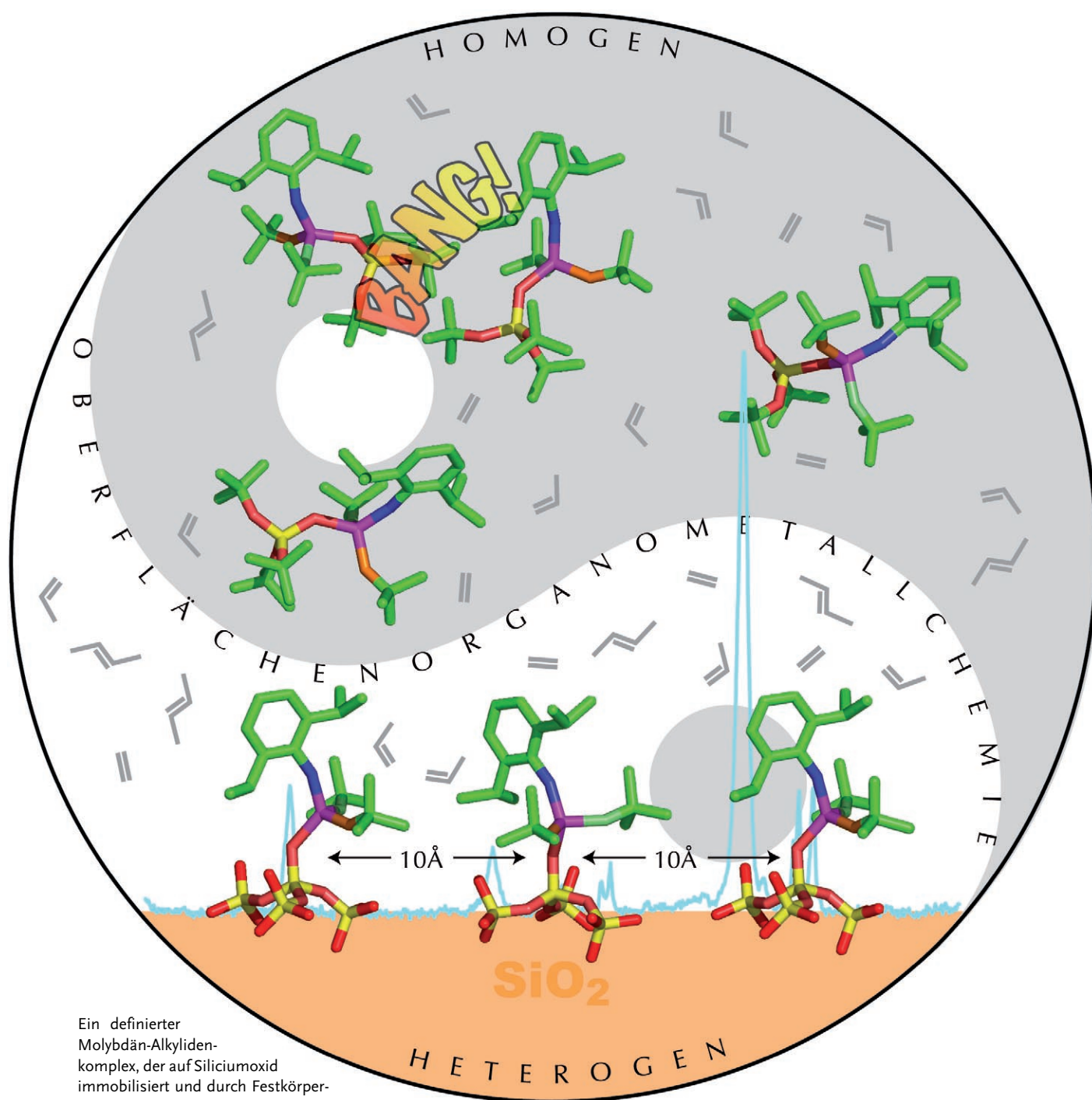


Zuschriften



Ein definierter Molybdän-Alkylidenkomplex, der auf Siliciumoxid immobilisiert und durch Festkörper-NMR-Spektroskopie charakterisiert wurde, erwies sich bei der Olefinmetathese als leistungsfähiger als entsprechende nichtimmobilisierte Katalysatoren mit Siloxy-Liganden. Das Auftreten isolierter aktiver Zentren auf dem Trägerkatalysator könnte dieses Verhalten erklären, denn so würde eine Zersetzung durch Dimerisierung verhindert. C. Copéret et al. erläutern dies in ihrer Zuschrift auf den folgenden Seiten.

