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

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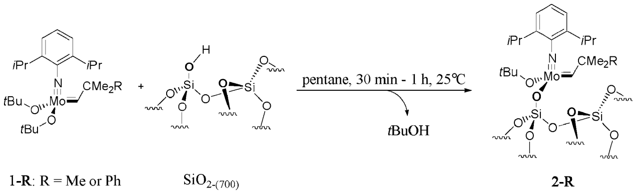
$[(\equiv SiO)Mo(\equiv NAr)(=CHCMe_2R)(OtBu)]$, a well-defined silica supported alkene metathesis catalyst precursor, shows a dramatic enhancement of activity and selectivity compared to $[Mo(\equiv NAr)(=CHCMe_2R)(OtBu)_2]$ and $[(\equiv SiO)Mo(\equiv NAr)(=CHCMe_2R)(CH_2tBu)]$, respectively.

Alkene metathesis is a key reaction to make carbon–carbon bonds, and it has been applied to a wide range of applications ranging from petrochemical to fine chemical products.[1] Despite tremendous advances in the past few years, there is still a challenge to prepare more active and more robust catalysts. With this in mind, we and others have worked on the development of well-defined heterogeneous alkene metathesis catalysts.[2] In particular, we have shown that silica supported Mo-, W- and Re-based catalyst precursors, of general formula $[(Y)M(\equiv ER)(=CHtBu)(X)]$ ($Y = \equiv SiO$), are highly active ($X = CH_2tBu$; M = Re, ER = $CtBu$;[3] M = Mo, ER = NR;[4] or M = W, ER = NAr[5]) and selective ($X = NPh_2$, M = Mo and ER = NR), and overall their performances—in term of activity and stability—often out-performed those of their homogeneous analogues.[6] These improved catalytic properties have been associated with the presence of a siloxy ligand ($Y = \equiv SiO$) in combination with one σ-donating ligand ($X = tCH_2R$ or NR_2)[7] as well as site isolation. Here, we show that the replacement of only one of the *t*BuO ligand in **1-R** by a siloxy ligand upon its grafting on silica partially dehydroxylated at 700 °C ($SiO_{2\text{-}(700)}$) is enough to yield a highly active well-defined alkene metathesis catalyst precursor **2-R** (Scheme 1).



Scheme 1

When a silica disk of $SiO_{2\text{-}(700)}$ was immersed in a pentane solution of **1-Ph**, the IR signal associated with the surface silanols at 3747 cm^{-1} mostly disappeared as new IR bands associated with the ν(C–H) and δ(C–H) of hydrocarbyl ligands appeared in the 3000–2700 and 1500–1350 cm^{-1} regions, respectively (Fig. S1 in the electronic supporting information, ESI†). Additional IR signals are also observed between 3000–3700 cm^{-1} and assigned as follows: the signals at 3088, 3065 and 3028 cm^{-1} correspond to aromatic C–H bonds, and the signal at 3609 cm^{-1} to residual OH groups interacting with aromatic ligands and not accessible for further grafting.[5] Moreover, when a mixture of **1-Ph** (109 mg, 0.20 mmol) in pentane (10 mL) was contacted and stirred for 30 min at 25 °C with $SiO_{2\text{-}(700)}$ (720 mg, 0.19 mmol of $\equiv SiOH$), silica turned yellow and *t*BuOH was formed. The Mo elemental analysis ($2.05\%_{wt}$) corresponds to 0.21 mmol of Mo g^{-1} of solids in agreement with the consumption of most surface silanols (*ca.* 82%), which is consistent with IR data. Moreover, these materials contain on average 27 ± 2 carbons and 1.0 ± 0.5 nitrogens per grafted Mo from elemental analysis, which is in good agreement with the proposed structure **2-Ph**, for which 26 C/Mo and 1 N/Mo are expected.

Further characterisation of this material was performed by solid state NMR spectroscopy. In the ^1H MAS NMR spectrum of **2-Ph** (Fig. S2†), the signals can be assigned as follows: 11.5 (=C*H*CMe$_2$Ph), 7.1 (Csp^2-H), 3.5 (C*H*Me$_2$), 1.1 (=CHC*Me*$_2$Ph, C*Me*$_3$ and CH*Me*$_2$). The ^{13}C CP MAS spectrum of **2-Ph** contains 10 resolved signals (Fig. S3†), assigned as follows: 22 {$CH(CH_3)_2$}, 27 {$=CHC(CH_3)_2Ph + C(CH_3)_3$}, 30 {$CH(CH_3)_2$}, 52 {$=CHC(CH_3)_2Ph$}, 78 {$C(CH_3)_3$}, 122–153 {Ar}. While no signal corresponding to the alkylidene carbon resonance {$=CHC(CH_3)_2Ph$} could be observed on **2-Ph**, a signal at 272 ppm is detected when grafting is performed with **1-Me**, $[Mo(\equiv NAr)(={}^*CHtBu)(OtBu)_2]$ 99% ^{13}C labeled at the alkylidene carbon (Fig. S4 and S5†). These assignments were further corroborated by 2D ^1H-^{13}C HETCOR experiment (Fig. 1),[8] and in particular a strong correlation was observed for the carbon signal at 272 ppm and the corresponding alkylidene proton at 11.2 ppm.

Overall, the disappearance of most of the band at 3747 cm^{-1} and the evolution of *t*BuOH upon grafting, the elemental analysis and the NMR data are fully consistent with the formation of **2-Ph**. Note that the grafting of **1-Ph** by sublimation on $SiO_{2\text{-}(200)}$ yields a mixture of surface complexes.[9] This shows the advantage of using $SiO_{2\text{-}(700)}$, a silica surface, which has isolated silanols and which thereby yields well-defined monosiloxy species.

