

Reactivity differences between molecular and surface silanols in the preparation of homogeneous and heterogeneous olefin metathesis catalysts

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Abstract

The reaction of $\text{Mo}(\equiv\text{N})(\text{CH}_2t\text{Bu})_3$ (**1**) and $\text{SiO}_{2-(700)}$ generates $(\equiv\text{SiO})\text{Mo}(\equiv\text{NH})(\equiv\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$ (**2**) when performed in C_6H_6 (material $[\text{1/SiO}_{2-(700)}]_{\text{C}_6\text{H}_6}$). The grafting occurs presumably by protonation of the nitrido ligand to form an intermediate $(\equiv\text{SiO})\text{Mo}(\equiv\text{NH})(\text{CH}_2t\text{Bu})_3$ (**3**), a pentacoordinated complex, which decomposes into **2** and 2,2-dimethylpropane. While $[\text{1/SiO}_{2-(700)}]_{\text{C}_6\text{H}_6}$ is highly active in olefin metathesis, $[\text{1/SiO}_{2-(700)}]_{\text{CH}_2\text{Cl}_2}$ and $[\text{1/SiO}_{2-(700)}]_{\text{THF}}$ are poorly active or inactive catalysts respectively. In contrast, when $\text{Mo}(\equiv\text{N})(\text{CH}_2t\text{Bu})_3$ reacts with a molecular silanol derivative, a soluble model of the surface of $\text{SiO}_{2-(700)}$, it yields a very stable complex, $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiO-Mo}(\equiv\text{NH})(\text{CH}_2t\text{Bu})_3$ (**3m**), which does not spontaneously generate 2,2-dimethylpropane and an alkylidene complex in contrast to the surface complex. Moreover, **3m** does not catalyse olefin metathesis at room temperature as it does not already contain the initiating carbene ligand, and it is necessary to heat up the reaction mixture to 110 °C to obtain low catalytic activity. Nevertheless, the complex **3m** generates well-defined metallocarbenes when heated in the presence of PMe_3 : $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiO-Mo}(\equiv\text{N})(\equiv\text{CH}t\text{Bu})(\text{P}(\text{CH}_3)_3)_2$ (**4m**) as a 10:1 mixture of its *syn* and *anti* rotamers with the loss of 2 equiv. of 2,2-dimethylpropane.

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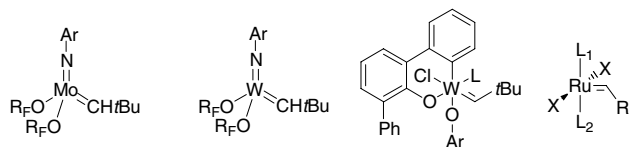
1. Introduction

Surface organometallic chemistry is aimed at generating well-defined active site precursors through the controlled reaction of an organometallic complex with an oxide support [1]. Since Herisson and Chauvin [2] pro-

posed that metallocarbenes were key intermediates in olefin metathesis, there has been a tremendous effort at preparing well-defined metallocarbenes as homogeneous catalyst precursors [3–14]. Of the different metals, Mo, W and Ru have emerged as the key elements to achieve highly active and selective catalysts. They can be classified in two different families. Mo- and W-based systems are typically d^0 metal complexes having a set of ligands which increases the electrophilicity of the metal centre, and Ru-based systems are d^4 metal complexes with basic

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Scheme 1. Examples of homogeneous olefin metathesis catalysts. $R_F = [(CF_3)_2(CH_3)C^-]$, $R = Ph$ or $CH=CMe_2$, $Ar =$ Aryl substituent, $L = OEt_2$ and $L_1/L_2 = PCy_3$ or NHC ligands.

ligands, which help the dissociation of one ligand to generate the active species (Scheme 1). In contrast, heterogeneous catalysts, which were historically the first olefin metathesis catalysts and which are still used in large scale industrial processes today [15], are usually metal oxides supported on an oxide support, typically silica, magnesia or alumina, for which the formation of the active sites is still unclear despite recent advances [16–19]. Within this area, we have been interested at preparing well-defined heterogeneous olefin metathesis catalysts by generating well-defined metallocarbenes supported on silica. Using this strategy, we have prepared and characterized $[(=SiO)Re(=CHtBu)(CH_2tBu)]$, probably the most active Re heterogeneous catalyst and of activity comparable to that of the best homogeneous Re-based catalysts [20]. In homogeneous catalysis, group 6 metals are usually more stable and more active. One of the best set of ligands has been discovered by Schrock et al. [3,4,21–25], and the corresponding complexes are imido alkoxy systems, $[(RO)_2Mo(=NR)(=CHtBu)]$. The closest well-defined surface organometallic complex is $[(=SiO)Mo(=NH)(=CHtBu)(CH_2tBu)]$, which was prepared by reaction of $[Mo(=N)(CH_2tBu)_3]$ (**1**) [26] and a silica partially dehydroxylated at 500 °C. However, it has only been prepared by sublimation in small quantities due to the thermal instability of **1** [27]. Its promising activities in olefin metathesis lead us to develop a preparation procedure for larger quantities, to investigate the synthesis of the corresponding molecular complex $[(RO)_3SiO-Mo(=NH)(=CHtBu)(CH_2tBu)]$, and to compare the corresponding surface *vs.* molecular complexes.

2. Experimental

2.1. General procedure

All experiments were carried out under dry and oxygen free Ar using either standard Schlenk or glovebox techniques for the organometallic synthesis. For the syntheses and the treatments of the surface species, reactions were carried out using high vacuum lines (1.34 Pa) and glovebox techniques. Silica (Aerosil Degussa, 200 m² g⁻¹) was compacted with distilled water, calcined at 500 °C under air for 2 h and treated under

vacuum (1.34 Pa) at 500 °C for 12 h and then at 700 °C for 4 h. In experiments requiring deuterated silica, a similar procedure was used, but after treatment under vacuum at 500 °C for 12 h, silica was contacted with D₂O (ca. 0.5 mL), heated at 80 °C for 30 min, treated under vacuum at 500 °C for 5 h (3–5 cycles) followed by a treatment under vacuum at 700 °C for 4 h (support referred to as deuterated SiO₂₋₍₇₀₀₎, 79–82% deuterated according to IR spectroscopy). $Mo(=N)(CH_2tBu)_3$ (**1**) was prepared according to the literature procedure [26]. $(c-C_5H_9)_7Si_7O_{12}SiOH$ (Aldrich, 99%) was dried under vacuum (1.34 Pa) at 60 °C for 12 h prior to use. Propene (N, Air Liquide) and H₂ (N, Air Liquide) were purified by passing them through R-3-11 BASF catalysts and 4 Å molecular sieves. Ethyl oleate (Aldrich, 99%) was purified according to the literature procedure [28]. 1-Octene (Aldrich, 99%) was distilled over Na under Ar prior to use. C₆H₆ was distilled from sodium benzophenone ketyl prior to use and stored over 3 Å molecular sieves. Hexane was distilled from NaK under N₂. Toluene was distilled from NaK under N₂ and stored over 3 Å molecular sieves. CH₂Cl₂ was distilled from P₂O₅ under N₂ and stored over 3 Å molecular sieves. THF was distilled from sodium benzophenone ketyl under N₂ prior to use. C₆D₆ was distilled from sodium benzophenone ketyl prior to use. Toluene-*d*₈ was dried over 3 Å molecular sieves prior to use. Octadecane (Aldrich, 99%) was used as received. Gas phase analysis was performed on a Hewlett–Packard 5890 series II gas chromatography (GC) apparatus equipped with a flame ionisation detector (FID) and a KCl/Al₂O₂ column (50 m × 0.32 mm). Liquid phase analysis was performed on a Hewlett–Packard 6890 series II GC apparatus equipped with a FID detector and an HP1 column (30 m × 0.32 mm). Products were identified by GC/MS (HP G1800A) equipped with a KCl/Al₂O₂ or an HP1 column. Elemental analyses were performed at the University of Bourgogne, Dijon (H, C and N) and at the SCA in Solaize (Mo).

