

Highly Active, Stable, and Selective Well-Defined Silica Supported Mo Imido Olefin Metathesis Catalysts

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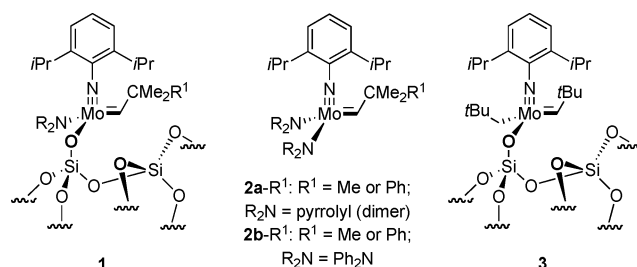
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We report here the synthesis, characterization, and catalytic properties of highly active well-defined silica supported heterogeneous olefin metathesis catalysts,^{1–5} [(≡SiO)Mo(≡NAr)(=CHCMe₂R¹)(NR₂)] (**1**). These catalysts are compatible with ethyl oleate and function without a cocatalyst.

In the past few years, we have shown that monosiloxy Mo-, W-, and Re-based catalysts, of general formula [(≡SiO)M(≡ER)(=CH*t*Bu)(CH₂*t*Bu)] are highly active olefin metathesis catalysts (M = Re, ER = C*t*Bu;^{6,7} M = Mo, ER = NH;^{8,9} M = Mo¹⁰ or W¹¹, ER = NAr), that often display reactivity and stability greater than their homogeneous analogues, [(RO)₂M(≡ER)(=CH*t*Bu)] (RO = Me(CF₃)₂CO^{12–14} or (RO)₂ = POSS¹⁵). Interestingly, complexes that are asymmetric at the metal center appear to provide optimum activity.¹⁶ Moreover, silica supported systems are less prone to deactivation¹⁰ as a consequence of being isolated on the surface, thereby eliminating bimolecular decomposition of alkylidenes.^{17,18} However, in the metathesis of propene, traces of 1-butene are found, which might be ascribed to side reactions that involve the neopentyl ligand. We were attracted to the possibility of adding recently reported bis(amido) complexes, [Mo(≡NAr)(=CHCMe₂R¹)(NR₂)₂] (**2**; Ar = 2,6-*i*Pr₂C₆H₃, R¹ = Me or Ph; NR₂ = pyrrolyl for **2a**¹⁹ and NPh₂ for **2b**²⁰) to partially dehydroxylated silica (SiO_{2–(700)}) to yield well-defined asymmetric systems **1** having no alkyl ligand present, in contrast to **3**, [(≡SiO)Mo(≡NAr)(=CH*t*Bu)(CH₂*t*Bu)] (Scheme 1).

The reaction between SiO_{2–(700)} and **2a-Ph** (NR₂ = pyrrolyl, R¹ = Ph), was monitored by IR spectroscopy. The IR peak associated with the surface silanols at 3747 cm⁻¹ 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 region, respectively (Supporting Information, Figure S1). The new IR peaks at 3088, 3065, and 3028 cm⁻¹ are attributed to the ν(=C–H) of arylimido group, and that at 3610 cm⁻¹ to residual OH interacting with aromatic ligands.¹¹ Overall, the disappearance of the band at 3747 cm⁻¹ during grafting is in agreement with a chemical grafting of **2a-Ph**. When a mixture of SiO_{2–(700)} (298 mg, 0.26 mmol SiOH per gram, 0.077 mmol) and **2a-Ph** (44 mg, 0.082 mmol) in C₆H₆ (8 mL) is stirred for 2 h at 25 °C, 0.9 equiv of pyrrole per grafted Mo (2.28 wt %) is formed in agreement with the formation of the surface complex **1a-Ph** (Scheme 1). The Mo elemental analysis (2.28 wt %) corresponds to 0.24 mmol of Mo per gram of solids in agreement with the consumption of most surface silanols (ca. 92%), and it is also consistent with the formation of a monomeric species. Moreover, the materials contain on the average 25 ± 2 carbons and 1.7 ± 0.5 nitrogens per grafted Mo (obtained from elemental analysis), which is consistent with the proposed structure

