Electronic Supplementary Information for Dalton Transactions

Supporting information

Dramatic enhancement of the alkene metathesis activity of Mo imido alkylidene complexes upon replacement of one *t*BuO by a surface siloxy ligand.[**]

Frédéric Blanc, Nuria Rendón, Romain Berthoud, Jean-Marie Basset, Christophe Copéret,* Zachary J. Tonzetich, Richard R. Schrock.[*]

Dr. F. Blanc, Dr. N. Rendón, Mr. R. Berthoud, Dr. J.-M. Basset, Dr. C. Copéret.

Université de Lyon, Institut de Chimie de Lyon, Laboratoire de Chimie, Catalyse, Polymères et Procédés

CNRS - ESCPE Lyon

43, Bd du 11 Novembre 1918

F-69616 Villeurbanne Cedex, France

Mr. Zachary J. Tonzetich, Dr. R. R. Schrock

Department of Chemistry, Massachussets Institute of Technology, Cambridge

Massachussets 02139, USA.

Experimental procedures.

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. $[Mo(\equiv NAr)(=CHCMe_2Ph)(OtBu)_2]$ (Ar = 2,6-iPr$_2$C$_6$H$_3$) (**1-Ph**) was synthetized according to literature procedure.[1] ^{13}C labeled $[Mo(\equiv NAr)(={}^*CHtBu)(OtBu)_2]$ (**1*-Me**) was synthesized as previously described using [(1-^{13}C 99 %) tBu^{13}CH$_2$MgCl] as alkylating agent. [(1-^{13}C 99 %) tBu^{13}CH$_2$MgCl] was prepared according to the literature procedure.[2] Silica (Aerosil Degussa, 200 m^{2}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 (support referred to as $SiO_{2-(700)}$). Pentane and toluene were distilled from NaK and sodium benzophenone ketyl under N_2, respectively. Propene (Scott, 99.95 %) was purified over R3-11 BASF catalyst/MS 4 Å prior to use. Ethyl oleate (NuChekPrep, 99 %) was used as received. Elemental analyses were performed at the University of Bourgogne, Dijon (C and N) and at the Service Central Analyse in Solaize (Mo). Infrared spectra were recorded on a Nicolet 550-FT by using an infrared cell equipped with CaF_2 windows, allowing *in situ* studies. Typically 16 scans were accumulated for each spectrum (resolution, 2 cm^{-1}). Liquid phase analyses were performed on a Hewlett Packard 5890 series II GC apparatus equipped with a FID detector and a Fame column (50m X 0.25 mm). Products were identified by GC/MS.

Solid State Nuclear Magnetic Resonance Spectroscopy. All solid state NMR spectra were recorded under MAS on a Bruker Avance 500 spectrometer at the European Large Scale Center for NMR in Lyon. A with a conventional double resonance 4 mm CP-MAS probe. The MAS frequency was set to 12.5 kHz for all of the experiments reported here. The samples were introduced in a 4 mm zirconia rotor in the glove box and tightly closed. Chemical shifts are reported in ppm downfield from liquid $SiMe_4$ (0 ppm) for ^1H and ^{13}C NMR. The ^{13}C CP spectra were performed according to the standard scheme using SPINAL-64 proton decoupling.[3] The proton rf field was set to $\nu_1^H = 100$ kHz for both the 90° pulses and decoupling. For the CP step, a ramp radio frequency (rf) field [4-5] centred at $\nu^{CP} = 70$ kHz was applied on protons, while the carbon rf field was matched to obtain optimal signal. The contact time for CP is indicated in the caption of the figures.

Preparation of [(≡SiO)Mo(≡NAr)(=CHCMe$_2$Ph)(O*t*Bu)] (2-Ph) followed by *in situ* IR spectroscopy. Silica (29 mg) was pressed into a 18 mm self-supporting disk and put into a sealed glass high vacuum reactor equipped with CaF_2 windows. After calcination at 500 °C under air for 2 h, the silica disk was treated under vacuum (1.34 Pa) at 500 °C for 12 h and then at 700 °C for 4 h. The silica support thus obtained, referred to as $SiO_{2-(700)}$ (29 mg, 7.5 μmol SiOH), was then immersed into a pentane (12 mL) solution of [Mo(≡NAr)(=CHCMe$_2$Ph)(O*t*Bu)$_2$] (**1-Ph**) (28 mg, 52 μmol, 7 equiv.) at 25 °C for 1 h. After washing three times with pentane (10 mL), the solid was dried under vacuum (1.34 Pa) at 25 °C for 1 h. IR: 3743, 3609, 3107, 3088, 3065, 3028, 2969, 2932, 2907, 2874, 2789, 1799, 1600, 1586, 1574, 1494, 1468, 1463, 1445, 1426, 1386, 1363, 1333 cm^{-1}. Elemental analysis: 1.47 $\%_{wt}$ Mo, 4.74 $\%_{wt}$ C, 0.20 $\%_{wt}$ N, 26 ± 3 C/Mo (26 expected), 0.9 ± 0.3 N/Mo (1 expected).