Liquid state NMR spectra were recorded in C₆D₆ or toluene-*d*₈ as a solvent in a Young type NMR tube. ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on a Bruker AC 300 spectrometer at 300.18, 75.47 and 121.49 MHz, respectively, using the solvent as an internal standard for ¹H and ¹³C. For ³¹P NMR, a solution of H₃PO₄ 85% in H₂O was used as an external standard. ¹³C, ¹⁵N and ²⁹Si{¹H} NMR spectra were recorded on a DRX-500 spectrometer at 115.78, 50.69 and 99.36 MHz, respectively. ¹H–¹⁵N 2D HMBC experiment was recorded with the standard Bruker inv4gplrnd sequence and processed in absolute mode (D6 = 100 ms, Gradient = 70–30–50). External NH₃ was used as a reference for ¹⁵N NMR. ¹H–¹³C 2D HSQC experiment was recorded without ¹H decoupling with the standard Bruker invietgs sequence and processed in phase mode (Gradient = 20–20–10). ¹H MAS (number of scans = 8, 90°

proton pulse length = 3.0 μ s, recycle delay = 2 s) solid state NMR spectra were recorded on a Bruker Avance 500 spectrometer with a conventional double resonance 4 mm CP-MAS probe. The rotation frequency was set to 10 kHz. The samples were introduced in a zirconia rotor in the glove box and tightly close with a kel-f cap. Chemical shifts are reported in ppm downfield from SiMe₄, and coupling constants are reported in Hz. ESR spectra were recorded on Varian E9 spectrometer at 77 K against DPPH ($H_o = 329.5$ mT, $g = 2.0036$). The samples were introduced in a quartz tube in the glove box and sealed under vacuum. Titration of Mo^(V) d^1 was performed by using VO(SO₄)₂ as a standard for d^1 system, (35.5 mg, V (wt%) = 3.52, 24.4 μ mol, $H = 334.2$ mT, $g = 1.975$). Mass spectra (ESI⁺) were recorded on a ThermoFinnigan LCQ Advantage instrument.

2.2. Preparation of surface organometallic complexes

2.2.1. Grafting of Mo(\equiv N)(CH₂tBu)₃ on a silica disk partially dehydroxylated at 700 °C (SiO₂₋₍₇₀₀₎) by impregnation in a solvent, and monitoring by in situ IR spectroscopy

2.2.1.1. General procedure.

Preparation of [1/SiO₂₋₍₇₀₀₎]_{C₆H₆}.

Silica (55 mg) was pressed into an 18 mm self-supporting disk, and it was introduced in an IR cell equipped with CaF₂ windows. After calcination at 500 °C under air for 2 h, and treatment under vacuum (1.34 Pa) at 500 °C for 12 h followed by a treatment at

700 °C for 4 h, the silica disk was then immersed into a C₆H₆ solution (12 mL) of **1** (28 mg, 0.087 mmol) at 25 °C. After 4 h of reaction in the dark followed by three C₆H₆ washing cycles and a drying step under dynamic vacuum (1.34 Pa) at 25 °C for 2 h, an IR spectrum was recorded (see Fig. 1, vide infra): 3722 (ν (OH)), 3396 (ν (NH)), 2958, 2906, 2869, 2827, 2713 (ν (CH)), 1473 (δ (NH)), 1463, 1363 cm⁻¹ (δ (CH)).

Preparation of [1/SiO₂₋₍₇₀₀₎]_{CH₂Cl₂}.

The same procedure was used as described above for which SiO₂₋₍₇₀₀₎ (37 mg) and a CH₂Cl₂ solution (12 mL) of **1** (20 mg) were used. IR for [1/SiO₂₋₍₇₀₀₎]_{CH₂Cl₂} (see Figure S1 in the Supplementary Material). IR for [1/SiO₂₋₍₇₀₀₎]_{CH₂Cl₂}: 3712 (ν (OH)), 3396, 3366 (ν (NH)), 2958, 2906, 2869, 2827 (ν (CH)), 1473 (δ (NH)), 1463, 1363 cm⁻¹ (δ (CH)).

2.2.2. Grafting of Mo(\equiv N)(CH₂tBu)₃ on SiO₂₋₍₇₀₀₎ by impregnation in a solvent

2.2.2.1. General procedure.

Preparation of [1/SiO₂₋₍₇₀₀₎]_{C₆H₆}.

A mixture of **1** (82 mg, 0.26 mmol) and SiO₂₋₍₇₀₀₎ (1.01 g, 0.27 mmol OH) in C₆H₆ (4 mL) was stirred at 25 °C for 4 h in the dark. All volatile compounds were then condensed in a reactor of known volume to quantify the 2,2-dimethylpropane released during grafting, and then C₆H₆ (25 mL) was distilled on the resulting solid to wash the excess of complex. After three washing cycles, the resulting brown solid [1/SiO₂₋₍₇₀₀₎]_{C₆H₆} (1.02 g) was dried under vacuum (1.34 Pa) at 25 °C for

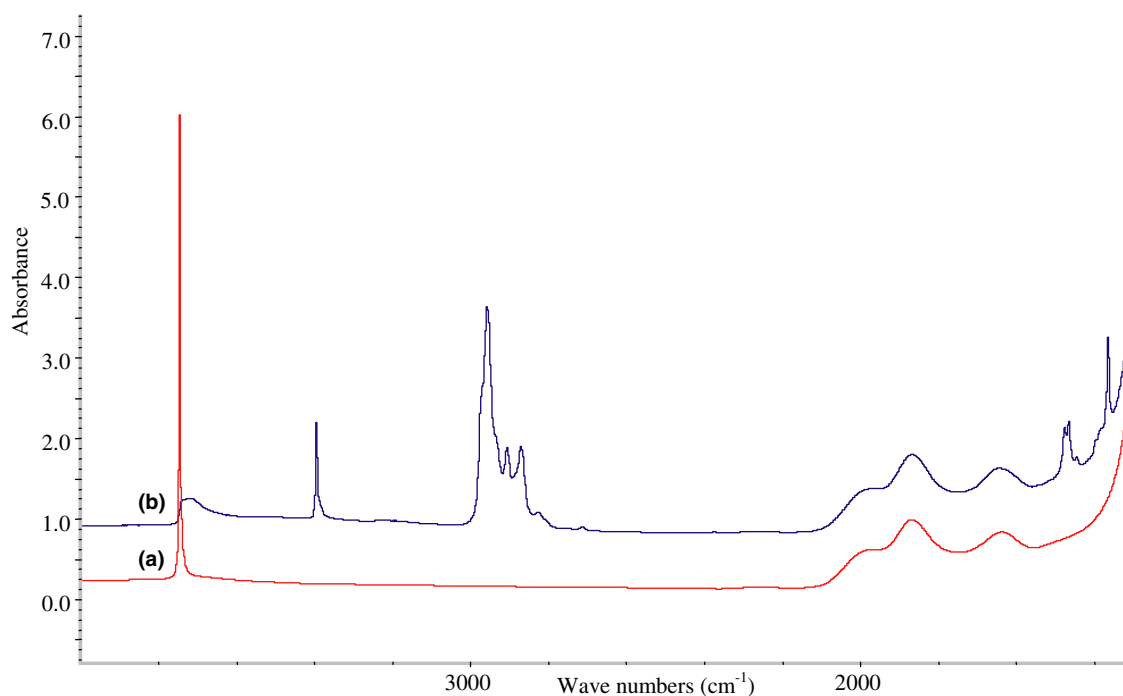


Fig. 1. Grafting of **1**, Mo(\equiv N)(CH₂tBu)₃, on a silica partially dehydroxylated at 700 °C, SiO₂₋₍₇₀₀₎, monitored by IR spectroscopy: (a) A silica disk of SiO₂₋₍₇₀₀₎ (55 mg). (b) The silica disk after grafting of **1** (28 mg) in C₆H₆.

1 h 30. Analysis by GC indicated the formation of 0.171 mmol of 2,2-dimethylpropane during grafting (1.0 *t*BuCH₃/Mo). Solid state NMR: $\delta_{\text{H}} = 1.1$ (CH₂(CH₃)₃), 2.1 (CH₂C(CH₃)₃). ESR: $H_0 = 333.9$ mT, $g = 1.977$ (27.0 mg, 4.47 μmol , 2.4% of total Mo). Elemental Anal. Found: C, 1.91; Mo, 1.59 wt% (9.6 C/Mo).

Preparation of [1/SiO₂₋₍₇₀₀₎]CH₂Cl₂.

A mixture of **1** (98 mg, 0.30 mmol) and SiO₂₋₍₇₀₀₎ (0.87 g, 0.24 mmol OH) in CH₂Cl₂ (15 mL) was stirred at 25 °C for 4 h in the dark. After filtration, the lightly colored solid was washed three times with CH₂Cl₂ and all volatiles were then condensed in a reactor of known volume to quantify the 2,2-dimethylpropane released during grafting. The resulting white solid was then dried under vacuum (1.34 Pa) at 25 °C for 30 min to yield 0.93 g of **2**CH₂Cl₂. Analysis by GC indicated the formation of 0.104 mmol of 2,2-dimethylpropane during grafting (0.8 *t*BuCH₃/Mo). Solid state NMR: $\delta_{\text{H}} = 0.8$ (CH₂(CH₃)₃), 2.2 (CH₂C(CH₃)₃), 4.0 (CH₂Cl₂). Elemental Anal. Found: C, 2.44; Mo, 1.43; Cl, 0.51 wt% (13.6 C/Mo, 1 Cl/Mo).

