W}(\text{O})(\text{CHtBu})(\text{OSi}(\text{OtBu})_3)(\text{PPhMe}_2)], \mathbf{1\text{-PPhMe}_2@\text{SiO}_2}$.

A solution of 65.5 mg of $[\text{W}(\text{O})(\text{CHtBu})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)]$ (0.07 mmol, 1.05 equiv.) in benzene (2 mL) was added to a suspension of SiO₂-(700) (256 mg, 0.067 mmol) in benzene (2 mL) at room temperature. The suspension was slowly stirred at room temperature for 2h, resulting in a fading of the color of the solution and a coloration of the silica to light yellow. The solid was collected by filtration, and was washed by four suspension/filtration cycles in benzene (4 x 2 mL). The resulting light yellow solid was dried thoroughly under high vacuum (10⁻⁵ mBar) at room temperature for 3h to afford 272 mg of the title compound. All the filtrate solutions were collected and analyzed by ¹H NMR spectroscopy in C₆D₆ using ferrocene as internal standard (12.4 mg, 1 equiv.), indicating quantitative reaction of the complex and that 0.05 mmol of HOSi(OtBu)₃ were released upon grafting (0.7 HOSi(OtBu)₃/W_{surf}). Elemental Analysis: W 2.81%, C 4.97%, H 0.82%, P 0.46% corresponding to 27 C/W (25 expected), 53.2 H/W (48 expected), 1 P (1 expected).

Synthesis [(≡SiO)W(O)(CH₂tBu)(OSi(OtBu)₃)₂], 1@SiO₂.

A solution of 119.6 mg of [W(O)(CHtBu)(OSi(OtBu)₃)₂] (0.15 mmol, 1.05 equiv.) in toluene (3 mL, -40°C) was added dropwise to a suspension of SiO₂₋₍₇₀₀₎ (549 mg, 0.14 mmol) in toluene (2 mL, -40°C). The suspension was slowly stirred at -40°C for 30 minutes, resulting in a fading of the color of the solution and a coloration of the silica to yellow. The yellow solid was collected by filtration, and was washed by four suspension/filtration cycles in benzene (4 x 2 mL). The resulting yellow solid was dried thoroughly under high vacuum (10⁻⁵ mBar) at room temperature for 3h to afford 599 mg of the title compound. All the filtrate solutions were collected and analyzed by ¹H NMR spectroscopy in C₆D₆ using ferrocene as internal standard (24.7 mg, 1 equiv.), indicating quantitative consumption of the molecular complex and that 0.05 mmol of HOSi(OtBu)₃ were released upon grafting (0.3 HOSi(OtBu)₃/W_{surf}). Elemental Analysis: W 3.15%, C 4.59%, H 0.75%, corresponding to 22.2 C/W (17 expected), 43.1 H/W (37 expected).

Synthesis [(≡SiO)W(O)(CHC₆H₄-*o*-OMe)(OSi(OtBu)₃)₂], 2@SiO₂.

A solution of 68 mg of [W(O)(CHC₆H₄-*o*-OMe)(OSi(OtBu)₃)₂] (0.08 mmol, 1.05 equiv.) in benzene (2 mL) was added dropwise to a suspension of SiO₂₋₍₇₀₀₎ (294 mg, 0.07 mmol, 1 equiv.) in benzene (1 mL). The suspension was slowly stirred at room temperature for 12 hours, resulting in a fading of the color of the solution and a coloration of the silica to pink orange. The solid was collected by filtration, and was washed by four suspension/filtration cycles in benzene (4 x 1 mL). The resulting pink orange solid was dried thoroughly under high vacuum (10⁻⁵ mBar) at room temperature for 3h to afford 311 mg of the title compound. All the filtrate solutions were collected and analyzed by ¹H NMR spectroscopy in C₆D₆ using ferrocene as internal standard (14.1 mg, 1 equiv.), indicating that 0.02 mmol of HOSi(OtBu)₃ were released upon grafting while 0.035 mmol of unreacted complex was still present in solution (release of 0.7 equiv. HOSi(OtBu)₃/W_{surf}). Elemental Analysis: W 2.35%, C 4.07%, H 0.55%, corresponding to 25.2 C/W (20 expected), 40.6 H/W (35 expected).

C) XRD crystallography.

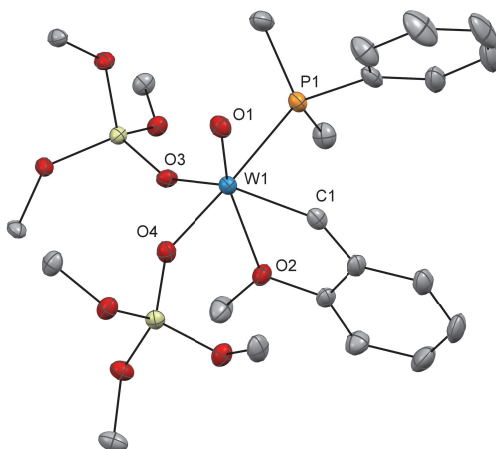


Figure S1. Thermal ellipsoid plot at the 50% probability of $[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-o-OMe})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)] \cdot \text{C}_6\text{H}_6$. Hydrogen atoms and methyl groups of the siloxide ligands have been omitted and co-crystallized solvent molecule was omitted for clarity.

Table S1. Selected bonds for $[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-o-OMe})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)] \cdot \text{C}_6\text{H}_6$ (distances are given in Å)

Structural parameters	$[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-o-OMe})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)]$
W1 – C1	1.973(3)
W1 – P1	2.5612(6)
W1 – O1	1.698(2)
W1 – O2	2.4838(19)
W1 – O3	2.006(2)
W1 – O4	1.958(2)

Table S2. Selected angles for $[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-o-OMe})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)]$ (given in °)

Structural parameters	$[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-o-OMe})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)]$
O1 – W1 – O2	167.98(9)
O1 – W1 – P1	87.75(7)
O1 – W1 – C1	98.54(11)
O1 – W1 – O3	117.14(9)
O1 – W1 – O4	99.69(9)

Table S3. Crystallographic data for **[W(O)(CHC₆H₄-o-OMe)(OSi(OtBu)₃)₂(PPhMe₂)]**

[W(O)(CHC₆H₄-o-OMe)(OSi(OtBu)₃)₂(PPhMe₂)].C₆H₆	
Formula	C ₄₆ H ₇₉ O ₁₀ PSi ₂ W
Crystal size (mm)	0.35 × 0.20 × 0.09
cryst syst	Monoclinic
space group	P2 ₁ /c
volume (Å ³)	5263.9(2)
<i>a</i> (Å)	22.8961(6)
<i>b</i> (Å)	12.9575(3)
<i>c</i> (Å)	17.8940(4)
α (deg)	90
β (deg)	97.449(2)
γ (deg)	90
<i>Z</i>	4
formula weight (g/mol)	1063.09
density (g cm ⁻³)	1.341
F(000)	2208.0
temp (K)	100.1(2)
total no. reflections	65586
unique reflections [R(int)]	17664 [0.0720]
Final R indices [<i>I</i> > 2 σ (<i>I</i>)]	R ₁ = 0.0457, wR ₂ = 0.0742
Largest diff. peak and hole (e.Å ⁻³)	1.01/-1.18
GOF	1.049

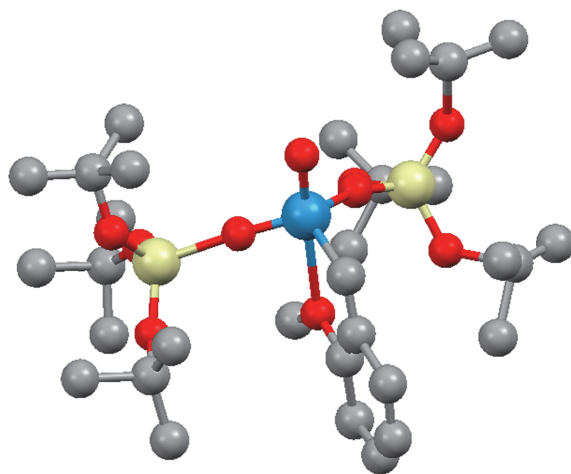


Figure S2. Structure plot of $[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-o-OMe})(\text{OSi}(\text{OtBu})_3)_2]$. 7 different crystals were measured but only data of relatively low quality could be acquired. However the data are of sufficient quality to unambiguously confirm the structure of the compound.