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[a] *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. E-mail: coperet@cpe.fr; Fax: +33472431795; Tel: +33472431811*

[b] *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139, USA*

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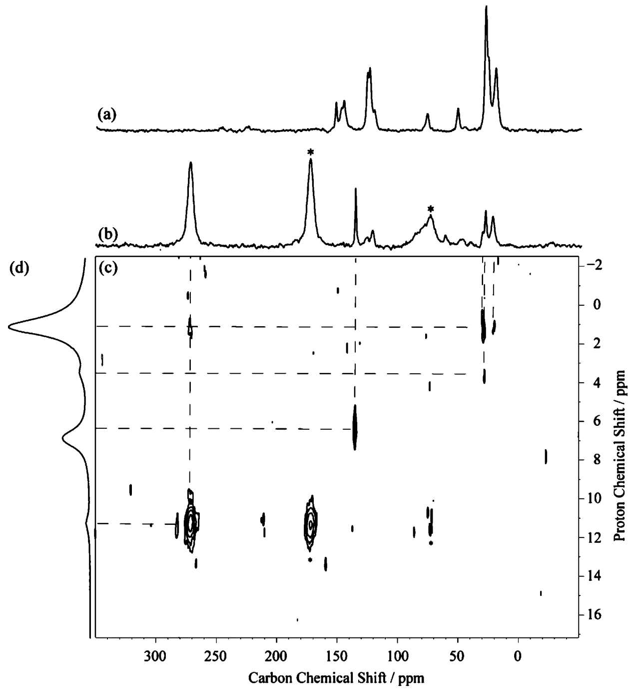

Fig. 1 Solid state NMR spectra of **2-R** recorded at a spinning rate of 12.5 kHz. The ^{13}C spectra were recorded under SPINAL-64 $^{1}H^{10}$ decoupling at $\nu_1^H = 100$ kHz. The recycle delay was set to 2 s. Stars (*) indicates spinning side bands of the alkylidene resonance. (a) ^{13}C CP spectrum of **2-Ph** acquired with 20 000 scans and a contact time of 10 ms. (b) ^{13}C CP MAS spectrum of **2-Me** acquired with 4 180 scans and a contact time of 1 ms. (c) ^{1}H-^{13}C HETCOR spectrum of **2-Me** acquired in 48 t_1 points with 512 scans each. A contact time of 1 ms was used for CP. (d) Single pulse ^{1}H MAS spectrum of **2-Me** acquired with 8 scans.

Finally, contacting **2-Ph** with propene in a flow reactor (*ca.* 400 mL min^{-1}; 32 mol propene mol Mo^{-1} s^{-1}) gives selectively ethene and 2-butenes (>99.9%, no other alkene is detected) with an initial activity of 1.9 s^{-1}, yielding overall a cumulated TON of 51200 over 1550 min (Fig. 2). The catalytic performances of this system are greatly improved by comparison with $[(\equiv SiO)(tBuCH_2)Mo(\equiv NAr)(=CHCMe_2R^2)]$[4c] in term of selectivity and stability, the latter displaying a butene selectivity of 99.6% (2-butenes/all butene isomers), an initial activity of 2 s^{-1} and a cumulated TON over 1 500 min of 20 000.[4d,g] This further shows that the formation of alkene by-products could be related to the presence of the pendant alkyl ligand. Moreover, using 0.05 mol% of **2-Ph** (Fig. S6†), it is possible to reach the thermodynamic equilibrium in the self-metathesis of ethyl oleate (EO) within 24 h with initial activity of 4.1 mol EO (mol Mo min)$^{-1}$, while **1-Ph** is nearly inactive (initial activity of 0.6 mol EO (mol Mo min)$^{-1}$ and only 4% conversion after 24 h).

These results nicely illustrate the activation of a Mo-based olefin metathesis catalyst precursor by the siloxy ligand and the importance in the choice of the ligands.

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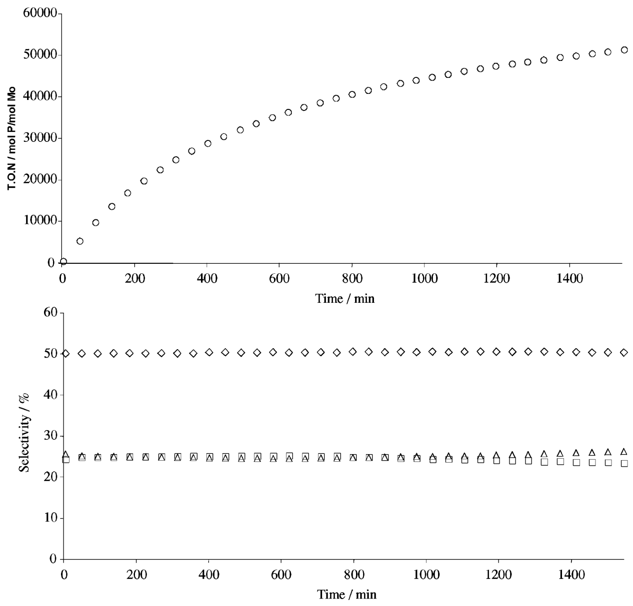

Fig. 2 Activity in propene metathesis catalysed by **2-Ph**. Top: cumulative TON as a function of time (min). Bottom: products selectivity as a function of time (min). Ethylene (◇), *E*-2-butene (□), *Z*-2-butene (△).

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