Preparation of [1/SiO₂₋₍₇₀₀₎]THF.

A mixture of **1** (99 mg, 0.31 mmol) and SiO₂₋₍₇₀₀₎ (0.85 g, 0.23 mmol OH) in THF (10 mL) was stirred at 25 °C for 4 h in the dark. After filtration, the white solid was washed three times with THF, and all volatiles were then condensed in a reactor of known volume. The resulting white solid was then dried under vacuum (1.34 Pa) at 25 °C for 1 h to yield 0.77 g of [1/SiO₂₋₍₇₀₀₎]THF. Analysis by GC showed that no 2,2-dimethylpropane was released during grafting (<0.01 *t*BuCH₃/Mo). Solid state NMR: $\delta_{\text{H}} = 0.9$ (CH₂(CH₃)₃), 1.8 (THF), 2.2 (CH₂C(CH₃)₃), 3.6 (THF). Elemental Anal. Found: Mo, 0.45 wt%.

2.2.3. Carbon analysis by treatment under H₂ of materials [1/SiO₂₋₍₇₀₀₎]

Solid [1/SiO₂₋₍₇₀₀₎]_{C₆H₆} (41 mg, 6.8 μmol Mo, 1.59 wt% Mo) was contacted with H₂ in a 472 mL reactor (550 Torr, 14.64 mmol). The reaction mixture was heated for 12 h at 150 °C, followed by 12 h at 250 °C and 12 h at 350 °C. Analysis by GC indicated the formation of 8.8 C/Mo (1.8 *t*BuCH₃/Mo) as a mixture of all alkanes (C₁–C₅).

2.3. Catalytic test for olefin metathesis with [1/SiO₂₋₍₇₀₀₎]solvent

2.3.1. Metathesis of propene on [1/SiO₂₋₍₇₀₀₎]_{C₆H₆}

2.3.1.1. General procedure (R = 780). Solid [1/SiO₂₋₍₇₀₀₎]_{C₆H₆} (38 mg, 6.3 μmol , 1.59 wt% Mo) was contacted with propene (200 Torr, 4.95 mmol, 780 equiv.) purified over R3-11 BASF catalyst/MS4A in a 472 mL reactor at 25 °C. Small aliquots were analysed by GC over time.

2.3.2. Metathesis of propene on [1/SiO₂₋₍₇₀₀₎]CH₂Cl₂

The same experimental procedure was used as described above in which [1/SiO₂₋₍₇₀₀₎]_{CH₂Cl₂} (42 mg, 6.3 mol, 1.43 wt% Mo) was used in place of [1/SiO₂₋₍₇₀₀₎]_{C₆H₆}.

2.3.3. Metathesis of propene on [1/SiO₂₋₍₇₀₀₎]THF

The same experimental procedure was used as described above in which [1/SiO₂₋₍₇₀₀₎]_{THF} (135 mg, 6.3 mol, 0.45 wt% Mo) was used in place of [1/SiO₂₋₍₇₀₀₎]_{C₆H₆}.

2.3.4. Metathesis of propene for substrate to catalyst ratio (R = 13000)

Solid [1/SiO₂₋₍₇₀₀₎]_{C₆H₆} (8 mg, 1.3 μmol Mo, 1.59 wt% Mo) was contacted at 25 °C with propene (720 Torr, 17.7 mmol, 13000 equiv.) purified over R3-11 BASF catalyst/MS4A in a 472 mL reactor. Small aliquots were analysed by GC over time.

2.3.5. Metathesis of propene purified by MnO/SiO₂ (R = 13000)

Solid [1/SiO₂₋₍₇₀₀₎]_{C₆H₆} (8 mg, 1.3 μmol Mo, 1.59 wt% Mo) was contacted at 25 °C with propene (720 Torr, 17.7 mmol, 13000 equiv.) purified over R3-11 BASF catalyst/MS4A and then over MnO/SiO₂ in a 472 mL reactor. Small aliquots were analysed by GC over time.

2.3.6. Metathesis of propene purified by MnO/SiO₂ (R = 185000)

Solid [1/SiO₂₋₍₇₀₀₎]_{C₆H₆} (8 mg, 1.3 μmol Mo, 1.59 wt% Mo) was contacted with propene (720 Torr, 0.25 mol, 185000 equiv.) purified over R3-11 BASF catalyst/MS4A and then over MnO/SiO₂ in a 6 L reactor. Small aliquots were analysed by GC over time.

2.3.7. Metathesis of liquid olefins with 2

2.3.7.1. General procedure.

Metathesis of 1-octene with [1/SiO₂₋₍₇₀₀₎]_{C₆H₆}.

A solution of known concentration of 1-octene (1.6 M, 1.6 mL, 4.59 mmol, 1300 equiv.) in toluene containing octadecane as an internal standard was freshly prepared, degassed with three freeze-pump-thaw cycles, and dried over freshly 3 Å activated molecular sieves. The solid [1/SiO₂₋₍₇₀₀₎]_{C₆H₆} (27 mg, 4.5 μmol Mo, 1.59 wt% Mo) was placed in a 5 mL batch reactor equipped with a magnetic stirring bar, and the reactor was closed with a cap equipped with a Teflon-septum. At $t = 0$, the solution was added at 25 °C under vigorous stirring via a syringe through the septum, and small aliquots (1–2 drops) were sampled, diluted in pure solvent (0.5 mL) and analysed by GC.

Metathesis of 1-octene with [1/SiO₂₋₍₇₀₀₎]CH₂Cl₂.

The same experimental procedure was used as described above: 1.6 M solution of 1-octene (1.6 mL,

4.59 mmol, 1300 equiv.), octadecane (16 mg, 6.0 μmol) and $2\text{CH}_2\text{Cl}_2$ (30 mg, 4.5 μmol Mo, 1.43 wt% Mo).

Metathesis of ethyl oleate (100 equiv.) with [I/SiO₂-(700)]C₆H₆.

The same experimental procedure was used as described above with ethyl oleate in place of 1-octene: a 0.123 M solution of ethyl oleate (3.5 mL, 0.43 mmol, 100 equiv.), octadecane (16 mg, 6.0 μmol) and [I/SiO₂-(700)]C₆H₆ (26 mg, 4.3 μmol Mo, 1.59 wt% Mo).

Metathesis of ethyl oleate (2000 equiv.) with [I/SiO₂-(700)]C₆H₆.

The same experimental procedure was used as described above: a 0.94 M solution of ethyl oleate (3.5 mL, 3.38 mmol, 2000 equiv.), octadecane (156 mg, 58.5 μmol) and $2\text{C}_6\text{H}_6$ (10 mg, 1.7 μmol Mo, 1.59 wt%).

2.4. Preparation and reactivity of molecular organometallic complexes

2.4.1. Reaction of Mo($\equiv\text{N}$)(CH₂tBu)₃ (1) with (c-C₅H₉)₇Si₇O₁₂SiOH

2.4.1.1. Formation of (c-C₅H₉)₇Si₇O₁₂SiO–Mo($\equiv\text{NH}$)(CH₂tBu)₃ (3m). A suspension of Mo($\equiv\text{N}$)(CH₂tBu)₃ (173 mg, 0.53 mmol) and (c-C₅H₉)₇Si₇O₁₂SiOH (497 mg, 0.54 mmol) in C₆H₆ (5 mL) was stirred at room temperature for 16 h. After filtration, the solvent was removed in vacuo yielding a brown powder (508 mg, 0.41 mmol, 76%). δ_{H} (C₆D₆) = 1.14 (s, [Mo](CH₂(C(CH₃)₃)₃), 27H), 1.23–1.37 (m, c-CH(CH₂)₄, 7H), 1.56–2.07 (m, c-CH(CH₂)₄, 56H), 2.39 (s, [Mo](CH₂(C(CH₃)₃)₃), 6H), 3.36 (s, [Mo]($\equiv\text{NH}$), 1H). δ_{C} (C₆D₆) = 22.8, 23.2, 27.4, 27.5, 27.9, 28.1, 32.7 ([Mo](CH₂(C(CH₃)₃)₃)), 34.9 ([Mo](CH₂(C(CH₃)₃)₃)), 84.2 ([Mo](CH₂(C(CH₃)₃)₃)). δ_{N} (C₆D₆) = 338.8. ^1H – ^{15}N 2D HMBC: δ_{N} (C₆D₆) = 338.8 (d, $^1J_{\text{H}-^{15}\text{N}}$ = 68.5 Hz). δ_{Si} (C₆D₆) = –105.11 (Q³, 1Si), –65.72 (T³, 3Si), –65.68 (T³, 1Si), –65.63 (T³, 3Si). Mass spectrometry ESI(CH₃CN matrix), *m/z* calculated for C₅₀H₉₇MoNO₁₃Si₈ = 1240.93, found: 1240 (100; [M – H][–]); 1168 (10; [M – H – C₅H₁₂][–]). Elemental Anal. Calc. for C₅₀H₉₇MoNO₁₃Si₈: C, 48.39; H, 7.88; Mo, 7.73; N, 1.13; Si, 18.11. Found C, 48.03; H, 6.20; Mo, 7.43; N, 1.21; Si, 18.47. IR (nujol): 3375 (ν(NH)), 1241, 1118, 1041, 908 cm^{–1}.