DOI: 10.1002/ange.200503205

Surface versus Molecular Siloxy Ligands in Well-Defined Olefin Metathesis Catalysts: $[(\text{RO})_3\text{SiO}]\text{Mo}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})$

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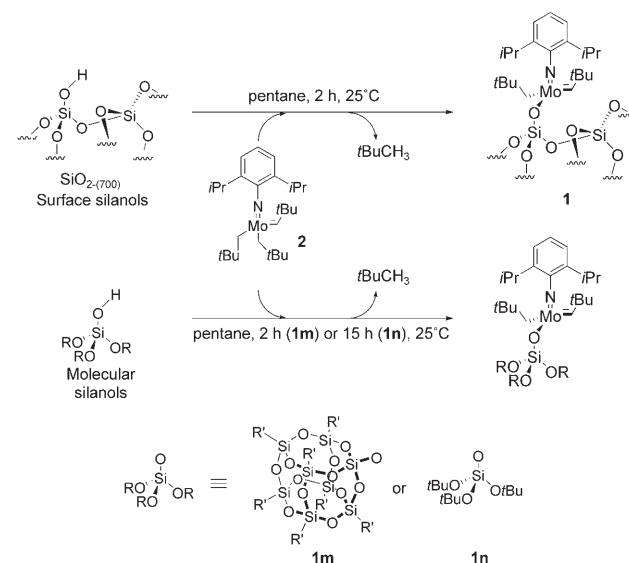
Dedicated to Professor Ei-ichi Negishi
on the occasion of his 70th birthday

We report herein the synthesis and characterization of $[(\text{SiO})\text{Mo}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})]$ (**1**), a well-defined heterogeneous catalyst for olefin metathesis, and its molecular equivalents **1m** and **1n**.

We recently reported the preparation and characterization of highly active heterogeneous olefin metathesis catalysts $[(\text{SiO})\text{Re}(=\text{C}t\text{Bu})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})]$.^[1–3] This system has shown better activity than the best Re-based homogeneous and heterogeneous catalysts and comparable initial activities to Mo- and W-based homogeneous olefin metathesis catalysts. In homogeneous catalysis, well-defined Mo complexes such as $[(\text{R}_f\text{O})_2\text{Mo}(=\text{NAr})(=\text{CH}t\text{Bu})]$ ^[4–7] ($\text{R}_f = (\text{CF}_3)_2(\text{CH}_3)\text{C}$) are much better catalysts than their Re equivalents $[(\text{R}_f\text{O})_2\text{Re}(=\text{C}t\text{Bu})(=\text{CH}t\text{Bu})]$.^[8,9] However, preparing a supported equivalent to $[(\text{R}_f\text{O})_2\text{Mo}(=\text{NAr})(=\text{CH}t\text{Bu})]$ has remained a challenge.^[10–15] In surface organometallic chemistry,^[16] the forma-

tion of a Mo alkylidene complex requires the use of well-defined Mo alkyl alkylidene molecular precursors, which have become available only recently as $[\text{Mo}(=\text{NAr})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})_2]$ (**2**; $\text{Ar} = 2,6\text{-diisopropylphenyl}$).^[17–19] Since the surface of silica partially dehydroxylated at 700 °C ($\text{SiO}_{2-(700)}$) can be compared to a bulky monodentate ligand,^[16] we investigated the reaction of **2** with $\text{SiO}_{2-(700)}$ in order to generate a well-defined supported olefin metathesis catalyst.

