On the interaction of Schrock Mo–alkylidene complexes with the surface of inorganic oxides

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Abstract

This work describes the reactivity of Schrock-type alkylidenemolybdenum(VI) complexes, $Mo(=CHCPhMe_2)(=NAr)(O^tBu)_2$, **I**, or $Mo(=CHCPhMe_2)(=NAr)[OCMe(CF_3)_2]_2$, **II**, with the surface of silica, silica–alumina and niobia. In situ FT-IR studies suggest that **I** and **II** are attached to the surface of silica via a Lewis acid base adduct; on silica–alumina, an OH addition to the Mo=N bond seems to take place. Grafting of **I** and **II** causes a decrease in their intrinsic catalytic activity as well as a change in the stereoselectivity of **II** in ROMP of norbornene. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The reactivity of organometallic complexes with the surface of partially dehydroxylated amorphous inorganic oxides has been extensively studied for more than 20 years [1–6]. Among the objectives of such studies is the synthesis of surface-anchored complexes with a defined coordination sphere. In such heterogeneous molecular complexes, the metal center bears two types of ligands: (a) the "solid" ligand, through which the metal is bonded to the surface, usually an oxy-type ligand, and (b) the "classical" ligands, responsible for the chemical reactivity of the metal complex via their steric and electronic properties. Therefore, in certain cases, a new catalytic material, which exhibits much higher activities and/or selectivities for a given reaction, can be obtained.

Alkylidene complexes are considered to be intermediates in the olefin metathesis reaction [7]. Although the presence of alkylidene species in heterogeneous metathesis catalysts has often been suggested [8–13], the actual surface organometallic species has never been fully characterized. The few well-defined surface alkylidenes already described are not active in olefin metathesis [14,15]. In this work, we describe our attempts to prepare a Schrock-type surface alkylidenemolybdenum(VI) complex via the reaction of alkoxy-containing alkylidenemolybdenum(VI) compounds with the surface OH groups of some inorganic oxides, which have different acid–base properties. This kind

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of reaction has been described for alkylidene-tungsten(VI) molecular complexes [16]:

$$(NpO)_2Br_2W[=CH(CMe_3)] + Ph_3SiOH$$
$$\rightarrow (NpO)(Ph_3SiO)$$
$$\times Br_2W[=CH(CMe_3)] + NpOH \qquad (1)$$
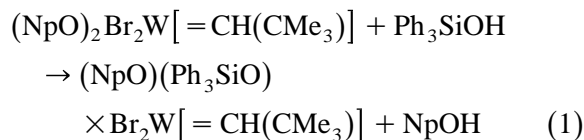
Therefore, the simple replacement of an alkoxy ligand by a surface $\equiv SiO$, $\equiv AlO$ or $\equiv NbO$ would be expected.

2. Experimental

The molybdenum complexes were purchased from Strem. SiO_2 (Degussa, 200 m^2 g^{-1}, ~ 2 OH per nm^2),[1] SiO_2–Al_2O_3 (Akzo, 24.3 wt.% Al_2O_3, 380 m^2 g^{-1}, ~ 0.2 OH per nm^2 [17,18]) and Nb_2O_5 (CBMM, ~ 100 m^2 g^{-1}, previously calcined under oxygen at 450°C, ~ 0.2 OH per nm^2 [19]) were treated under vacuum ($\sim 10^{-4}$ Torr) overnight at the desired temperature. Solvents (Merck) were distilled under argon over Na-benzophenone. *cis*-2-pentene and 1-hexene (Fluka) were purified by passing through a column of activated alumina. Norbornene (Aldrich) was distilled from molten sodium. Acetone was dried with $MgSO_4$ and distilled under argon.

2.1. Catalyst preparation

The catalysts were prepared in situ by impregnation of the support with a refluxing toluene solution of the molybdenum complex, using Schlenk techniques. After washing several times with toluene followed by drying under vacuum ($\sim 10^{-2}$ Torr) at room temperature, no complex could be extracted with THF. Molybdenum loadings were determined by ICP-EAS.