2.4.1.2. Single crystal X-ray experiments. Suitable single crystals for X-ray diffraction study were grown from a saturated solution of **3m** in hexane cooled at –30 °C. C₅₀H₉₇MoNO₁₃Si₈, *M_r* = 1240.95, colorless plate (0.20 × 0.56 × 0.71 mm³), triclinic, *P*₁ (No.: 2), *a* = 13.9353(1) \AA , *b* = 14.4781(1), *c* = 17.5167(1) \AA , α = 84.0715(5)°, β = 77.9965(5)°, γ = 88.5791(3)°, *V* = 3438.33(4) \AA^3 , *Z* = 2, *d*_{calc} = 1.199 g cm^{–3}, *F*₀₀₀ = 1324, μ Mo K α = 0.381 mm^{–1}. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3 κ -CCD) at the window of a

rotating anode (NONIUS, FR591) and graphite monochromated Mo K α radiation (λ = 0.71073 \AA). The unit cell parameters were obtained by full-matrix least-squares refinement of 12399 reflections [29]. Data collection were performed at 123 K within a θ -range of 1.2° < θ < 25.2°. Nine data sets were measured in rotation scan modus with $\Delta\phi/\Delta\omega$ = 1.0°. A total of 82454 intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects [30]. After merging (*R*_{int} = 0.064), 12400 [10805: *I*_o > 2 σ (*I*_o)] independent reflections remained and all were used to refine 681 parameters. The refinements converged with *R*1 = 0.0388 [*I*_o > 2 σ (*I*_o)], *wR*2 = 0.0930, and *GOF* = 1.04. The final difference-Fourier map showed no striking feature ($\Delta e_{\text{min/max}}$ = +0.73/–0.57 e \AA^{-3}). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography [31]. All calculations were performed with the STRUX-V [32] system including the programs PLATON [33], SIR92 [34], and SHELXL-97 [35].

2.4.2. Thermal stability of 3m in the absence of 1-octene at 60 °C

In a NMR tube, a light yellow solution of **3m** (21 mg, 0.017 mmol) in C₆D₆ (0.5 mL) was heated at 60 °C for 4 days, and no evolution in the spectrum of **3m** was observed during that time as monitored by ¹H NMR spectroscopy.

2.4.3. Thermal stability of 3m in the absence of 1-octene at 110 °C

In a NMR tube, a light yellow solution of **3m** (25 mg, 0.020 mmol) in toluene-*d*₈ (0.4 mL) was heated at 110 °C, and the reaction was monitored by ¹H NMR spectroscopy. 2,2-Dimethylpropane was slowly formed over time, and after 4 days, it was the major product along with numerous unidentified Mo species.

2.4.4. Thermal stability of 3m in the presence of 1-octene

To a NMR tube containing a light yellow solution of **3m** (32 mg, 0.026 mmol) in toluene-*d*₈ (0.4 mL) was added 1-octene (50 μL , 0.318 mmol, 12 equiv.). The reaction mixture was heated at various temperatures for 2 h. No reaction was observed at 25, 60 and 80 °C according to ¹H NMR spectroscopy. Heating the sample to 110 °C for 4 h shows the disappearance of 1-octene and the formation of ethylene and 7-tetradecene according to ¹H and ¹³C{¹H} NMR and GC analysis.

2.4.5. Thermal stability of 3m in the presence of PMe₃: formation of (c-C₅H₉)₇Si₇O₁₂SiO–Mo($\equiv\text{N}$)(=CHtBu)(P(CH₃)₃)₂ (4m)

P(CH₃)₃ (170 μmol , 10 equiv.) was condensed into an NMR tube containing a solution of (c-C₅H₉)₇Si₇O₁₂–

SiO–Mo(=NH)(CH₂*t*Bu)₃ (20 mg, 17 μmol) in C₆D₆ (0.5 mL). Monitoring the reaction by ¹H NMR showed that no reaction takes place at 25 °C. Heating the sample for 24 h at 70 °C shows the quantitative formation of (*c*-C₅H₉)₇Si₇O₁₂SiO–Mo(≡N)(=CH*t*Bu)(PMe₃)₂ as a mixture of 2 rotamers along with 30 μmol of 2,2-dimethylpropane (2.0 CH₂*t*Bu/Mo) as measured by GC. (*c*-C₅H₉)₇Si₇O₁₂SiO–Mo(≡N)(=CH*t*Bu)(PMe₃)₂ was obtained as an inseparable mixture of its *syn* and *anti* rotamers in a 10/1 ratio. *syn*-(*c*-C₅H₉)₇Si₇O₁₂SiO–Mo(≡N)(=CH*t*Bu)(PMe₃)₂: δ_H = 0.81 (t, ²J_{HP} = 3.6 Hz, [Mo](P(CH₃)₃), 18H), 1.20 (s, [Mo](=CH)(C(CH₃)₃), 9H), 1.12–1.28 (m, *c*-CH(CH₂)₄, 7H), 1.48–1.91 (m, *c*-CH(CH₂)₄, 56H), 13.67 (t, ³J_{HP} = 6.5 Hz, [Mo](=CH)(C(CH₃)₃), 1H). δ_C = 15.5 (qt, ²J_{CP} = 11.1 Hz, ¹J_{CH} = 135 Hz, [Mo](P(CH₃)₃), 23.0, 23.4 (*c*-CH(CH₂)₄), 27.8, 28.1, 28.3, (*c*-CH(CH₂)₄), 32.3 (q, ¹J_{CH} = 125 Hz, [Mo](=CH(C(CH₃)₃))), 44.2 (s, [Mo](=CH(C(CH₃)₃))), 313.0 (d, ¹J_{CH} = 110 Hz, [Mo](=CH(C(CH₃)₃))). δ_P = –8.0. δ_{Si} = –100.79 (Q³, 1Si), –66.21 (T³, 3Si), –65.64 (T³, 4Si). *anti*-(*c*-C₅H₉)₇Si₇O₁₂SiO–Mo(≡N)(=CH*t*Bu)(PMe₃)₂: δ_H = 0.80 (t, ²J_{HP} = 3.6 Hz, [Mo](P(CH₃)₃), 18H), 1.20 (s, [Mo](=CH(C(CH₃)₃), 9H), 1.12–1.28 (m, *c*-CH(CH₂)₄, 7H), 1.48–1.91 (m, *c*-CH(CH₂)₄, 56H), 14.23 (t, ³J_{HP} = 5.5 Hz, [Mo](=CH(C(CH₃)₃), 1H). δ_C = 15.9 (qt, ²J_{CP} = 11.1 Hz, ¹J_{CH} = 135 Hz, [Mo](P(CH₃)₃), 23.0, 23.4 (*c*-CH(CH₂)₄), 27.8, 28.1, 28.3, (*c*-CH(CH₂)₄), 31.8 (q, ¹J_{CH} = 125 Hz, [Mo](=CH(C(CH₃)₃))), 321.0 (d, ¹J_{CH} = 136 Hz, [Mo](=CH(C(CH₃)₃))). δ_P = –9.3. δ_{Si} = –100.79 (Q³, 1Si), –66.21 (T³, 3Si), –65.64 (T³, 4Si).