When immersed in a solution of **2** in pentane, a $\text{SiO}_{2-(700)}$ disk immediately turned yellow. After 2 h, the disk was washed three times with pentane, dried under vacuum for 1 h at 25 °C, and analyzed by IR spectroscopy. The IR peaks associated with the surface silanol groups at 3747 cm^{-1} had disappeared while new IR bands associated with $\nu(\text{C-H})$ and $\delta(\text{C-H})$ of hydrocarbyl ligands appeared in the regions of 3000–2700 and 1500–1350 cm^{-1} , respectively (see Supporting Information). Furthermore, the IR bands at 3065 and 3027 cm^{-1} are attributed to $\nu(\text{C-H})$ of the arylimido group. During these steps the surface silanol groups reacted, as their corresponding IR bands at 3747 cm^{-1} did not reappear. Preparation of larger quantities of this solid was performed by using calibrated silica (40–60 mesh) partially dehydroxylated at 700 °C. When a mixture of $\text{SiO}_{2-(700)}$ (0.26 mmol g^{-1} SiOH) and **2** in pentane was stirred for 2 h at 25 °C, surface organometallic complex **1** was formed together with 1 equivalent of 2,2-dimethylpropane (Scheme 1). The



Scheme 1. Formation of surface complex **1** and its homogeneous analogues **1m** and **1n** ($\text{R}' = \text{c-C}_3\text{H}_7$).

yellow solid thus obtained contains 1.7–2.1 wt % of Mo, which corresponds to 0.17–0.21 mmol of Mo per gram of solids, in agreement with consumption of most of the surface silanol groups (70–80 %). Moreover, the materials contain on average $23 \pm 3\text{C}$ and $1.0 \pm 0.3\text{N}$ per grafted Mo (as obtained from elemental analysis), consistent with the proposed structure **1**, for which 22C/Mo and 1N/Mo are expected. Furthermore, the ^1H magic-angle spinning (MAS) solid-state NMR spectrum of **1** (Figure 1 a) displays distinct signals at $\delta = 11.7$ ($=\text{CH}t\text{Bu}$, 1H), 6.8 ($\text{C}_{\text{sp}^2}\text{-H}$, 3H), 3.5 (CHMe_2 , 2H), and

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[**] F.B. is grateful to the French Ministry of Education, Research, and Technology (MENRT) for a predoctoral fellowship. We thank B. Fenet for recording solution-state $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra. We are also indebted to the CNRS, ESCPE Lyon, and the National Science Foundation (R.R.S.) for financial support.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