For infrared studies, the samples were prepared by sublimation, using standard break-and-seal techniques.

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[1] As determined by titration with $LiAlH_4$, according to Degussa's Technical note.

2.2. Activity measurements

Catalytic experiments with acyclic olefins were carried out under argon in glass batch reactors (Schlenk flasks) using *n*-pentane as an internal standard. Analysis of the gas phase was performed on an HP 5890 series II gas chromatograph equipped with a flame ionization detector and using an Al_2O_3/KCl-on-fused-silica capillary column (50 m $\times$ 0.32 mm). Conversions were calculated as follows for metathesis of *cis*-2-pentene:

$$\text{Conv.}(\%) = \frac{2[\text{butenes}]}{2[\text{butenes}] + [\text{pentenes}]} \times 100$$

For ROMP experiments, a solution of norbornene in 5 ml toluene was added to the catalyst in a Schlenk flask. After 5 min, 3 ml of acetone was added to terminate the reaction. The polymer was precipitated in ethanol and dried in vacuum. ^{13}C and ^{1}H NMR spectra of the polymers dissolved in $CDCl_3$ were recorded in a 300 MHz Bruker AC 300P spectrometer. GPC analyses were performed using Waters Styragel HT columns, calibrated with standards of polystyrene, and THF as the solvent, in a Waters 410 chromatograph equipped with an optic differential refractometer.

2.3. Infrared studies

In situ infrared spectra were recorded on a Nicolet 520 Fourier Transform spectrometer (16 scans, 4.0 cm^{-1} resolution), using special cells already described in the literature [20].

2.4. CP-MAS NMR studies

Solid state NMR spectra were recorded on a Bruker AC 300P spectrometer, operating at 75.45 MHz. The probehead was a commercial double-tuned 7 mm double-bearing system from Bruker, allowing spinning frequencies up to 4 kHz. The samples were introduced in the zirco-

nia rotors under a dry argon atmosphere in a glove box and tightly closed. The cross-polarization parameters were acquisition time: 0.16 s; pulse length: 9.5 μs; contact time = 5 ms; delay between each scan = 5 s. Typically, 11,000 scans were accumulated. Chemical shifts are given with respect to Me_4Si. The following resonances were observed after reaction of I or II with silica, niobia or silica–alumina: δ 22(= N{Ph[o-CH(**CH$_3$**)$_2$]$_2$}); 28.5 (= CHC(Ph)-(**CH$_3$**)$_2$; = N{Ph[o-**CH**(CH$_3$)$_2$]$_2$}); OC(**CH$_3$**)$_3$); 60–80 (O**C**(CH$_3$)$_3$); 115–130 (= CHC(**Ph-2, 3, 4, 5, 6**)(CH$_3$)$_2$; = N{**Ph-3, 4, 5**}); 145–160 (= CHC(**Ph-1**)(CH$_3$)$_2$; = N{**Ph-1, 2, 3**}).

2.5. Reaction of Mo(= CHCPhMe$_2$)(= Nar)-(O^{t}Bu)$_2$ / SiO$_2$ with 2,2′-bipyridine

Mo(= CHCPhMe$_2$)(= NAr)(O^{t}Bu)$_2$/SiO$_2$ was prepared by adding 32 mg (0.058 mmol) of the molybdenum complex dissolved in 5 ml of toluene to a Schlenk flask containing 400 mg of pretreated silica. The system was refluxed for 2 h and then the solvent was filtered off. After washing three times with 3 ml of toluene, the beige solid was dried under vacuum. A 4 ml dried THF was then added to the reactor followed by 2 ml of a THF solution of bipyridine (9.0 mg; 0.058 mmol). After 1 h under reflux, the slightly yellow solution was filtered off and an orange solid was obtained.