Table S4. Crystallographic data for $[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-o-OMe})(\text{OSi}(\text{OtBu})_3)_2]$

$[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-o-OMe})(\text{OSi}(\text{OtBu})_3)_2]$	
Formula	$\text{C}_{32}\text{H}_{62}\text{O}_{10}\text{Si}_2\text{W}$
Crystal size (mm)	$0.40 \times 0.35 \times 0.17$
cryst syst	Monoclinic
space group	$\text{P}2_1/\text{m}$
volume ($\text{\AA}^3$)	2107.3(10)
a ($\text{\AA}$)	9.505(3)
b ($\text{\AA}$)	26.354(4)
c ($\text{\AA}$)	9.567(2)
α (deg)	90
β (deg)	118.43(3)
γ (deg)	90
Z	1
formula weight (g/mol)	846.85
density (g cm^{-3})	1.521
$F(000)$	980.0
temp (K)	100.1(2)
total no. reflections	5975

unique reflections [R(int)]	4019 [0.0665]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1094$, $wR_2 = 0.2651$
Largest diff. peak and hole (e. $\text{\AA}^{-3}$)	2.70/-1.39
GOF	1.087

D) IR spectra.

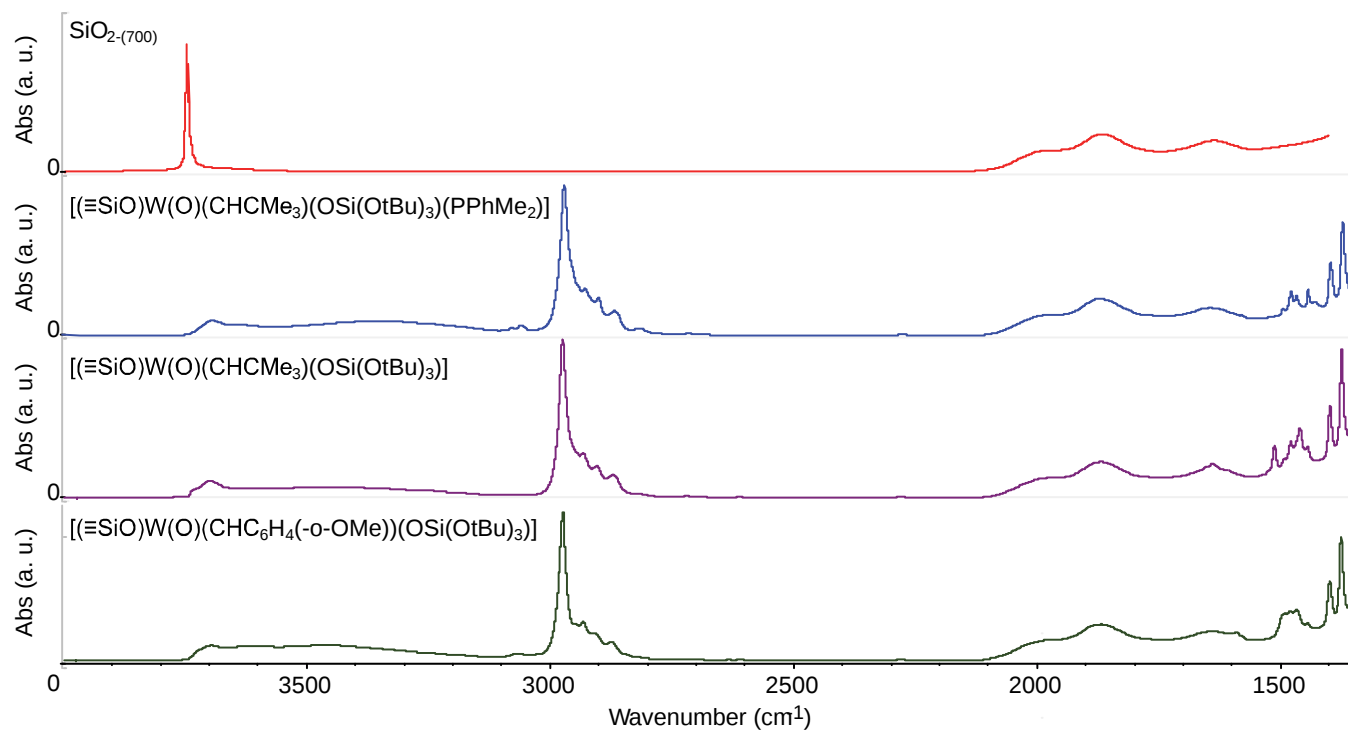


Figure S3. FTIR transmission spectra of **1-PMe₂Ph@SiO₂**, **1@SiO₂**, **2@SiO₂** and **SiO₂-(700)**

E) NMR spectra.

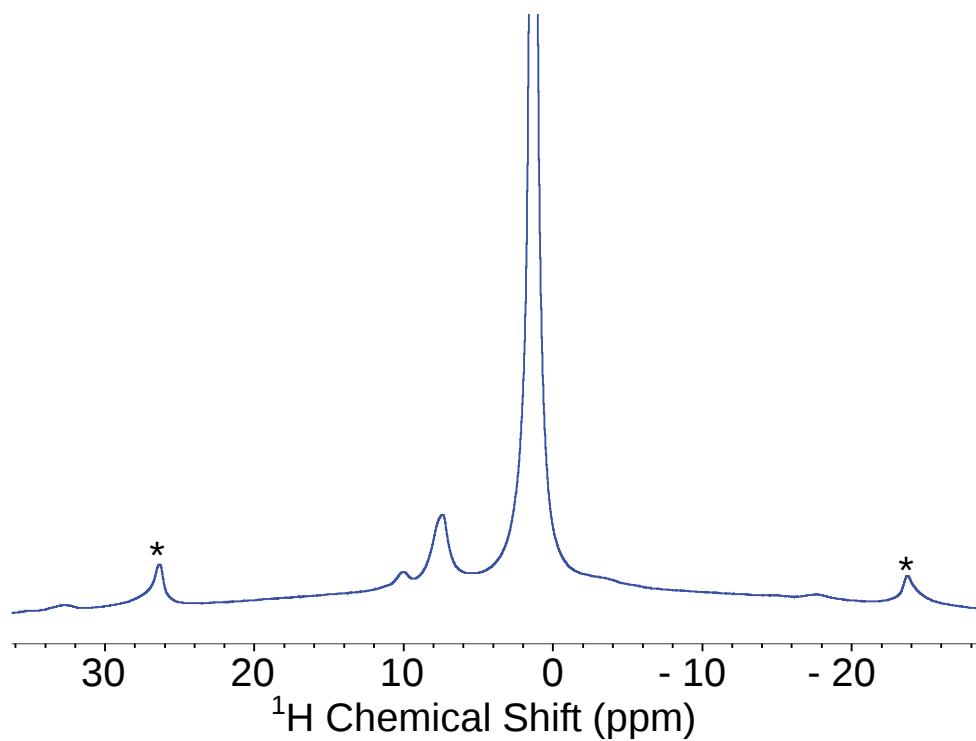


Figure S4. ^1H NMR spectrum (400 MHz, spinning rate 10 kHz, ns = 128) of **1-PPhMe₂@SiO₂** (*: spinning side bands).