Scheme 1



1a-Ph, for which 26 C/Mo and 2 N/Mo are expected. Furthermore, all the distinct signals in ¹H MAS solid-state NMR spectra and, more clearly, in constant time (CT) ¹H MAS NMR spectra (Figures 1 and S2)²¹ are fully consistent with the proposed structure of **1a-Ph**. These resonances are found at 11.9 (=CHCMe₂Ph), 6.8 (Csp²-H), 5.7 (pyrrolyl-Csp²-H), 3.2 (CHMe₂), 1.8 (unreacted SiOH), 1.4 (=CHCMe₂Ph) and 0.7 (CHMe₂) ppm. The resonance at 1.8 ppm is assigned to residual silanols since it almost disappears when deuterated silica is employed (Figure S3).

The ¹³C CP MAS spectrum contains nine resolved peaks (Figure S4a; Table S1), which can be assigned as follows: 22 {CH(CH₃)₂}, 28 {=CHC(CH₃)₂Ph + CH(CH₃)₂}, 54 {=CHC(CH₃)₂Ph}, 122–153 {Ar}. However, the alkylidene carbon resonance was not observable for **1a-Ph** at natural abundance. Therefore the corresponding ¹³C labeled neopentylidene complex, **1a*-Me** [(≡SiO)Mo(≡NAr)(=CHCMe₂R¹)(NR₂)] (R¹ = Me), 99% ¹³C labeled on the α-carbon to Mo (Figures S4b–S5; Table S1) was prepared. This surface complex unambiguously displays a large isotropic signal at 285 ppm in the ¹³C CP MAS NMR spectrum, consistent with the presence of an alkylidene carbon (Mo=CHR¹). This has been confirmed in 2D ¹H-¹³C dipolar HETCOR NMR spectra,^{22,23} which show that the carbon at 285 ppm is correlated with a proton at 11.9 ppm (Figure S6).

Similarly, **2b-Ph** (NR₂=NPh₂, R¹ = Ph) reacts with a silica surface to yield the corresponding monosiloxy complex **1b-Ph** according to mass balance analysis, IR, and ¹H and ¹³C solid-state NMR spectroscopies (Figure S7–S11; Table S2). The ¹H, ¹³C, and 2D NMR spectra of **1b*-Me** display the expected proton and carbon signals for the carbene, observed at 11.4 and 288 ppm, respectively. A small amount of the anti isomer is also observed in this case, which proton and carbon signals appear at 12.9 and 302 ppm. The maximum Mo loading in this case has been only 1 wt % (0.11 mmol/g), which corresponds to the consumption of ~40% of the surface silanols of SiO_{2–(700)} (0.26 mmol/g). The remaining silanols are interacting with the ligand of **1b-Ph** according to IR spectroscopy (Figure S7) and therefore are not accessible. Considering a calculated projected area of 2.1 nm² for the [Mo(≡NAr)-

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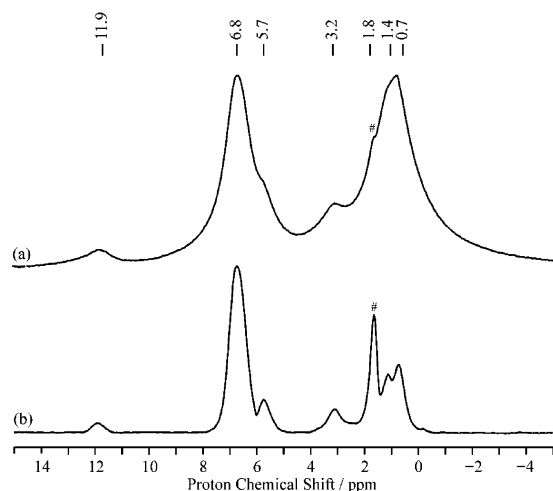


Figure 1. Proton NMR spectra of **1a-Ph** recorded on a Bruker Avance 500-MHz spectrometer at a MAS frequency of 12.5 kHz: (a) single pulse spectrum (8 scans); (b) CT spectrum ($T = 4$ ms, 64 t_1 points of 16 scans each) (# indicates residual silanol).²¹