Preparation of [(≡SiO)Mo(≡NAr)(=CHCMe$_2$Ph)(O*t*Bu)] (2-Ph) by impregnation of [Mo(≡NAr)(=CHCMe$_2$Ph)(O*t*Bu)$_2$] (1-Ph) onto SiO$_{2\text{-}(700)}$. A mixture of [Mo(≡NAr)(=CHCMe$_2$Ph)(O*t*Bu)$_2$] (**1-Ph**) (109 mg, 0.20 mmol) and SiO$_{2\text{-}(700)}$ (720 mg, 0.19 mmol SiOH) in pentane (10 mL) was stirred at 25 °C for 30 min. the volatiles were distilled off and pentane was added. The yellow-orange solid was then washed, filtrated and the volatiles distilled off. This was repeated three times and finally the resulting yellow powder was dried thoroughly under vacuum (1.34 Pa) at 25 °C for 2 h to yield [(≡SiO)Mo(≡NAr)(=CHCMe$_2$Ph)(O*t*Bu)] (**2-Ph**). ^{1}H MAS NMR: 11.5, 7.1, 3.5 and 1.1. ^{13}C CP MAS NMR: 153, 147, 128, 125, 122, 107, 78, 52, 30, 27, 22. Elemental analysis: 2.05 %wt Mo, 6.92 %wt C, 0.31 %wt N, 27 ± 2 C/Mo (26 expected), 1.0 ± 0.3 N/Mo (1 expected).

Preparation of [(≡SiO)Mo(≡NAr)(=*CH*t*Bu)(O*t*Bu)] (2*-Me) by impregnation of [Mo(≡NAr)(=*CH*t*Bu)(O*t*Bu)$_2$] (1*-Me) onto SiO$_{2\text{-}(700)}$. This compound was prepared as described above using [(1-^{13}C 99%) Mo(≡NAr)(=*CH*t*Bu)(O*t*Bu)$_2$] (**1*-Me**) (36 mg, 74 μmol) and SiO$_{2\text{-}(700)}$ (246 mg, 64 μmol SiOH) in pentane (6 mL). ^{1}H MAS NMR: 11.2, 7.0, 3.7 and 1.2 ^{13}C CP MAS NMR: 272, 150-118, 135, 52, 31, 28, 22. Elemental analysis: 2.12 %wt Mo, 5.33 %wt C, 0.31 %wt N, 20 ± 2 C/Mo (21 expected), 1.0 ± 0.3 N/Mo (1 expected).

Propene metathesis in a flow reactor. [(≡SiO)Mo(≡NAr)(=CHCMe$_2$Ph)(O*t*Bu)] (**2-Ph**) (40 mg, 8.5 μmol) was loaded in a flow reactor in the glove box, the isolated reaction chamber was then connected to the propene line, the propene pressure was set to 1 bar, and the tubes were flushed with propene for 2 h. The flow rate was set to 400 mL.min^{-1} (32 mol propene.molMo^{-1}.s^{-1}), the temperature was set to 30 °C and the opening of the valve corresponds to the beginning of the catalysis. The reaction was monitored by GC using an auto-sampler.

Metathesis of ethyl oleate (2000 equiv). Representative procedure. A 1.16 M solution of ethyl oleate in toluene was freshly prepared, degassed with freeze-pump-thaw cycles, and dried over freshly 3 Å activated molecular sieves. At t = 0 min, the solution (3 mL, 3.5 mmol) was added at 25 °C *via* a syringe through a septum to the catalyst (1.8 μmol) placed in a Schlenk flask, and the reaction mixture was stirred vigorously. Small aliquots (1 – 3 drops) were sampled, diluted with toluene (0.5 – 1 mL) and analysed by GC over time.