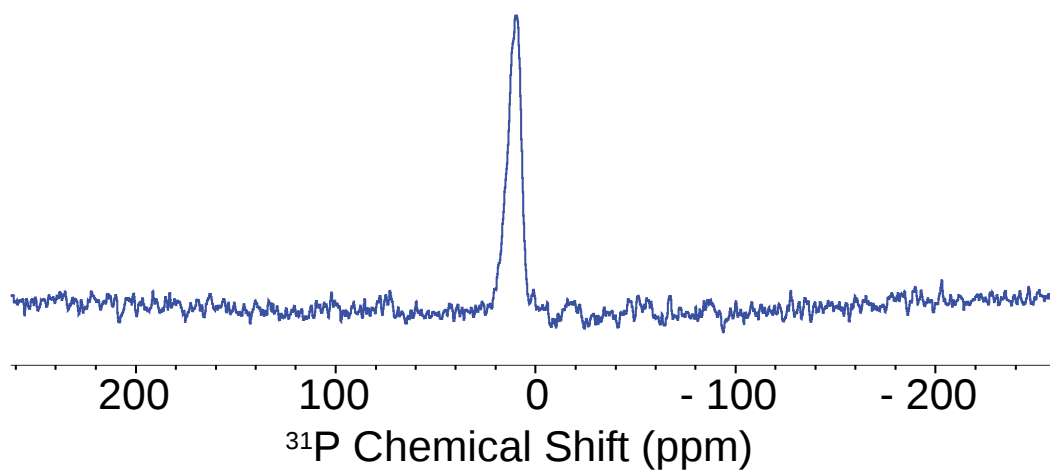


Figure S5. ^{31}P NMR spectrum (400 MHz, spinning rate 10 kHz) of **1-PPhMe₂@SiO₂**.

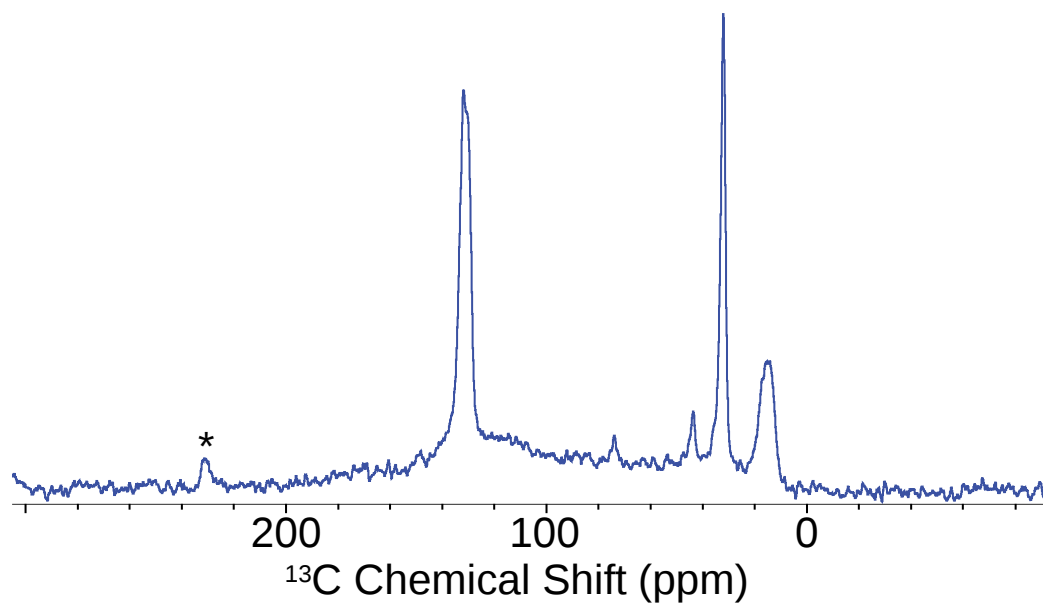
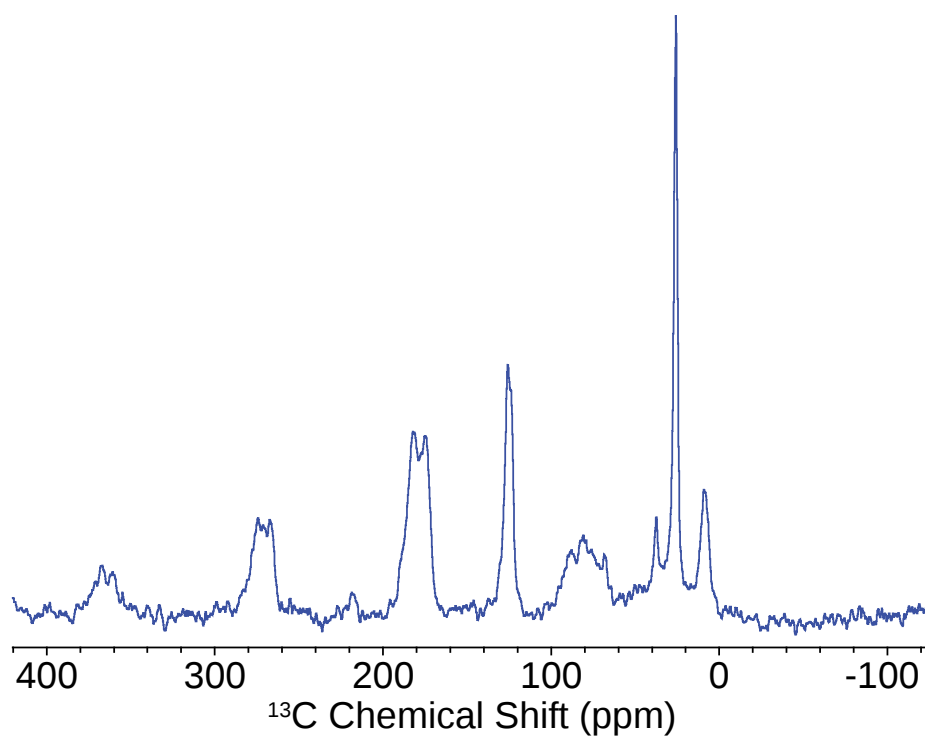


Figure S6. ^{13}C NMR spectrum (400 MHz, spinning rate 10 kHz, contact Time = 1 ms, recycle delay = 2 sec, ns = 80k) of **1-PPhMe₂@SiO₂**.

a)



b)