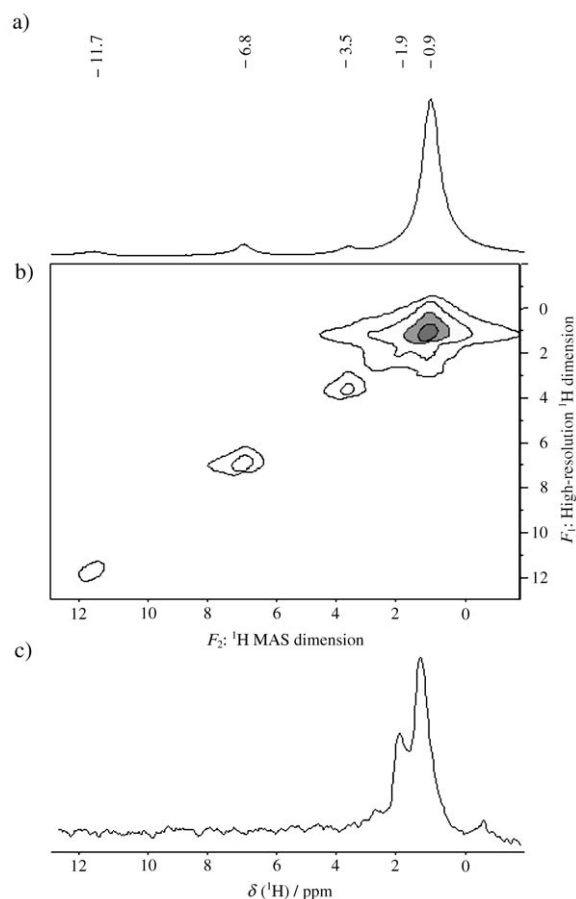


Figure 1. Solid-state NMR spectra of **1**. a) ^1H NMR spectrum acquired at a MAS frequency of $\nu_R = 12.5$ kHz with eight scans and a recycle delay of 2 s. The ^1H rf field was 83 kHz. b) 2D ^1H - ^1H NMR spectrum recorded at a MAS frequency of $\nu_R = 10.0$ kHz with the DUMBO-1 homonuclear dipolar decoupling sequence^[20] in t_1 . c) Trace parallel to F_1 extracted along F_2 at $\delta_H = 1.9$ ppm.

0.9 ppm (CH_3 , 30H). The signal of the methylene protons in the position α to Mo is only observed as a shoulder centered around $\delta = 1.9$ ppm. The presence of relatively sharp signals for a solid-state NMR spectrum ($\Delta\nu_{1/2} = 390$ Hz) shows that ^1H - ^1H dipolar coupling is weak, the ligands undergo rapid restricted motion, and the species are dispersed. A 2D ^1H - ^1H homonuclear correlation NMR spectrum recorded with the DUMBO-1 homonuclear dipolar decoupling sequence^[20] in t_1 resulted in a slight improvement in the line width of the ^1H NMR spectrum ($\Delta\nu_{1/2} = 260$ Hz; Figure 1 b), in contrast to the much larger effect that is observed for bulk materials. This results, however, in a better resolution of the signal at $\delta = 1.9$ ppm (Figure 1 c).

The ^{13}C cross-polarization (CP) MAS spectrum contains 11 resolved peaks (see Figure 2 a and Supporting Information), which can be tentatively assigned as follows: $\delta = 22$ ($\text{CH}(\text{CH}_3)_2$), 29 ($=\text{CHC}(\text{CH}_3)_3$), 31 ($\text{CH}_2\text{C}(\text{CH}_3)_3$), 36 (CH_2CMe_3), 46 ($=\text{CHCMe}_3$), 56 (CH_2tBu), 122

(C_{para}), 126 (C_{meta}), 145 (C_{ortho}), 153 (C_{ipso}), and 279 ppm ($=\text{CHtBu}$); the signal of the alkylidene carbon atom at $\delta = 279$ ppm is barely observable. $[(\equiv\text{SiO})\text{Mo}(=\text{NAr})(=\text{CHtBu})(=\text{CH}_2\text{tBu})]$ (**1***), 33% ^{13}C -labeled on the carbon atom α to Mo, unambiguously displays signals for both the methine ($\text{Mo}=\text{CHtBu}$) and methylene carbon atoms ($\text{Mo}-\text{CH}_2\text{tBu}$) at $\delta = 279$ and 56 ppm, respectively (Figure 2 a). Furthermore, using the 2D ^1H - ^{13}C dipolar HETCOR NMR method^[21,22] (see Figure 2 b and Supporting Information) with different contact times (1 and 5 ms) allowed resolution and assignment of all signals of the ^{13}C spectrum (see Supporting Information).^[22,23] The carbene ($=\text{CHtBu}$) and methylene (CH_2tBu) signals gave correlations (δ_H [ppm] in F_1 ; δ_C [ppm] in F_2) at (11.7; 279) and (1.9; 56), respectively. A cross-peak is observed between the proton at $\delta = 3.5$ ppm (CHMe_2) and the carbon atom at $\delta = 29$ ppm, showing that CHMe_2 (not observed before) also appears at this chemical shift.