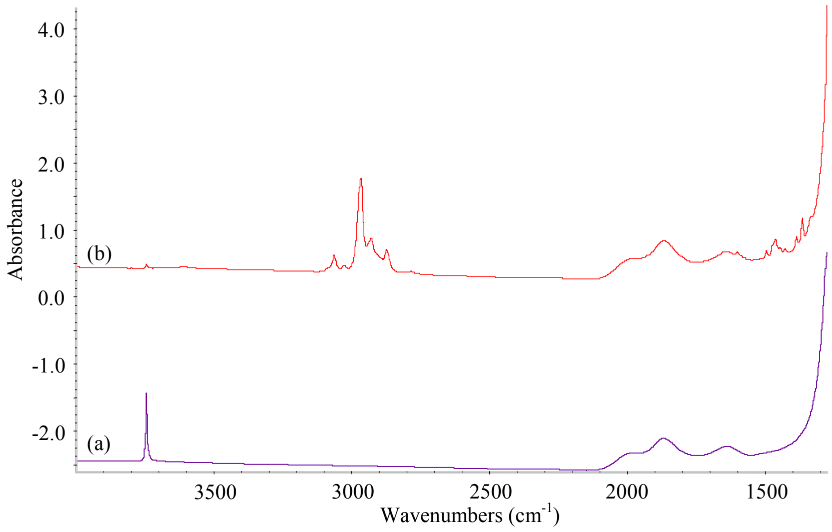

Figure S1. Grafting of [Mo(≡NAr)(=CHCMe$_2$Ph)(O*t*Bu)$_2$] (**2-Ph**) (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) on a silica partially dehydroxylated at 700 ºC, SiO$_{2\text{-}(700)}$, monitored by IR spectroscopy. (a) SiO$_{2\text{-}(700)}$ pellet (29 mg). (b) After impregnation of [Mo(≡NAr)(=CHCMe$_2$Ph)(O*t*Bu)$_2$] (**1-Ph**) (29mg) in pentane (10 mL) (1 h, 25 ºC), followed by three washings (30 min, 25 ºC) in pentane and a drying step under vacuum (1.34 Pa, 1 h, 25 ºC).

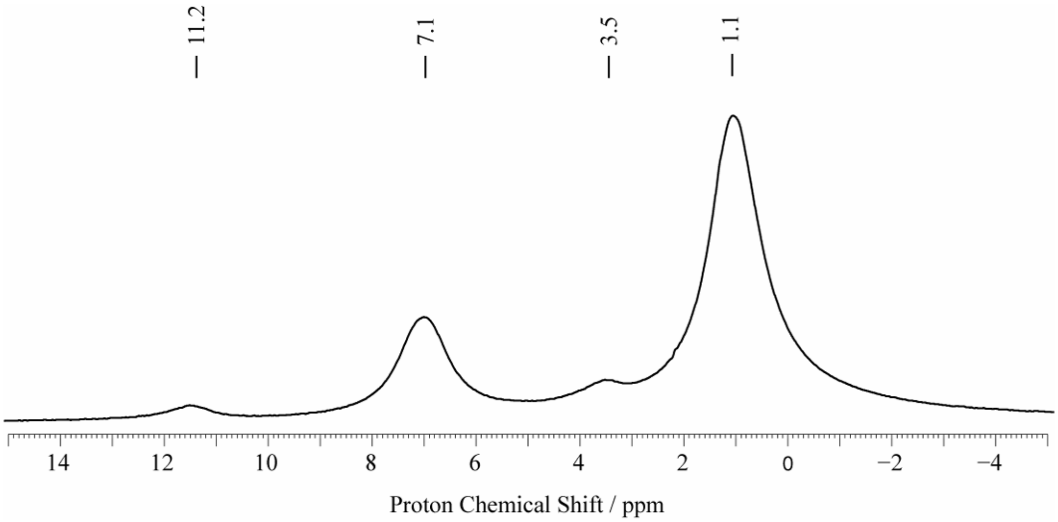

Figure S2. One-dimensional solid state proton single pulse spectrum of [(≡SiO)Mo(≡NAr)(=CHCMe$_2$Ph)(O*t*Bu)] (**2-Ph**) (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) recorded under MAS frequency of 12.5 kHz. 8 scans were coadded at a recycle rate of 3 s.