3. Results and discussions

3.1. Grafting monitored by infrared spectroscopy

A disk of SiO₂₋₍₇₀₀₎ (55 mg) was immersed into a solution of [Mo(≡N)(CH₂*t*Bu)₃] (**1**), (6 equiv.) in C₆H₆ for 4 h. After washing three times with C₆H₆ and a drying step under vacuum, an IR spectrum was recorded and showed the following features (Fig. 1). The band assigned to the isolated silanol groups ν(OH) at 3747 cm^{–1} disappears, but a broad band centred at 3722 cm^{–1} appears in agreement with the presence of residual silanols, which are in interaction with surrounding ligands (70% of silanols have reacted as measured by IR spectroscopy). Moreover, a sharp band with a broad base appears at 3396 cm^{–1} assigned to ν(=NH); the corresponding δ(=NH) is found at 1473 cm^{–1}. Finally, two groups of bands appear in the 3000–2700 and 1500–1300 cm^{–1} regions, respectively, assigned to ν(CH) and δ(CH). The same features are observed when impregnation is carried out in CH₂Cl₂ (see Figure S1 in supplementary materials). Some silanols do not react and are

in interaction with the ligands bound to Mo (the broad signal centred at 3722 cm^{–1}). This is in contrast to what has been observed during the grafting of Mo(≡C-*t*Bu)(CH₂*t*Bu)₃ [36] and most of the corresponding perhydrocarbyl transition metal complexes on SiO₂₋₍₇₀₀₎ [37,38]. This data is however consistent with the low Mo loading (vide infra). The major difference is the presence of NH bands, and it is possible that the residual OH's are in fact hydrogen bonded to nearby N centres, which would also explain the slight broadening of the base of this N–H signal. Additionally, when a deuterated SiO₂₋₍₇₀₀₎ is used (ν(SiO–D) = 2762 cm^{–1}, 79% deuterated according to IR, see Figure S2 in supplementary materials), the band at 3396 cm^{–1} appears shifted at 2526 cm^{–1} as expected. The appearance of ν(CH), δ(CH), ν(=NH) and δ(=NH) as well as the disappearance of the isolated ν(OH) and the formation of 2,2-dimethylpropane is consistent with a chemical grafting of Mo(≡N)(CH₂*t*Bu)₃ on silica.

3.2. Influence of the solvent in the grafting of **1** on SiO₂₋₍₇₀₀₎

In order to obtain larger quantities of the material, grafting was performed by contacting at 25 °C Mo(≡N)(CH₂*t*Bu)₃ (≈1 equiv./SiOH) and 0.5–1.0 g of silica (SiO₂₋₍₇₀₀₎) in the presence of a solvent. Three different solvents, C₆H₆, CH₂Cl₂ and THF, are used, and the resulting supported materials [1/SiO₂₋₍₇₀₀₎]_{solvent} are characterised by mass balance analysis of the grafting step, elemental analysis and ¹H MAS solid state NMR spectroscopy. While Mo(≡N)(CH₂*t*Bu)₃ is soluble in CH₂Cl₂ or THF, it is only sparingly so in C₆H₆. Therefore, in the latter case, only a small quantity of C₆H₆ was used to disperse the two solids, Mo(≡N)(CH₂*t*Bu)₃ and SiO₂₋₍₇₀₀₎, and several washings were used to remove the excess of **1**. The Mo loading varies between 0.4 and 1.6 wt%, which corresponds to 0.04–0.17 mmol of Mo/g of silica, while the concentration of silanols is about 0.26 mmol OH/g on SiO₂₋₍₇₀₀₎ [39–41]. This shows that 20–70% of the silanols has been consumed during grafting, which is consistent with what has been observed by IR spectroscopy, i.e., the presence of residual silanols (vide supra). Moreover, during this process, 0.7 and 1.0 ± 0.1 mol of 2,2-dimethylpropane (*t*BuCH₃) per grafted Mo is formed when grafting is performed in CH₂Cl₂ and C₆H₆, respectively, while none is observed in THF (Table 1). Moreover, when grafting is performed in CH₂Cl₂, the resulting solid contains about 12.5 ± 1.1 carbons/Mo, which correspond to more than 2 neopentyl-like ligands/Mo (neopentyl or neopentylidene), and whose quantity has been confirmed by the treatment under H₂ (carbon analysis by hydrogenolysis). However, elemental analysis also reveals the presence of 0.51 wt% of Cl, that is 1 Cl/Mo, which corresponds to 0.5 equiv. of remaining CH₂Cl₂ per total grafted Mo.

Table 1
Grafting of Mo(\equiv N)(CH₂*t*Bu)₃ on SiO₂₋₍₇₀₀₎

Entry	Solvent	wt% Mo ^a	<i>t</i> BuCH ₃ /Mo ^b (grafting)	wt% C ^a	C/Mo (<i>t</i> BuCH _x [#] /Mo) ^c	C/Mo (<i>t</i> BuCH _x [#] /Mo) ^d
1	THF	0.45	0	–	–	–
2	CH ₂ Cl ₂	1.43	0.8	2.44	13.6 (2.7)	13.2 (2.6)
3	CH ₂ Cl ₂	1.46	–	2.09	11.4 (2.3)	–
4	C ₆ H ₆	1.59	1.0	1.91	9.6 (1.9)	8.8 (1.8)
5 ^e	C ₆ H ₆	1.56	0.7	–	–	–

^a As determined by elemental analysis.

^b 2,2-Dimethylpropane evolved during grafting as determined by GC analysis.

^c Number of neopentyl-like ligands around Mo as determined by elemental analysis.

^d Number of neopentyl-like ligands around Mo as determined by the quantification of alkanes formed upon treatment under a large excess of H₂ at high temperatures.

^e Grafting on deuterated SiO₂₋₍₇₀₀₎.

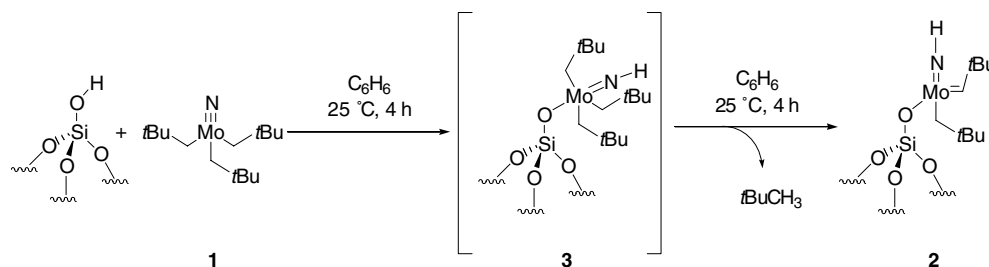
Additionally, when pure CH₂Cl₂ is contacted with silica and then evaporated under the same conditions used for impregnation, no CH₂Cl₂ is observed by ¹H solid state NMR, thus showing that in the case of [1/SiO₂₋₍₇₀₀₎]_{CH₂Cl₂}, CH₂Cl₂ is probably coordinated to Mo. During grafting in C₆H₆ (Table 1, entry 3–4), the resulting solid contains 9.6 ± 0.5 and 8.8 ± 0.5 carbons/Mo as measured by elemental analysis and hydrogenolysis, respectively (10 C/Mo expected for the structure 2). Additionally, when SiO_{2-D-(700)} (82% D according to IR) was used, 2,2-dimethylpropane evolved mainly as a non-labeled isotopomer (93%) along with small amounts of the monodeuterated one (7%). These data are consistent with a grafting occurring mainly via protonation of the nitrido ligand to yield an intermediate species 3, (\equiv SiO)–Mo(\equiv NH)(CH₂*t*Bu)₃, which evolves towards (\equiv SiO)–Mo(\equiv NH)(=CH*t*Bu)(CH₂*t*Bu) (2) via a selective α -H abstraction by a neopentyl ligand of an H borne by an adjacent neopentyl ligand as proposed previously when this compound was prepared by sublimation on small quantities (Scheme 2) [27]. The ¹H MAS solid state NMR spectrum of [1/SiO₂₋₍₇₀₀₎]_{C₆H₆} shows only two peaks at 1.1 and 2.1 ppm corresponding to the CH₂ (2H) and *t*Bu (18H) signals, respectively (Figure S3, see supplementary materials). No other peak corresponding to the NH and the alkylidene ligands, expected in the 3–7 [42] and 4–15 ppm [8] regions, respectively, is detected even though the NH fragment has been clearly identified

by IR spectroscopy, suggesting that these signals are probably broad and not observable by solid state NMR. For [1/SiO₂₋₍₇₀₀₎]_{THF} and [1/SiO₂₋₍₇₀₀₎]_{CH₂Cl₂}, extra signals appear, and they correspond to remaining coordinating solvent molecules (see supplementary materials). In the case of [1/SiO₂₋₍₇₀₀₎]_{C₆H₆} ESR spectroscopy showed only traces of Mo(V) species (<3%), which is consistent with the presence of mainly Mo^(VI) species as in the starting material. Therefore, when C₆H₆ is used as a solvent, around one 2,2-dimethylpropane evolved during grafting, and the resulting solid contains about 1.8–2.0 neopentyl-like ligands per grafted Mo (9–10 C/Mo), which is consistent with the formation of 2, [(\equiv SiO)–Mo(\equiv NH)(=CH*t*Bu)(CH₂*t*Bu)], as proposed already when this compound was prepared by sublimation [27].