The corresponding molecular complexes **1m** and **1n**, with a molecular monosiloxy equivalent, were prepared by using $(\text{RO})_3\text{SiOH}$ in place of a siloxy group of the silica surface (Scheme 1).^[24-26] The reaction of **2** with 1 equivalent of $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiOH}]$ in C_6D_6 or pentane for 2 h at 25°C quantitatively gave $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{SiO})\text{Mo}(=\text{NAr})(=\text{CHtBu})(\text{CH}_2\text{tBu})]$ (**1m**) and tBuCH_3 . The closeness of the NMR data of **1m** to those of **1** fully supports the assignments (see Supporting Information). Complex **1m** shows resonances at $\delta = 12.05$ and 281.2 ppm ($^1J_{\text{CH}} = 110$ Hz) for the alkylidene ligand in the ^1H and ^{13}C NMR spectra, respectively, which is

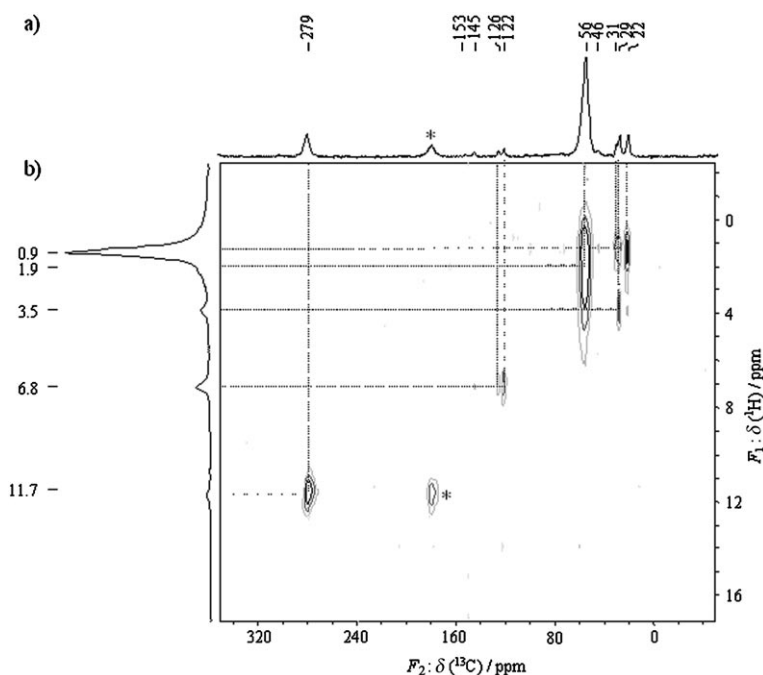
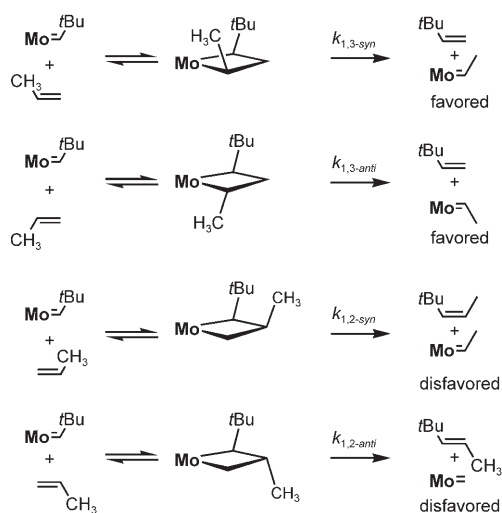


Figure 2. Solid-state NMR spectra acquired at a MAS frequency of $\nu_R = 12.5$ kHz. a) ^{13}C CP MAS NMR spectrum of **1*** recorded with TPPM-15^[31] ^1H decoupling at $\nu_1^H = 83$ kHz with 56 000 scans. The recycle delay was set to 1 s, and the contact time for the CP step was 1 ms. An exponential line broadening of 80 Hz was applied before Fourier transformation. b) 2D ^1H - ^{13}C dipolar HETCOR solid-state NMR spectrum of **1*** with a contact time of 1 ms (short-range HETCOR). A total of 32 t_1 were collected with 4096 scans each. Left: Projection along F_2 . Asterisks denote spinning side bands.

consistent with a *syn*-alkylidene complex.^[17] A similar reaction carried out over 15 h between **2** and [(*t*BuO)₃SiOH] yielded [(*t*BuO)₃SiO]Mo(=NAr)(=CH*t*Bu)(CH₂*t*Bu) (**1n**), which displayed similar NMR data and whose X-ray crystal structure (not shown) showed it to be the expected *syn* isomer.