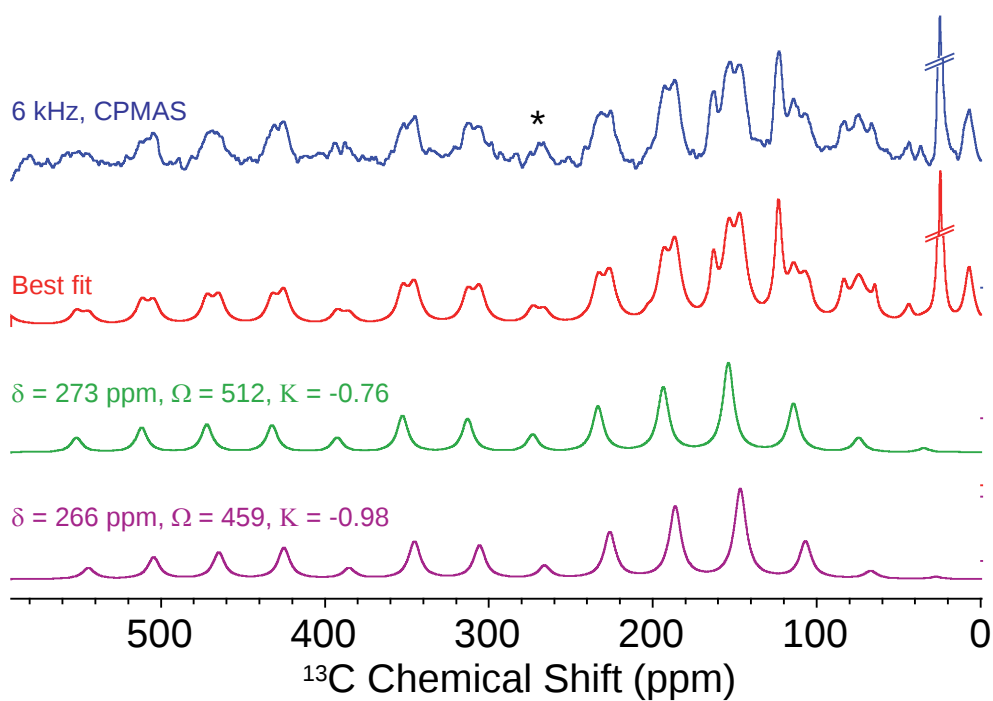


Figure S7. ^{13}C NMR spectrum of $1^*\text{-PPhMe}_2\text{@SiO}_2$ measured at 600 MHz. Spinning rate 14 kHz, contact Time = 1.2 ms, recycle delay = 2 sec, ns = 80k (a) and spinning rate 6 kHz, contact Time = 3 ms, recycle delay = 2 sec, ns = 50k (b).

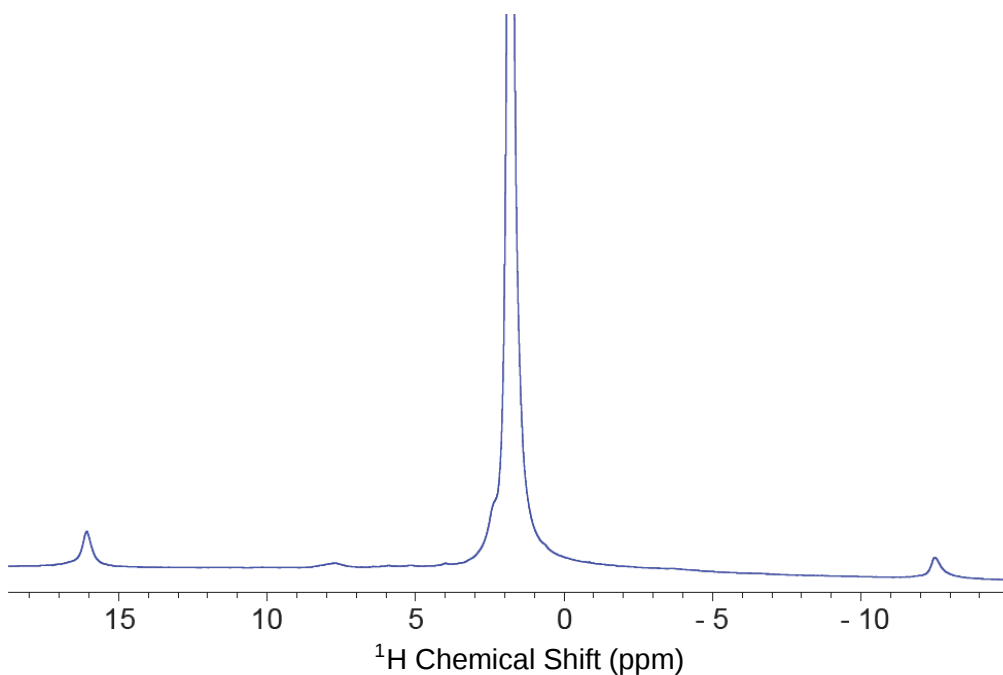


Figure S8. ^1H NMR spectrum (400 MHz, spinning rate 10 kHz, ns = 128) of 1@SiO_2 (*: spinning side bands).

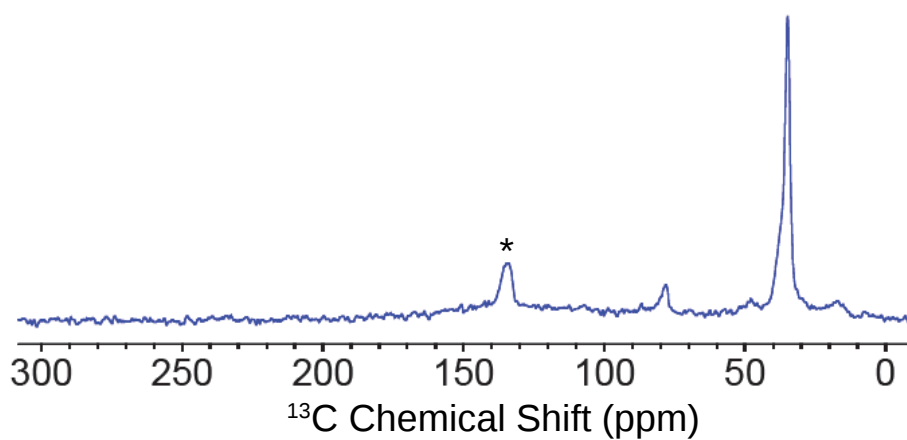


Figure S9. ^{13}C NMR spectrum (600 MHz, spinning rate 16 kHz, contact Time = 1ms, recycle delay = 2 sec, ns = 80k) of **1@SiO₂**.