3.3. Reactivity towards olefins of materials

[1/SiO₂₋₍₇₀₀₎]_{solvent}

The activity in olefin metathesis of the different materials highly depends on the method of preparation. While the material prepared in C₆H₆, [1/SiO₂₋₍₇₀₀₎]_{C₆H₆}, is highly active in the metathesis of propene (TOF_(5 min) = 0.89 s⁻¹ with equilibrium reached within 25 min), [1/SiO₂₋₍₇₀₀₎]_{CH₂Cl₂} is much less active (TOF_(5 min) = 0.001 s⁻¹), and [1/SiO₂₋₍₇₀₀₎]_{THF} is completely inactive (Table 2). These observations are fully consistent with the decrease of activity of d⁰ catalysts



Scheme 2. Reaction of Mo(\equiv N)(CH₂*t*Bu)₃ (1) with SiO₂₋₍₇₀₀₎.

Table 2
Initial rates and TON for the metathesis of propene (25 °C)

Entry	Catalysts	wt% M	P (Torr)	Ratio (propene/M)	TOF _(5 min) ^a (s ⁻¹)	TON _{max} ^b (time)
1	[1/SiO ₂ -(700)]THF	0.45	200	780	0	0
2	[1/SiO ₂ -(700)]CH ₂ Cl ₂	1.43	200	780	0.001	230 (24 h)
3	[1/SiO ₂ -(700)]C ₆ H ₆	1.59	200	780	0.89	300 (0.5 h)
4	(≡SiO)–Mo(≡C <i>t</i> Bu)(CH ₂ <i>t</i> Bu) ₂	2.55	500	500	0.50	170 (-)
5	(≡SiO)–Re(≡C <i>t</i> Bu)(=CH <i>t</i> Bu)(CH ₂ <i>t</i> Bu)	4.05	500	500	0.25	170 (-)

^a Initial rate in mol of propene converted per mol of metal per second measured after 5 min.

^b Number of turnovers in mol of propene converted per mol of metal.

in the presence of coordinating solvents, but it is worth mentioning that in the original paper [27], all the reactions were carried out in CH₂Cl₂, which probably slowed down the reaction rate dramatically. Furthermore, when [1/SiO₂-(700)]CH₂Cl₂ was contacted with propene a second time after evacuation of the gas phase (1 h, 30 °C, 1.34 Pa), the initial rate slightly increases (0.13 s⁻¹), which is consistent with a displacement of CH₂Cl₂ as the first loading of propene was evacuated.

The initial rate of [1/SiO₂-(700)]C₆H₆ is comparable to those reported for (≡SiO)–Mo(≡C*t*Bu)(CH₂*t*Bu)₂ and (≡SiO)–Re(≡C*t*Bu)(=CH*t*Bu)(CH₂*t*Bu) (Table 3) [36,38,43]. Moreover, the rate is much greater than those observed for Mo-based heterogeneous catalysts, MoO₃/S (S = SiO₂, Al₂O₃), which typically work under much higher temperature conditions, ca. 150–250 °C. It is however still lower than those reported for comparable molybdenum homogeneous catalysts [44,45].

Moreover, 3,3-dimethyl-1-butene (*t*BuCH=CH₂) and *trans* 4,4-dimethyl-2-pentene (*t*BuCH=CHMe) are formed in a 2.5:1 ratio, albeit only in small amounts, i.e., 0.15 equiv./Mo. 3,3-Dimethyl-1-butene is the major cross-metathesis product, as observed for homogeneous catalysts and (≡SiO)Re(≡C*t*Bu)(=CH*t*Bu)(CH₂*t*Bu) [38,43], because the favoured pathway involves the metallacyclobutane intermediate for which [1,2]-interactions are avoided and [1,3]-interactions are minimised (Scheme 3) [46].

When [1/SiO₂-(700)]C₆H₆ is contacted with 13000 equiv. of propene using the standard procedure, only 7% conversion are reached, thus showing that deactivation occurred. However, it is possible to reach the thermodynamic equilibrium (34% conversion) when propene is purified over both R3-11 BASF catalyst/Zeolithe and MnO/SiO₂. The catalyst [1/SiO₂-(700)]C₆H₆ yields up to 35000 productive TON in less than 35 min when 185000 equiv. of propene is used. Under

Table 3
Initial rates and TON for the metathesis of oleate esters (100 equiv.) at 25 °C

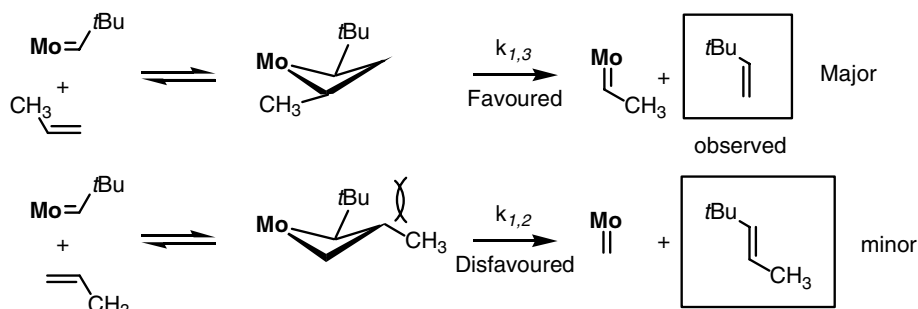
Entry	Catalysts	wt% M	TOF _(5 min) ^a (s ⁻¹)	TON ^b (time)
1	[1/SiO ₂ -(700)]C ₆ H ₆ ^c	1.59	0.11	49 (0.3 h)
2	(≡SiO)–Mo(≡C <i>t</i> Bu)(CH ₂ <i>t</i> Bu) ₂ ^d	2.55	0.014	25 (1 h)
3	(≡SiO)–Re(≡C <i>t</i> Bu)(=CH <i>t</i> Bu)(CH ₂ <i>t</i> Bu) ^d	4.05	0.07	49 (3.5 h)

^a Initial rate in mol of oleate converted per mol of metal per second after 5 min.

^b Number of turnovers in mol of oleate converted per mol of metal.

^c Data obtained with ethyl oleate.

^d Data obtained with methyl oleate.



Scheme 3. Production of cross-metathesis products in the metathesis of propene on 2.

these optimised conditions (using highly purified propene), $(\equiv\text{SiO})\text{-Mo}(\equiv\text{C}t\text{Bu})(\text{CH}_2t\text{Bu})_2$ and $(\equiv\text{SiO})\text{-Re}(\equiv\text{C}t\text{Bu})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$ reach 38 000 and 2000 in 1 h 30 and 1 h, respectively.

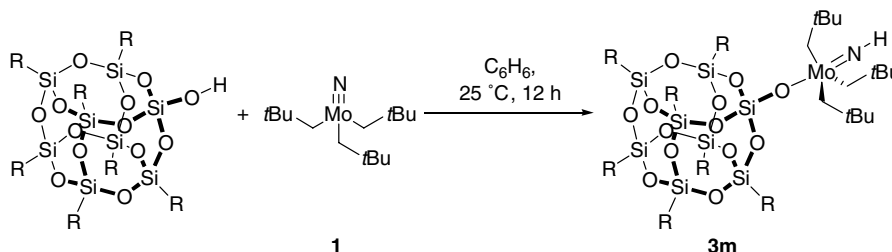
The material $[\mathbf{1}/\text{SiO}_2\text{-}(700)]_{\text{C}_6\text{H}_6}$ also catalyses the metathesis of liquid olefins such as 1-octene, for which 1300 equiv. are equilibrated in only 1 h, which is similar to what is usually observed for homogenous Mo-based catalysts [44,45], and much lower than those observed with the best Ru-catalysts [28]. Moreover, 100 equiv. of ethyl oleate are equilibrated in only 20 min by $[\mathbf{1}/\text{SiO}_2\text{-}(700)]_{\text{C}_6\text{H}_6}$ with an initial rate of 0.11 mol/mol/s. For comparison, 3 h 30 are necessary to obtain an equilibrated mixture for $(\equiv\text{SiO})\text{-Re}(\equiv\text{C}t\text{Bu})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$ under the same experimental conditions, while $(\equiv\text{SiO})\text{-Mo}(\equiv\text{C}t\text{Bu})(\text{CH}_2t\text{Bu})_2$ deactivates before reaching 25 TON. Finally, 700 productive TON's are reached in 24 h when 2000 equiv. of ethyl oleate are used, which is a little lower than what was found for $(\equiv\text{SiO})\text{-Re}(\equiv\text{C}t\text{Bu})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$. Those results are quite remarkable since classical heterogeneous catalysts are often incompatible with functional groups such as esters [20,47,48].