When **1** is contacted with 1350 equivalents of propene at 25 °C (batch reactor), equilibrium is reached within 20 min (around 30 % conversion, *E/Z*-butene ratio = 2.6) with a turnover frequency (TOF) of 1.0 mol(mol_{Mo})⁻¹ s⁻¹, which is four times faster than with [(≡SiO)Re(≡C*t*Bu)(=CH*t*Bu)(CH₂*t*Bu)] (TOF = 0.25 mol(mol_{Re})⁻¹ s⁻¹).^[1,2] Moreover, roughly 0.7 equivalents of a 2.7:1 mixture of 3,3-dimethylbutene and 4,4-dimethyl-2-pentene is formed, as previously observed for [(≡SiO)Re(≡C*t*Bu)(=CH*t*Bu)(CH₂*t*Bu)],^[1,2] and shows that initiation is almost quantitative, in agreement with a well-defined system. Moreover, the ratio of cross-metathesis products is in full agreement with the following model: the favored pathway involves reaction intermediates that minimize the interaction between the alkyl substituents (Scheme 2).^[27]



Scheme 2. Application of the metallacyclobutane model propene metathesis to explain the favored $k_{1,3}$ pathway.

Moreover, the self-metathesis of 0.5 M solutions of 1-octene and ethyl oleate in toluene in the presence of 1 % of **1** gives the equilibrated mixture in 10 and 60 min, respectively (Table 1). The respective initial TOFs are 0.06 and 0.04 mol(mol_{Mo})⁻¹ s⁻¹, which is very close to those obtained for [(≡SiO)Re(≡C*t*Bu)(=CH*t*Bu)(CH₂*t*Bu)].^[28] The initial rates with the corresponding molecular complex **1m** are similar, but the reaction times needed to reach the same conversion (thermodynamic equilibrium) are much longer, which shows that, in this case, decomposition is faster. On the other hand, the quasi-inactivity of molecular complex **2** illustrates the activating effect of the siloxyl group.^[3,29]

In conclusion, we have shown that the molecular and surface complexes **1** and **1m** are electronically very similar in terms of both their comparable NMR data and initial TOFs in olefin metathesis. Nonetheless, the supported catalyst has a

Table 1: Olefin metathesis activity at room temperature for **1**, **1m**, and **2**.^[a]

Olefin	1		1m		2	
	TOF [s ⁻¹] ^[b]	<i>t</i> [h] ^[c]	TOF [s ⁻¹] ^[b]	<i>t</i> [h] ^[c]	TOF [s ⁻¹] ^[b]	<i>t</i> [h] ^[c]
1-Octene	0.06	1/6	0.06	1	0.02	48 ^[d]
Ethyl oleate	0.04	1	0.03	24	0.005	— ^[e]

[a] Experimental conditions: 1 % Mo, 25 °C, 0.5 M solution of olefin in toluene under Ar atmosphere. All reactions were monitored by gas chromatography. [b] Initial TOF measured after 5 min of reaction and expressed in moles of substrate per mole of Mo per second. [c] Time to reach equilibrium (around 50 % conversion). [d] 40 % conversion. [e] Deactivation after 2 % conversion.

longer lifetime under catalytic conditions, which shows that the effect of active-site isolation prevents some deactivation pathways such as dimerization of reactive intermediates.^[30] Moreover, the formation of about 0.7 equivalents of cross-metathesis product shows that most of the surface complex generates the active species, in agreement with a well-defined heterogeneous catalyst.

Experimental Section

See Supporting Information for full experimental procedures, the IR and ¹³C CP MAS NMR spectra of **1**, and the ¹³C CP MAS NMR spectra, 2D ¹H–¹³C dipolar HETCOR spectra with 1- and 5-ms contact times, and a full assignment of **1***.

Received: September 8, 2005

Published online: January 16, 2006

Keywords: carbene ligands · heterogeneous catalysis · metathesis · molybdenum

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