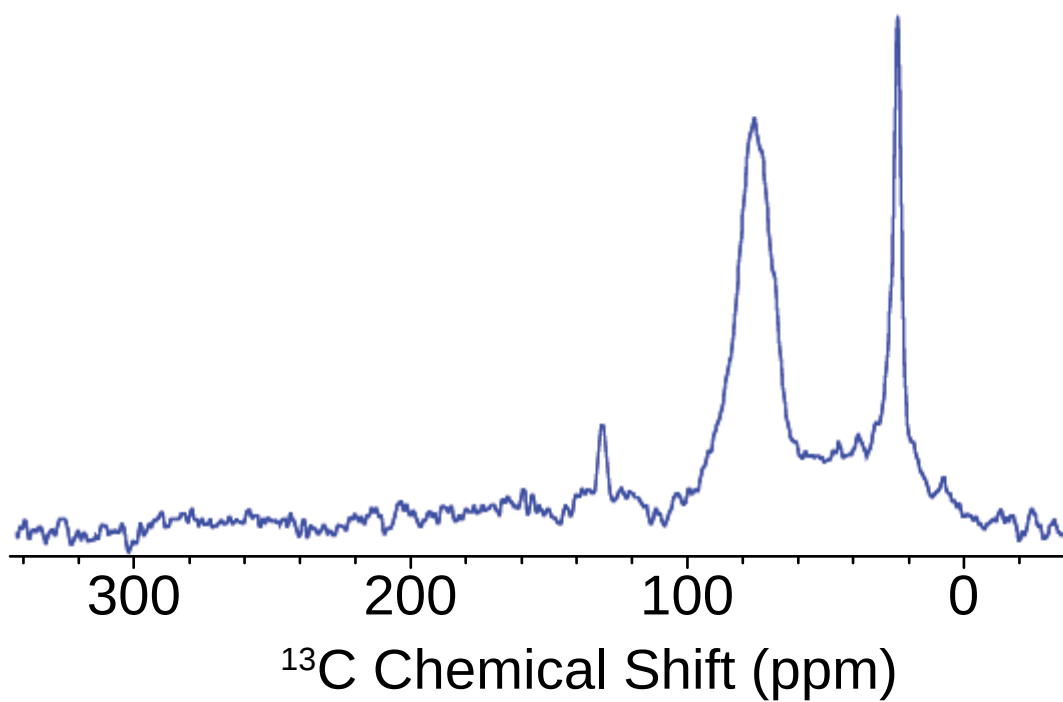


Figure S10. ^{13}C NMR spectrum (600 MHz, spinning rate 16 kHz, contact Time = 1.2 ms, recycle delay = 2 sec, ns = 90k) of **1*@SiO₂**.

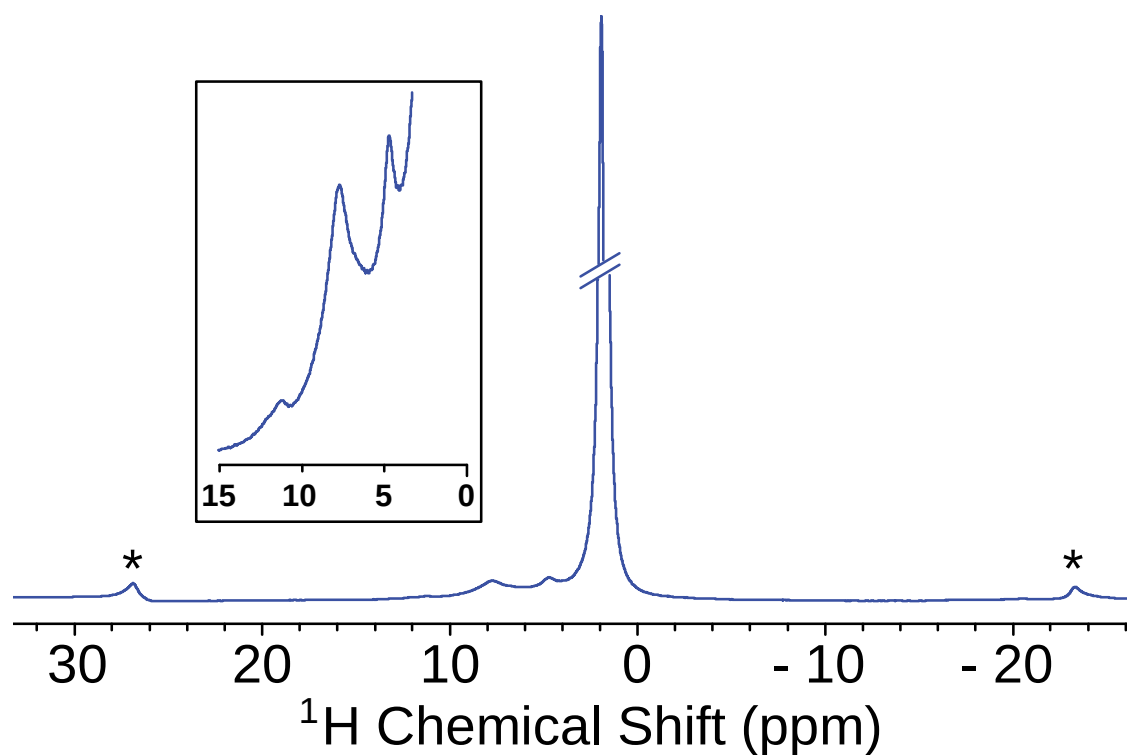


Figure S11. ^1H NMR spectrum (400 MHz, spinning rate 10 kHz, ns = 128) of $2@\text{SiO}_2$ (*: spinning side bands).

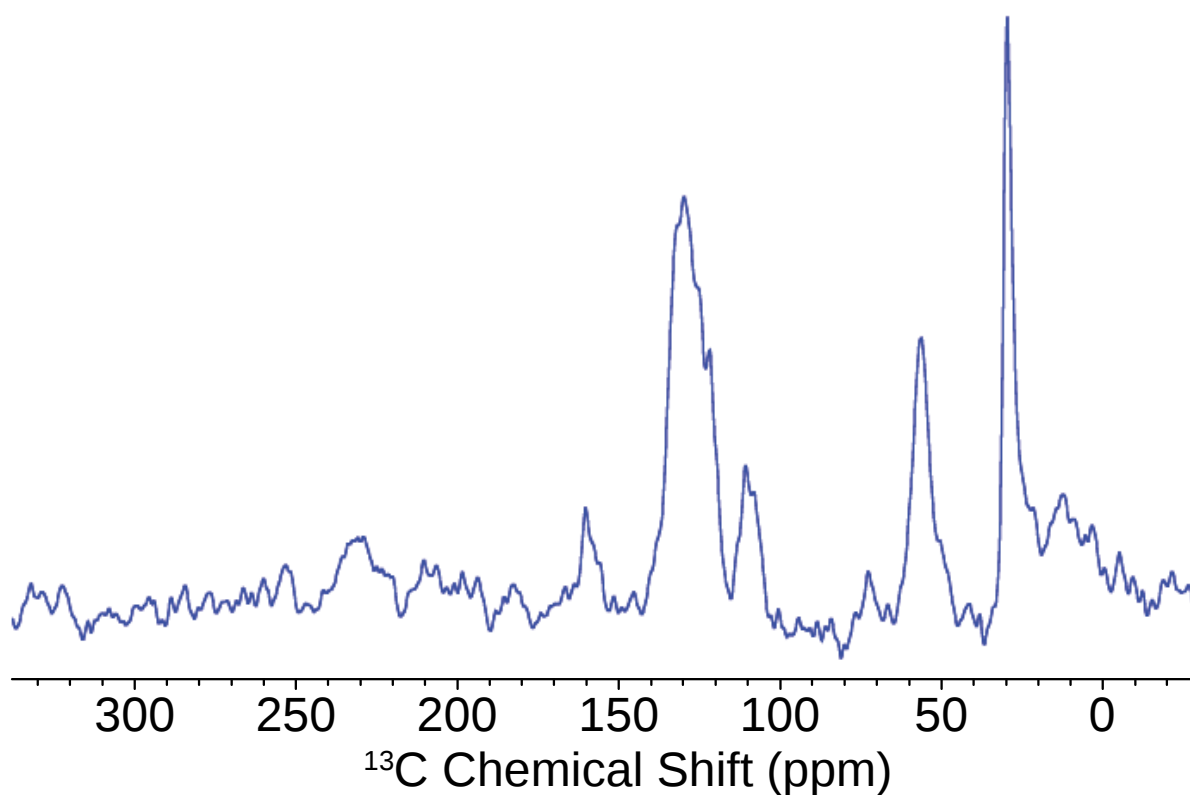


Figure S12. ^{13}C NMR spectrum (400 MHz, spinning rate 10 kHz, contact Time = 1 ms, recycle delay = 2 sec, ns = 80k) of $2@\text{SiO}_2$ (*: spinning side bands).