3.4. Development of an equivalent homogeneous olefin metathesis catalysts

In order to further characterize this system, we have also investigated the reaction of $\text{Mo}(\equiv\text{N})(\text{CH}_2t\text{Bu})_3$ with a soluble model of $\text{SiO}_2\text{-}(700)$ [1,49–52]. A previous study has used triphenylsilanol [27], but polyhedral oligomeric silsesquioxanes (POSS) are considered better models since they display $\text{p}K_a$ values closer to that of silica [53]. Of the various POSS's, $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOH}$ is considered as a good model for $\text{SiO}_2\text{-}(700)$ [37,38,54]. Therefore, under similar reaction conditions as those used for the preparation of $[\mathbf{1}/\text{SiO}_2\text{-}(700)]_{\text{C}_6\text{H}_6}$, a suspension of $\text{Mo}(\equiv\text{N})(\text{CH}_2t\text{Bu})_3$ and $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOH}$ stirred in C_6H_6 yields a yellow solution of $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOMo}(\equiv\text{NH})(\text{CH}_2t\text{Bu})_3$ (**3m**), pure (>98%) by NMR of the crude material (Scheme 4). The ^1H NMR spectrum of **3m** in C_6D_6 exhibits all the ^1H resonance of the cyclopentyl substituents of the POSS derivative as well as resonances at 3.36, 2.39 and 1.14 ppm in a

1:6:27 ratio, corresponding, respectively, to the NH, the methylene and the *t*Bu protons. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows signals at 22.8, 23.2, 27.4, 27.5, 27.9, 28.1 assigned to the carbon associated with the cyclopentyl ligands of the POSS derivative and some others at 32.7, 34.9, 84.2 characteristics of neopentyl groups. Moreover, the $^1\text{H}\text{-}^{15}\text{N}$ 2D HMBC NMR spectrum shows one correlation between the signals at 3.36 ppm (F_1 , ^1H) and 338.8 ppm (F_2 , ^{15}N), confirming its assignments to the NH fragment (Fig. 2). The trace at 338.8 ppm in the F_2 dimension shows a doublet with a $^1J_{\text{H-}^{15}\text{N}} = 65.4$ Hz. The chemical shift and the $J_{\text{H-N}}$ coupling constant are consistent with its assignment to an imido group, $\text{Mo}=\text{NH}$ [42,55,56]. IR spectroscopy in nujol shows a peak at 3375 cm^{-1} also in agreement with the presence of the $\text{Mo}=\text{NH}$ group. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of this compound contains 4 signals in a 3:1:3:1 ratio: three at -65.63 , -65.68 , -65.72 ppm in 3:1:3 ratio, characteristic of three different T^3Si , assigned to the three different types of alkyl substituted Si atoms, and one at -105.11 ppm characteristic of a Q^4 , that is a silicon bound to 4 O atoms [57]. Suitable single crystals were grown from a saturated solution of **3m** in hexane cooled at -30°C , and the structure was confirmed by X-ray analysis (Fig. 3). The complex **3m** has a bipyramidal trigonal geometry with the three alkyl substituents in the basal positions; the N and the O atoms occupying the two apical positions. The Mo–C and Mo–O bond distances are 2.119–2.124 and 1.984 Å, respectively, as expected [26,27] and the Mo–N bond distance (1.727 Å) is fully consistent with an imido group [26,27,58]. The salient features are also the very wide Mo=N–H (177°) and Mo–O–Si (172.2°) angles, the former clearly showing that the N acts as a LX type ligand to stabilize the otherwise highly unsaturated Mo centre.

In contrast to the surface complex **2** and other related systems (vide infra), the molecular species does not spontaneously release one equiv. of 2,2-dimethylpropane at room temperature to generate the alkylidene complex **3m**. For example, $\text{Re}(\equiv\text{C}t\text{Bu})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_2$ reacts with $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOH}$ to yield $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiORe}(\equiv\text{C}t\text{Bu})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$ as a 10:1 mixture if its *syn* and *anti* rotamers, for which



Scheme 4. Reaction of $\text{Mo}(\equiv\text{N})(\text{CH}_2t\text{Bu})_3$ (**1**) with a polyhedral oligomeric silsesquioxane ($\text{R} = c\text{-C}_5\text{H}_9$).

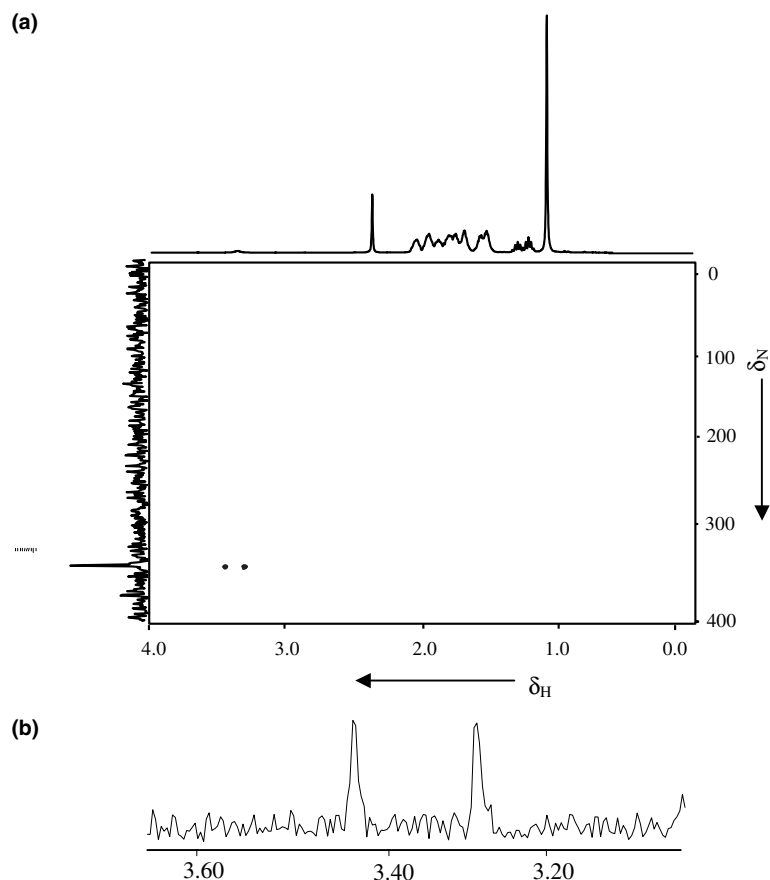


Fig. 2. (a) ^1H - ^{15}N 2D HMBC NMR spectrum of **3m** (500 MHz, 25 °C, C_6D_6). Top: ^1H NMR spectrum. Left: $^{15}\text{N}\{^1\text{H}\}$ NMR spectrum. (b) Proton trace of the signal at $\delta_{\text{N}} = -338.8$ ppm in the 2D HMBC ^1H - ^{15}N NMR spectrum.

no intermediate was observed [38,54]. Even in the case of $\text{Ta}(\text{=CH}t\text{Bu})(\text{CH}_2t\text{Bu})_3$, its reaction with $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOH}$ generates an intermediate $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOTa}(\text{CH}_2t\text{Bu})_4$, which readily decomposes at room temperature into $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiO-Ta}(\text{=CH}t\text{Bu})(\text{CH}_2t\text{Bu})_3$ and $t\text{BuCH}_3$ [37]. The complex **3m** is stable up to 60 °C in C_6D_6 solution for weeks, and it slowly decomposes at 110 °C over several hours. Furthermore, when **3m** is heated at a temperature as high as 80 °C in the presence of 1-octene, the NMR spectrum is unaltered, and no olefin metathesis takes place. It is necessary to carry out this reaction at 110 °C to observe a quantitative transformation of 1-octene (12 equiv.) into ethylene and 7-tetradecene along with the decomposition of **3m** into a complex reaction mixture. Note that this is in sharp contrast to the surface complex **2**, which can transform 1300 equiv. of 1-octene in 1 h at room temperature (vide supra).