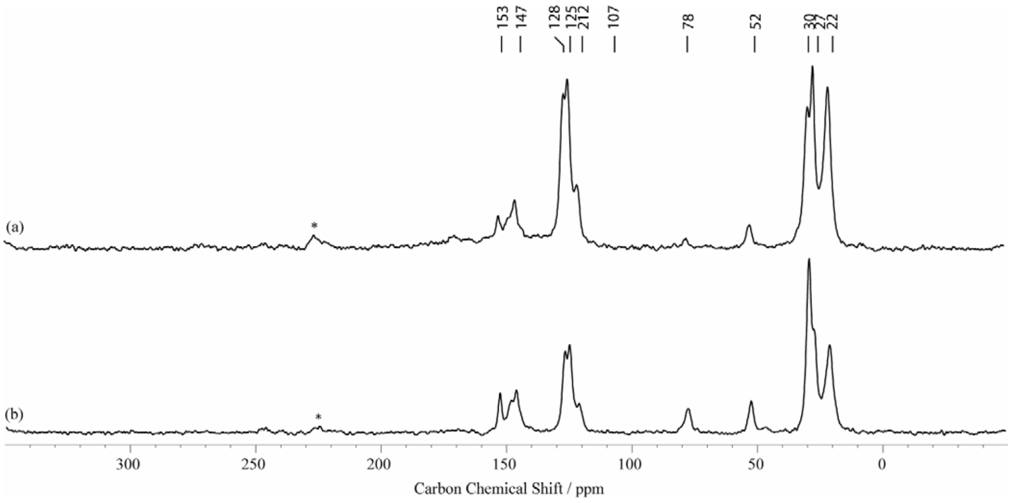

Figure S3. ^{13}C CP solid state NMR spectra of [(≡SiO)Mo(≡NAr)(=CHCMe$_2$Ph)(O*t*Bu)] (**2-Ph**) (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) acquired under SPINAL-64 ^{1}H[4] decoupling at ν_1^H = 100 kHz. The recyle delay was set to 2 s in both experiments. An exponential line broadening of 80 Hz was applied before Fourier transform. Spectrum (a) was recorded with 32000 scans with a contact time for CP of 1 ms while spectrum (b) was recorded with 20000 scans and a contact time of 10 ms.

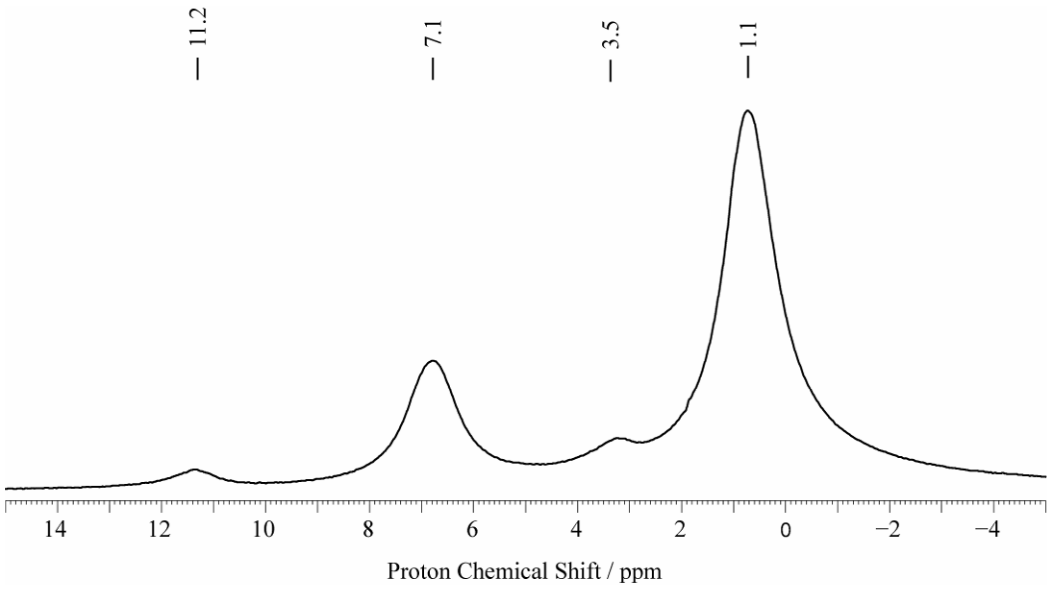

Figure S4. One-dimensional solid state proton single pulse spectrum of [(1-99 % ^{13}C) (≡SiO)Mo(≡NAr)(=*CH*t*Bu)(O*t*Bu)] (**2*-Me**) (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) recorded under MAS frequency of 12.5 kHz. 8 scans were coadded at a recycle rate of 3 s.

