

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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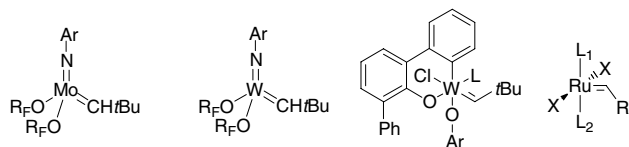
1. Introduction

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°

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