Table 1. Comparative Reactivity in Olefin Metathesis

catalyst	propene ^{a,b}		ethyl oleate ^{b,c}	
	TOF	time	TOF	time
1a-Ph	2.2	180 ^d	0.11 ^e	30
2a-Ph			0.01	<i>f</i>
1b-Ph	4.0 ^e	20	0.15 ^e	10
2b-Ph			<i>g</i>	<i>g</i>

^a Experimental conditions: 0.017 mol % Mo, 25 °C. ^b TOF is the initial turn over frequency measured after 5 min of reaction expressed in mol of substrate converted per mol of Mo per second. Time is the time (in minutes) to reach the equilibrium conversion (34% for propene and ca. 50% for EO). ^c Experimental conditions: 0.5 M solution of EO in toluene, 1 mol % of Mo. ^d The reaction stops after 30% conversion (thermodynamic conversion: 34%). ^e In these cases, the conversion is already high after 5 min, and the initial TOFs are probably greater than measured. ^f Deactivation after 30% conversion (4 h). ^g Less than 0.1% conversion.

(=CHCMe₂Ph)(NPh₂) fragment, the maximum Mo loading should have been 0.15 mmol/g (1.5 wt %), which shows that the silanols of a SiO₂-₍₇₀₀₎ are not evenly distributed on the surface of the solid.¹¹

When propene is contacted with **1a-Ph** or **1b-Ph** (0.017 mol %), equilibrium is reached in 60 min for **1b-Ph**, while only 30% conversion is achieved for **1a-Ph** (Table 1). The initial turnover frequencies are 2.2 (**1a-Ph**) and > 4 mol/mol Mo/s (**1b-Ph**), so that **1b-Ph** is slightly faster than **1a-Ph** and **3** [(≡SiO)Mo(=NAr)(=CH*t*Bu)(CH₂*t*Bu)] (3–4 mol/mol Mo/s under similar reaction conditions).¹⁰ Moreover, with catalyst **1**, no 1-butene was observed even after 24 h (<0.01% if any) in contrast to **3** (0.06%). We ascribe this beneficial effect to absence of an alkyl group.

The self-metathesis of ethyl oleate (EO) was investigated as a test substrate for functionalized olefins. Under identical conditions, 0.5 M solution of EO are equilibrated within 30 and 10 min with 1 mol % of **1a-Ph** and **1b-Ph**, respectively (Figure S12). In comparison, equilibrium is reached in 60 min for [(R_{F6}O)₂Mo(=NAr)(=CHCMe₂Ph)] under similar reaction conditions. Using 0.05 mol % of catalyst **1b-Ph**, equilibrium is reached within 3 h, while **1a-Ph** deactivates faster so that only 20% of the EO has been converted after 8 h (Figure S13). Finally, ring-closing metathesis of diallylmalonate can be achieved with 1 mol % of **1a-Ph** and **1b-Ph** in 2 h and 30 min, respectively.

In conclusion, we have shown that bisdiphenylamido and dipyrrolyl Mo complexes serve as precursors^{24,25} to well-defined

supported catalysts for olefin metathesis that are asymmetric at the metal.^{16,26} We believe that the remaining amido ligand in the supported catalyst is responsible for greater stability and selectivity compared to catalysts prepared from dineopentyl precursors, as evidenced by the absence of formation of 1-butene in the metathesis of propene. The diphenylamido system appears to be the most promising, although many possibilities remain. We will continue to explore this new generation of well-defined active silica-supported catalysts.

Acknowledgment. F.B. thanks le Ministère de la Recherche et de l'Education for a graduate fellowship. C.C. and J.M.B. thank the CNRS and CPE Lyon for financial support. This research was also sponsored by the ANR for a young investigator fellowship to C.C. (ANR JC05_46372). R.R.S. is also grateful to the National Science Foundation (Grant CHE-0138495) for support.