Additionally, heating the complex **3m** at 70 °C in the presence of 10 equiv. of PMe_3 generates 2 equiv. of 2,2-dimethylpropane and a new red complex $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiO-Mo}(\text{=N})(\text{=CH}t\text{Bu})(\text{P}(\text{CH}_3)_3)_2$ (**4m**) as a 10:1 mixture of its *syn* and *anti* rotamers (Scheme 5). In the ^1H NMR, the signal at 2.39 ppm associated

with the CH_2 of the $t\text{BuCH}_2$ ligands in **3m** disappear, while two triplets appear in a 10:1 ratio at 13.67 ($J_{\text{P-H}} = 6.5$ Hz) and 14.23 ($J_{\text{P-H}} = 5.5$ Hz) ppm in agreement with the formation of two metallocarbenes, each of them coordinated with two equivalent P atoms per Mo. Moreover, performing an HSQC experiment showed that the signals at 13.67 and 14.23 displayed, respectively, a correlation with signals in the ^{13}C dimension at 313.0 ($^1J_{\text{CH}} = 110$ Hz) and 321.0 ($^1J_{\text{CH}} = 136$ Hz) ppm as resolved doublets. These data are fully consistent with the presence of two alkylidene rotamers, *syn* and *anti*-(**4m**). (8) Additionally, the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **4m** contains 3 signals in a 4:3:1 ratio: two at -65.64 , -66.21 ppm (T^3), one at -100.79 ppm (Q^4 , the Q^4 being downfield with respect to this observed for **3m**). Its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows two singlets at -8.0 and -9.3 ppm in a 10:1 ratio corresponding to coordinated PMe_3 of *syn*-(**4m**) and *anti*-(**4m**), respectively. The formation of **4m** from **3m** is in fact quite similar to what has been found for other bis-alkyl complexes upon addition of PMe_3 , for which the extrusion of one neopentyl ligand is observed upon coordination of extra donor ligands [59–62]. This probably shows that the surface might play the role of this

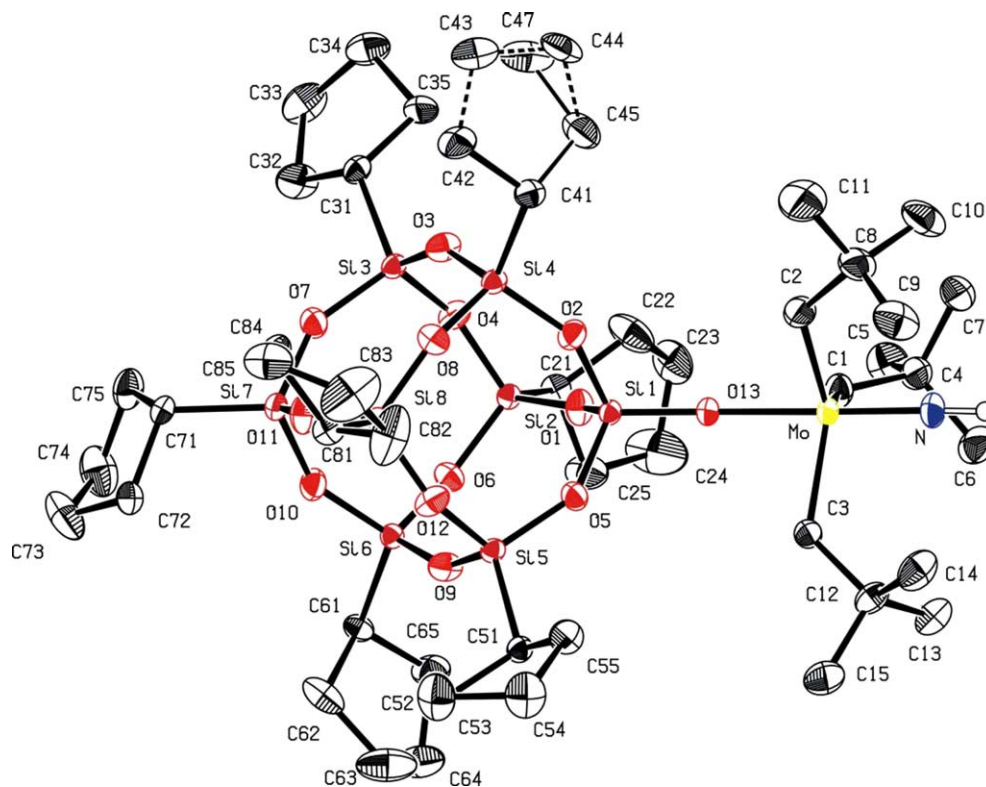
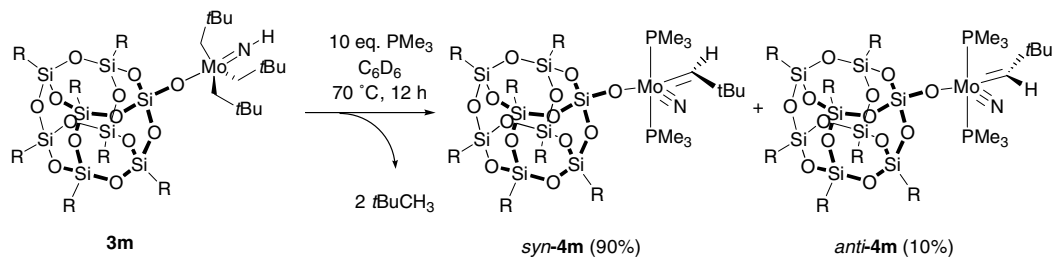


Fig. 3. ORTEP representation of compound **3m** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms but H are omitted for clarity. Selected bond distances and angles: Mo–N = 1.727(2) Å, N–H = 0.86(4) Å, Mo–C(1) = 2.119(3) Å, Mo–C(2) = 2.123(3) Å, Mo–C(3) = 2.124(2) Å, Mo–O(13) = 1.9837(16) Å, Mo–N–H = 177(3)°, N–Mo–C(1) = 95.52(10)°, N–Mo–C(2) = 95.13(11)°, N–Mo–C(3) = 95.86(10)°; Mo–O(13)–Si(1) = 172.20(11)°.



Scheme 5. Reaction of $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOMo}(\text{=NH})(\text{CH}_2t\text{Bu})_3$ (**3m**) with PMe_3 ($\text{R} = c\text{-C}_5\text{H}_{12}$).

ligand in generating directly **2** at room temperature in place of **3**.

4. Conclusion

The reaction of $\text{Mo}(\text{=N})(\text{CH}_2t\text{Bu})_3$ and $\text{SiO}_{2-(700)}$ generates $(\text{=SiO})\text{Mo}(\text{=NH})(\text{=CH}t\text{Bu})(\text{CH}_2t\text{Bu})$ (**2**) when performed in C_6H_6 $[\text{1/SiO}_{2-(700)}]_{\text{C}_6\text{H}_6}$. The grafting occurs presumably by protonation of the nitrido ligand to the form an intermediate $(\text{=SiO})\text{Mo}(\text{=NH})(\text{CH}_2t\text{Bu})_3$ (**3**), a pentacoordinated complex, which decomposes into **2** and 2,2-dimethylpropane. While $[\text{1/SiO}_{2-(700)}]_{\text{C}_6\text{H}_6}$ is highly active in olefin metathesis,

the preparation of $[\text{1/SiO}_{2-(700)}]$ in THF or CH_2Cl_2 yields inactive or poorly active catalysts. The preparation of this material can be easily performed on 1 g scales, but it can be readily scale-up to 10–100 g scale, replacing C_6H_6 by toluene since **1** and $\text{SiO}_{2-(700)}$ are readily accessible.

In contrast, when $\text{Mo}(\text{=N})(\text{CH}_2t\text{Bu})_3$ reacts with a molecular silanol derivative, which we and others have typically used to model the surface of $\text{SiO}_{2-(700)}$, it yields a very stable complex, $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiO-Mo}(\text{=NH})(\text{CH}_2t\text{Bu})_3$ (**3m**), which does not spontaneously generate 2,2-dimethylpropane and an alkylidene complex in contrast to the surface complex. Moreover, **3m** does not catalyze olefin metathesis at room temperature as it does

not already contain the initiating carbene ligand, and it is necessary to heat up the reaction mixture to 110 °C to obtain some catalytic activity, presumably because an unstable carbene has been generated. In trying to trap this reactive intermediate complex, **3m** was heated in the presence of trimethylphosphine, and it generated (*c*-C₅H₉)₇Si₇O₁₂SiO–Mo(≡N)(=CH*t*Bu)(P(CH₃)₃)₂ (**4m**) as a 10:1 mixture of its *syn* and *anti* carbene rotamers with the liberation of 2 *t*BuCH₃/Mo. While a metallo-carbene was generated, it also suffers from the loss of the imido ligand.

Finally, while molecular silanols derivatives can help to understand surface structures [49–52], the aforementioned differences illustrate that it can be misleading to determine surface structures solely through solution chemistry. Moreover, it also shows that it is possible to generate on surfaces highly unsaturated species, which is probably the basis for the high reactivity of heterogeneous catalysts prepared via surface organometallic chemistry.

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-273010 (**3m**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk.

All ¹H, ¹³C, ²⁹Si, ³¹P NMR data of **3m** and **4m** can be found in the supporting information. Bond distances and bond angles for the X-ray crystal structure of **3m** are listed in Table S1–3. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.04.028.

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