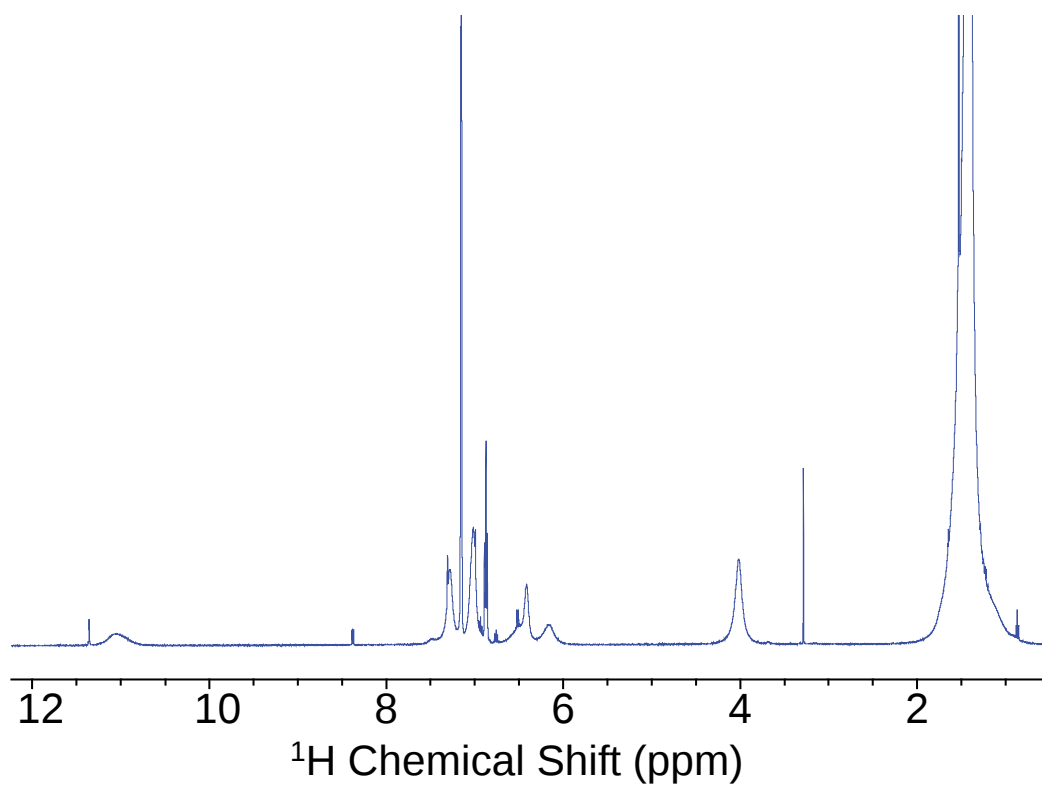


Figure S13. ^1H NMR spectrum (500 MHz) of 2- PMe_2Ph .

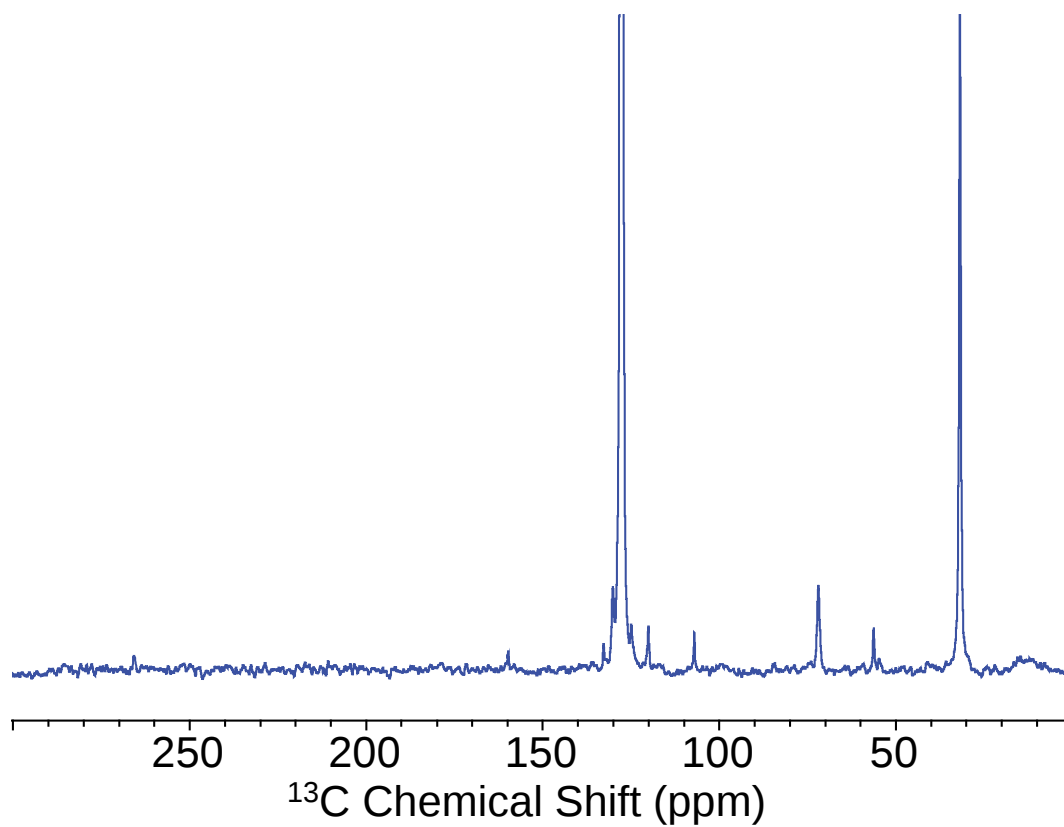


Figure S14. ^{13}C NMR spectrum (500 MHz) of 2- PMe_2Ph .