Supporting Information Available: Full experimental details, Tables S1–2, and Figure S1–13. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Hultzsck, K. C.; Jernelius, J. A.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 589–593.
- Kroell, R. M.; Schuler, N.; Lubbad, S.; Buchmeiser, M. R. *Chem. Commun.* **2003**, 2742–2743.
- (a) Copéret, C.; Chabanas, M.; Petroff Saint-Arroman, R.; Basset, J.-M. *Angew. Chem., Int. Ed.* **2003**, *42*, 156–181. (b) Copéret, C. *New J. Chem.* **2004**, *28*, 1–10.
- Dolman, S. J.; Hultzsck, K. C.; Pezet, F.; Teng, X.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **2004**, *126*, 10945–10953.
- Wang, D.; Kroell, R.; Mayr, M.; Wurst, K.; Buchmeiser, M. R. *Adv. Synth. Catal.* **2006**, *348*, 1567.
- Chabanas, M.; Baudouin, A.; Copéret, C.; Basset, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 2062–2063.
- Chabanas, M.; Copéret, C.; Basset, J.-M. *Eur. J. Chem.* **2003**, *9*, 971–975.
- Herrmann, W. A.; Stumpt, A. W.; Priemeier, T.; Bogdanovic, S.; Dufaud, V.; Basset, J.-M. *Angew. Chem., Int. Ed.* **1997**, *35*, 2803–2805.
- Blanc, F.; Chabanas, M.; Copéret, C.; Fenet, B.; Herdweck, E. *J. Organomet. Chem.* **2005**, *690*, 5014–5026.
- Blanc, F.; Copéret, C.; Thivolle-Cazat, J.; Basset, J.-M.; Lesage, A.; Emsley, L.; Sinha, A.; Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 1216–1220.
- Rhers, B.; Salameh, A.; Baudouin, A.; Quadrelli, E. A.; Taoufik, M.; Copéret, C.; Lefebvre, F.; Basset, J.-M.; Solans-Monfort, X.; Eisenstein, O.; Lukens, W. W.; Lopez, L. P. H.; Sinha, A.; Schrock, R. R. *Organometallics* **2006**, *25*, 3554–3557.
- Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875–3886.
- Fox, H. H.; Schrock, R. R.; O'Dell, R. *Organometallics* **1994**, *13*, 635–639.
- Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748–3759.
- Feher, F. J.; Tajima, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 2145–2146.
- Solans-Monfort, X.; Clot, E.; Copéret, C.; Eisenstein, O. *J. Am. Chem. Soc.* **2005**, *127*, 14015–14025.
- Lopez, L. P. H.; Schrock, R. R. *J. Am. Chem. Soc.* **2004**, *126*, 9526–9527.
- Sinha, A.; Lopez, L. P. H.; Schrock, R. R.; Hock, A. S.; Mueller, P. *Organometallics* **2006**, *25*, 1412–1423.
- Hock, A.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 16373–16375.
- Sinha, A.; Schrock, R. R.; Mueller, P.; Hoveyda, A. H. *Organometallics* **2006**, *25*, 4621–4626.
- Blanc, F.; Copéret, C.; Thivolle-Cazat, J.; Basset, J.-M.; Lesage, A.; Emsley, L.; Sinha, A.; Schrock, R. R. *Inorg. Chem.* **2006**, *45*, 9587–9592.
- Petroff Saint-Arroman, R.; Chabanas, M.; Baudouin, A.; Copéret, C.; Basset, J.-M.; Lesage, A.; Emsley, L. *J. Am. Chem. Soc.* **2001**, *123*, 3820–3821.
- (a) Chabanas, M.; Baudouin, A.; Copéret, C.; Basset, J.-M.; Lukens, W.; Lesage, A.; Hediger, S.; Emsley, L. *J. Am. Chem. Soc.* **2003**, *125*, 492–504. (b) Lesage, A.; Emsley, L.; Chabanas, M.; Copéret, C.; Basset, J.-M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4535–4538.
- Weissman, H.; Plunkett, K. N.; Moore, J. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 585–588.
- Cho, H. M.; Weissman, H.; Wilson, S. R.; Moore, J. S. *J. Am. Chem. Soc.* **2006**, *128*, 14742–14743.
- Ballard, D. G. H. *Adv. Catal.* **1973**, *23*, 263–325.

JA068249P