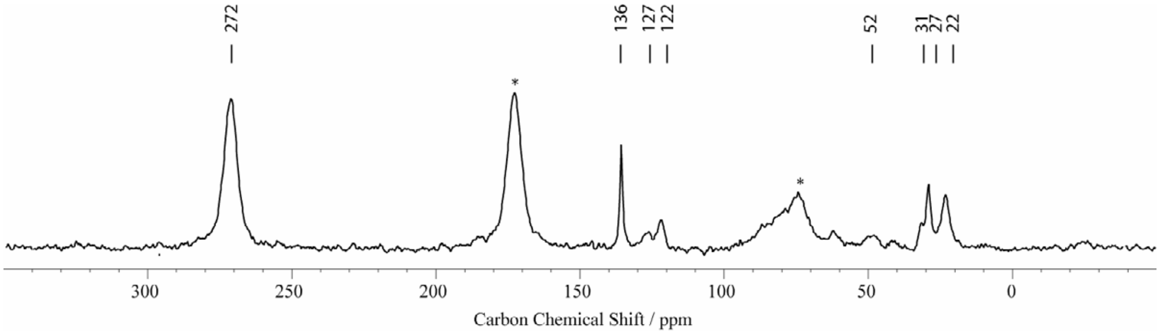

Figure S5. ^{13}C CP solid State NMR spectra of [(1-99 % ^{13}C) (≡SiO)Mo(≡NAr)(=*CH*t*Bu)(O*t*Bu)] (**2*-Me**) (Ar = 2,6-iPr$_2$C$_6$H$_3$) acquired under SPINAL-64 ^{1}H[4] decoupling at ν_1^H = 100 kHz. The recycle delay and contact time for CP were set to 2 s and 1 ms, respectively. An exponential line broadening of 80 Hz was applied before Fourier transform. A total of 5210 scans was collected. Stars (*) indicates spinning side bands of the alkylidene resonance.

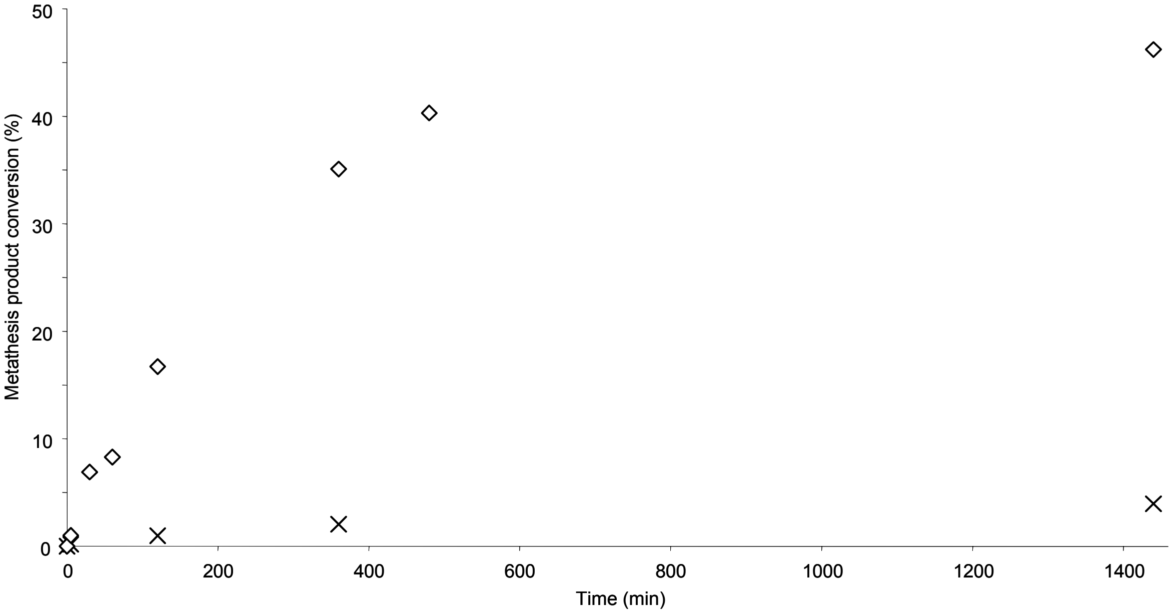

Figure S6. Conversion versus time in the self metathesis of ethyl oleate (2000 eq) with [Mo(≡NAr)(=CHCMe$_2$Ph)(O*t*Bu)$_2$] (**1-Ph**) (x) and [(≡SiO)Mo(≡NAr)(=CHCMe$_2$Ph)(O*t*Bu)] (**2-Ph**) (◊) under identical reaction conditions.

References.

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