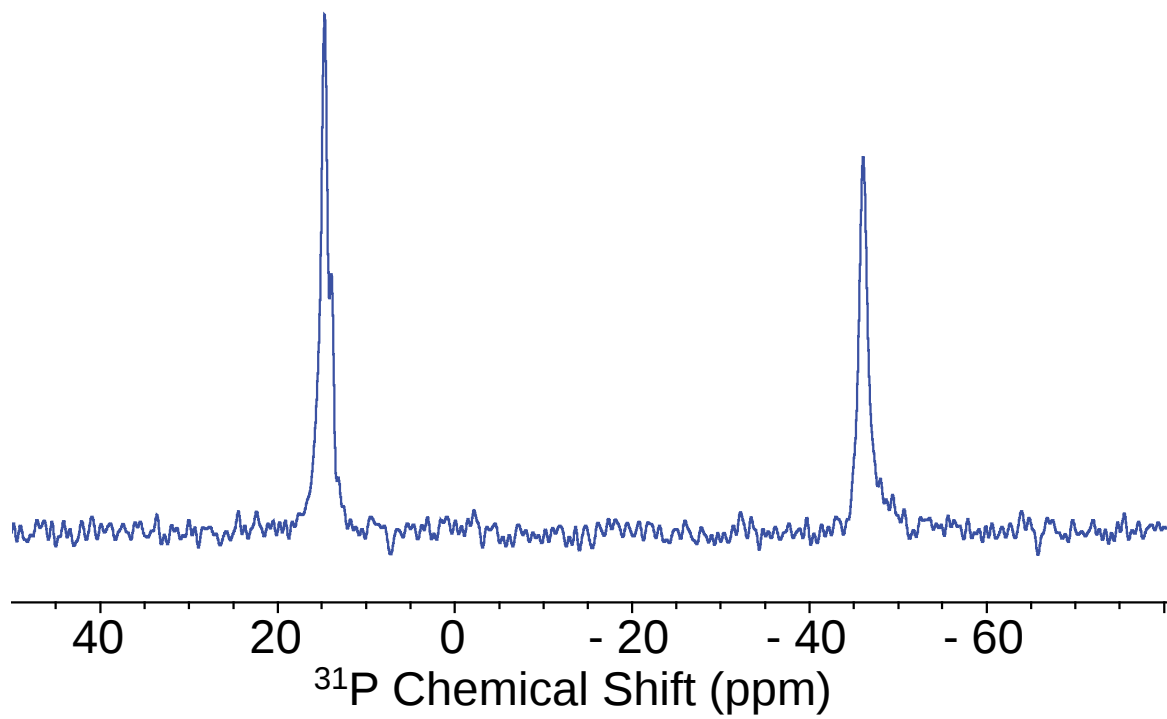


Figure S15. ^{31}P NMR spectrum (500 MHz) of 2-PMe₂Ph.

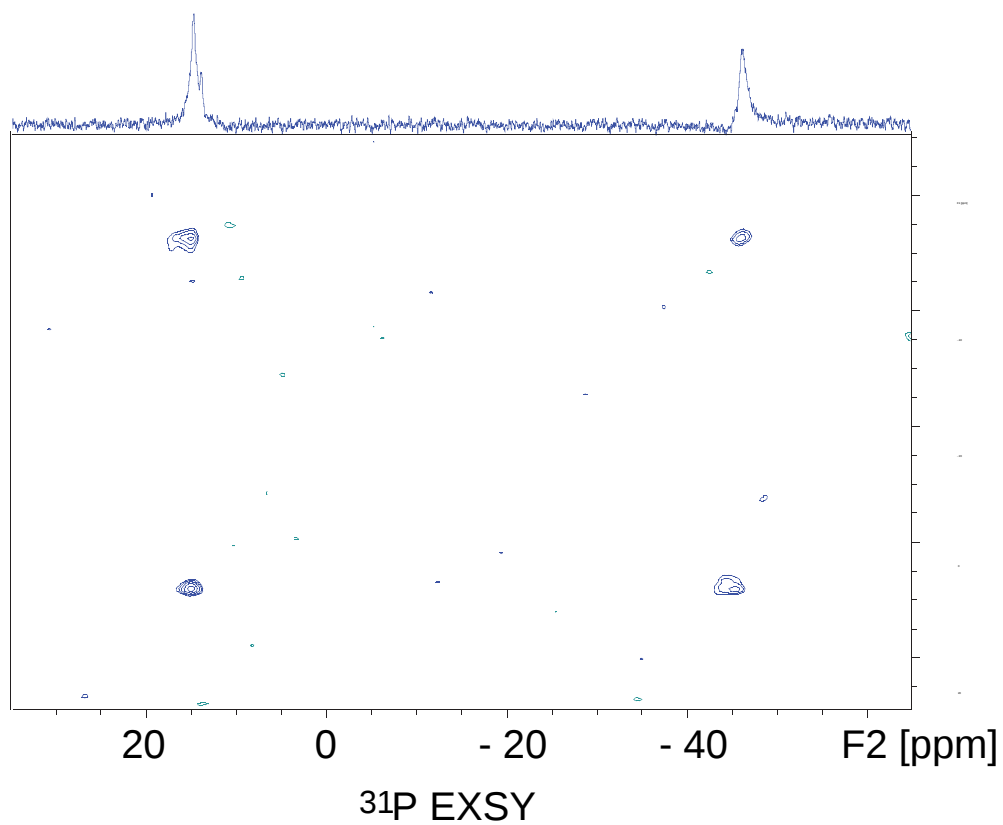


Figure S16. ^{31}P EXSY NMR spectrum (500 MHz) of 2-PMe₂Ph.

F) Analysis of 1@SiO₂

Analysis of the material by IR spectroscopy revealed a quantitative consumption of surface silanols, as indicated by the disappearance of the signal at 3747 cm⁻¹ together with the appearance of $\nu(\text{C-H})$ and $\delta(\text{C-H})$ vibrations (figure S3). However, mass balance analysis of the filtrate recovered after grafting revealed the release of only 0.3 equiv. of protonated silanolate ligand, indicating different grafting mechanism. ¹H MAS NMR of 1@SiO₂₋₍₇₀₀₎ presents a single peak at 1.45 ppm, corresponding to the tris-tert-butoxysilanolate ligand, but no clear signal of an alkylidene proton could be identified (see NMR section). ¹³C CP MAS NMR of the material presented two main signals at 35.1 and 77.8 ppm respectively corresponding to the quaternary and methyl carbons of the silanolate ligand, but no signal of an alkylidene carbon could be observed (Figure S9). 50% ¹³C labeled analogue, 1*¹³@SiO₂₋₍₇₀₀₎ displayed however a strong additional signal centered at 85 ppm, indicating the presence of a methylene carbon atom in the main species (W-CH₂tBu) (Figure S10). No alkylidene signature could be detected by solid state NMR. This information, combined with the mass balance analysis, confirmed the full protonation of the carbene moiety upon grafting.

G) Catalytic tests

Metathesis of cis-4-nonene:

A t=0, a 0.95 M solution of cis-4-nonene in toluene containing heptane as internal standard (0.1 M) was added to the catalyst introduced in a conical base vial containing a wing shaped magnetic stirred, and the reaction mixture was stirred at 600 rpm and kept at 30°C using an aluminum heating block. 10 μL aliquots of the solution were sampled, diluted with pure toluene (100 μL) and quenched by the addition of 1 μL of a 1 M solution of ethyl acetate in toluene. The resulting solution was analyzed by GC/FID (Agilent Technologies 7890 A) equipped with an HP-5 (Agilent Technologies) column. An error of $\pm 10\%$ was estimated for the analysis of a given metathesis reaction based on the reproducibility of data from duplicate and triplicate experiments. Conversion was determined from product formation that is without taking cis/trans isomerization of the substrate into consideration (eq. 1). In that case, equilibrium conversion is reached at ca. 50%.