3. Results and discussion

Preliminary experiments were carried out in order to determine the maximum amounts of the complexes Mo(= CHCPhMe$_2$)(= NAr)-(O^{t}Bu)$_2$, **I**, or Mo(= CHCPhMe$_2$)(= NAr)-[OCMe(CF$_3$)$_2$]$_2$, **II**, where Ar = 2,6-isopropylphenyl, which could react with the OH groups of silica, niobia and silica–alumina. Therefore, an excess of complex (with respect to the known concentration of OH groups of each inorganic oxide), dissolved in toluene, was

added to a sample of the pre-treated support. After 2 h under reflux, the solvent was removed and the resulting solid washed several times with toluene until no complex could be detected in the washing solution. In further experiments, the amounts of I or II employed were slightly lower than the determined maximum, in order to assure that the reaction was complete (typical values are shown in Table 1). The fact that the white inorganic oxides became colored (beige) suggested that a chemical reaction had taken place. However, when the reaction solution was analyzed through GC-MS, the presence of alcohols (t-BuOH, in the case of **I**, or CMe(CF$_3$)$_2$OH, in the case of **II**) could never be detected. This result rules out the exchange reaction expected from Eq. (1).

Since preliminary qualitative experiments showed that I and II supported on silica or silica–alumina (but not on niobia) were active in metathesis of 1-hexene, thus suggesting that for these inorganic oxides the Mo=C bond had not been affected by the surface reaction, we decided to further characterize these systems by NMR and in situ infrared experiments.

3.1. IR experiments

When **I** was sublimed onto a disk of silica pre-treated under vacuum at 500°C, SiO$_2$(500), followed by a thermal treatment at 80°C, the infrared spectrum showed that the band at 3747 cm^{-1}, assigned to isolated silanol groups, almost disappeared. At the same time, a group of bands appeared in the regions 3090–2878 and 1600–1370 cm^{-1}, which can be assigned to ν(C–H) and δ(C–H) vibrations of the organic groups. A band at 3593 and a large one centered in 3290 cm^{-1} were also observed. Heating at 120°C had almost no effect on the spectrum, besides a small increase in the band at 3747 cm^{-1}. However, after evacuation at 120°C, the band at 3747 cm^{-1} was almost completely recovered, and the bands assigned to ν(C–H) and δ(C–H) vibrations nearly disappeared. A similar behavior was observed for **II**/SiO$_2$(500)

Table 1
Catalytic activity of I and II when supported on different inorganic oxides[a]

	Mo content (wt.%)	cis-2-pentene conversion (%)[b]	Norbornene polymerization[c]			
			$Mn_{theor.}$	Mn_{found}^d	PDI	cis/trans[e]
I/silica	1.8	< 1	9437	196,168	1.82	1.6
I/niobia	0.3	0	–	–	–	–
I/silica–alumina	0.9	4.7	9209	221,773	1.93	1.5
II/silica	1.4	∼ 6	9793	206,508	1.86	1.7
II/niobia	0.4	0	–	–	–	–
II/silica–alumina	1.0	31	9510	217,598	1.96	3.0
I						1.5
$Mo(CH^tBu)(NAr)[OCMe(CF_3)_2]_2$			9580[f]	10,045[f]	1.06[f]	n.r.[g]
II			9331	18,430	1.42	4.7

[a][Olefin]:[Mo] ∼ 100; room temperature.
[b]Solvent = hexanes; reaction time = 2 h.
[c]Solvent = toluene; reaction time = 5 min, quenched with benzaldehyde.
[d]Corrected ($Mn_{found}/2.2$).
[e]Determined through ^1H NMR analysis in $CDCl_3$.
[f]Ref. [24].
[g]Not reported.