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

Molecular precursors

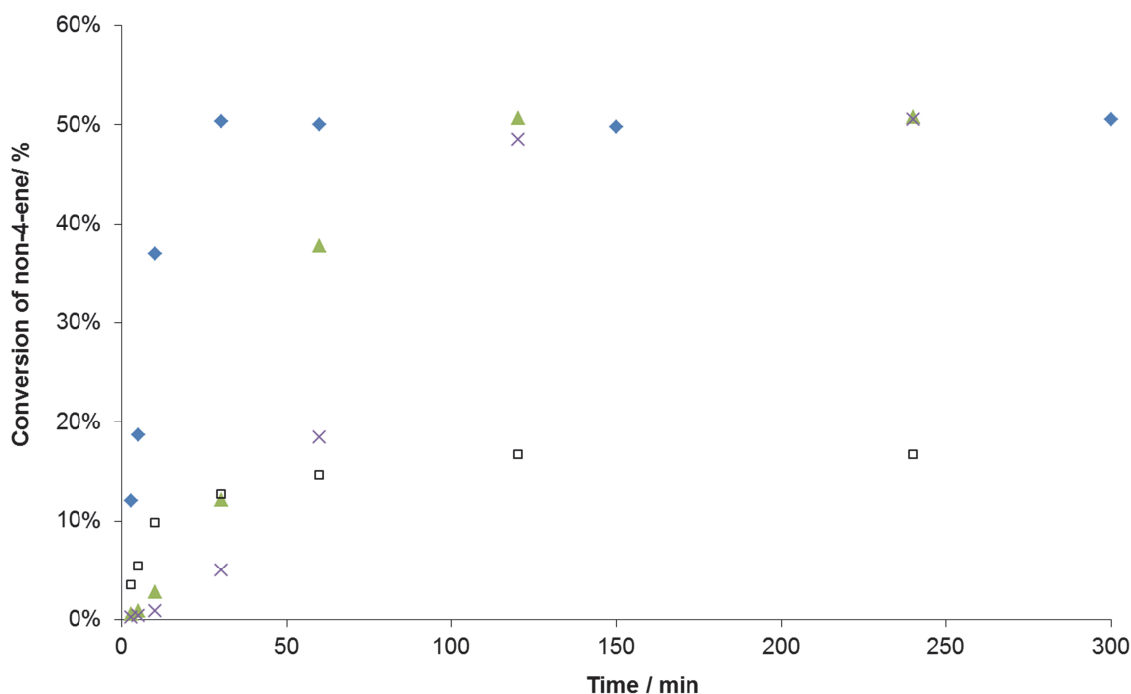


Figure S17. Metathesis of cis-4-nonene by the molecular precursors $[\text{W}(\text{O})(\text{CHtBu})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)]$ (Blue diamonds), $[\text{W}(\text{O})(\text{CHtBu})(\text{OSi}(\text{OtBu})_3)_2]$ (white squares) $[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-}o\text{-OMe})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)]$ (purple crosses) and $[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-}o\text{-OMe})(\text{OSi}(\text{OtBu})_3)_2]$ (green triangles) (0.1 mol%, 30°C)

Table S5. Metathesis of cis-4-nonene by the molecular precursors $[\text{W}(\text{O})(\text{CHtBu})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)]$, $[\text{W}(\text{O})(\text{CHtBu})(\text{OSi}(\text{OtBu})_3)_2]$ $[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-}o\text{-OMe})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)]$ and $[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-}o\text{-OMe})(\text{OSi}(\text{OtBu})_3)_2]$ (0.1 mol%, 30°C)

complex	TOF (min^{-1})	Time to equilibrium	Z:E ratio at 45% conversion
$[\text{W}(\text{O})(\text{CHtBu})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)]$	43	30 min	90/10
$[\text{W}(\text{O})(\text{CHtBu})(\text{OSi}(\text{OtBu})_3)_2]$	12	17% conversion after 24 h	-
$[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-}o\text{-OMe})(\text{OSi}(\text{OtBu})_3)_2(\text{PPhMe}_2)]$	1	180 min	85/15
$[\text{W}(\text{O})(\text{CHC}_6\text{H}_4\text{-}o\text{-OMe})(\text{OSi}(\text{OtBu})_3)_2]$	2	120 min	90/10

Supported complexes

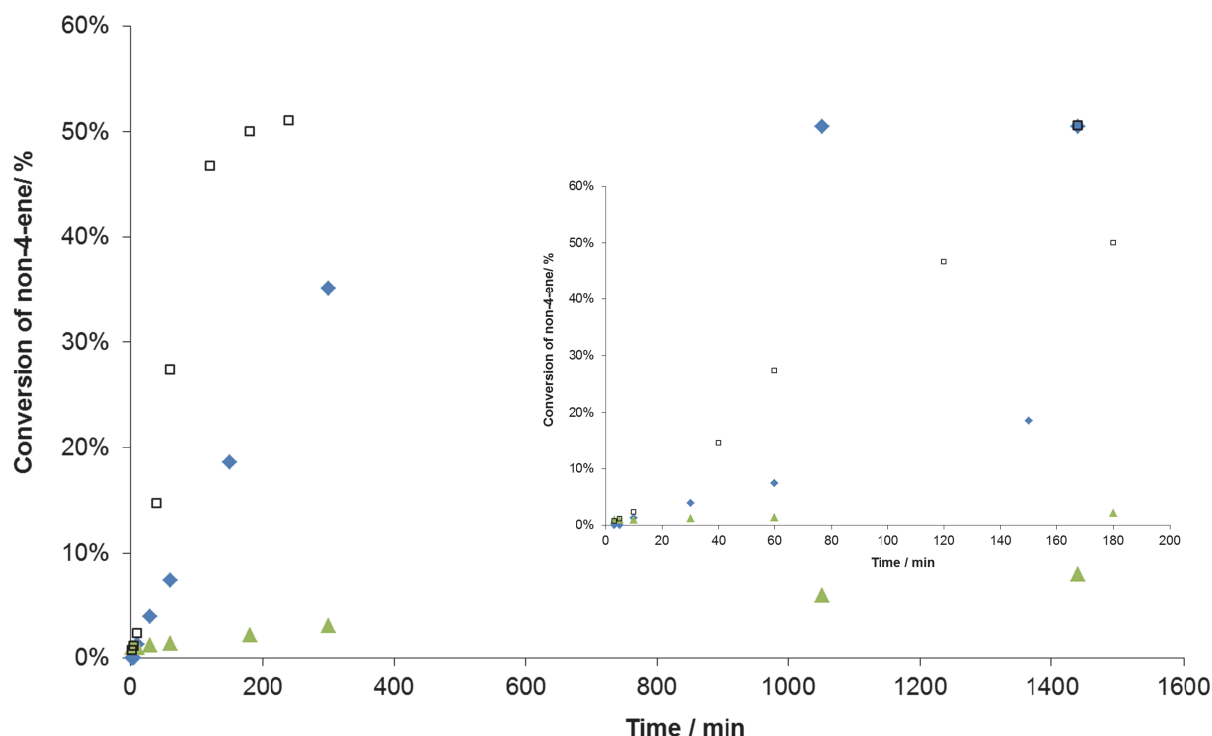


Figure S18. Metathesis of cis-4-nonene by complexes **1-PPhMe₂@SiO₂** (blue diamonds), **1@SiO₂** (green triangles) and **2@SiO₂** (White squares) (0.1 mol%, 30°C)

Table S6. Metathesis of cis-4-nonene by complexes **1-PPhMe₂@SiO₂**, **1@SiO₂**, **2@SiO₂** and **WO₃/SiO₂** (0.1 mol%, 30°C)

complex	TOF (min ⁻¹)	Time to equilibrium
1-PPhMe₂@SiO₂	<1	18 h
1@SiO₂	1	8 % conversion at 24h
2@SiO₂	2	3 h
WO₃/SiO₂	0	<1% conversion after 24h

H) References

- (1)Peryshkov, D. V.; Schrock, R. R. *Organometallics* **2012**, *31*, 7278-7286.
- (2)Conley, M. P.; Mougél, V.; Peryshkov, D. V.; Forrest, W. P.; Gajan, D.; Lesage, A.; Emsley, L.; Copéret, C.; Schrock, R. R. *J. Am. Chem. Soc.* **2013**, *135*, 19068-19070.
- (3)Ross-Medgaarden, E. I.; Wachs, I. E. *Journal of Physical Chemistry C* **2007**, *111*, 15089-15099.