(Fig. 1).[1] The same behavior was observed in parallel experiments when pentane solutions of the complexes were added to the IR cell. A
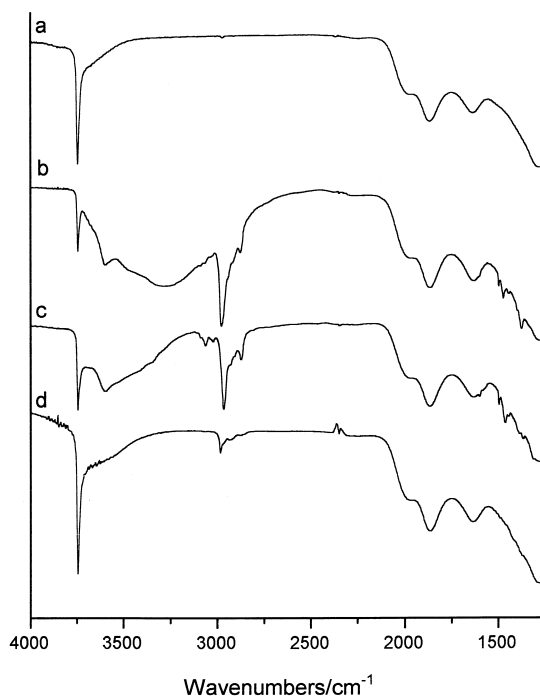

Fig. 1. Infrared spectra of (a) $SiO_2(500)$; (b) $I/SiO_2(500)$ after heating at 120°C; (c) $II/SiO_2(500)$ after heating at 120°C; and (d) $I/SiO_2(500)$ after evacuation at 120°C.

comparison between the spectra obtained for $I/SiO_2(500)$ and $II/SiO_2(500)$ suggests that the band at 3593 cm^{-1} ($I/SiO_2(500)$) or at 3600 cm^{-1} ($II/SiO_2(500)$) might be due to hydrogen bonding involving CH_3 (from t-BuO or from $CHCMe_2Ph$) and ≡SiOH groups.
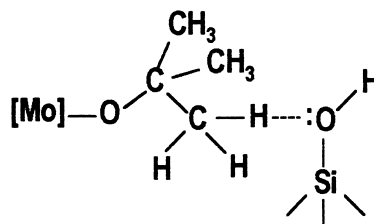
This type of interaction has been described for $SnBu_4$ physisorbed on $SiO_2(500)$ in which case a band at 3698 cm^{-1} was observed [21].

On the other hand, all resonances expected in the ^{13}C CP-MAS NMR spectra of $I/SiO_2(500)$ and $II/SiO_2(500)$ were broadened, suggesting that the complexes were not simply physically adsorbed on the silica surface. Therefore, the broad band centered at 3290 cm^{-1} ($I/SiO_2(500)$) could be due to a weakened OH stretching vibration, suggesting a complexation of the molybdenum compounds to the silica

surface through the formation of Lewis acid–base adducts, involving one or two $\equiv$SiOH groups:

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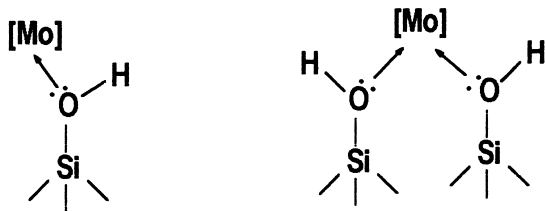
This kind of complexation has already been described for I and II with dimethoxyethane [22].[2]

In the case of I and II/SiO$_2$–Al$_2$O$_3$(500), infrared spectra show some differences (Fig. 2): I and II could not be removed from the surface of silica–alumina even after 32 h under vacuum at 120°C. This result suggests that bridging OH groups ($\equiv$Si(OH)Al$\equiv$), not observed in the infrared spectra, might be involved in a surface reaction, probably through an addition to the Mo=N bond, in agreement with the presence of bands in the 3400–3200 cm^{-1} region and at 1577 cm^{-1}, which can be ascribed to ν(N–H) and δ(N–H) vibrations, respectively, of an amino ligand. These bands are not observed in the spectra of I and II/SiO$_2$(500). The isolated $\equiv$Si–OH groups would be responsible mainly for hydrogen bonding since the band at 3747 cm^{-1} is not completely recovered after evacuation at 120°C, while a broad band centered at ca. 3600 cm^{-1} is still present.

3.2. Chemical reactivity

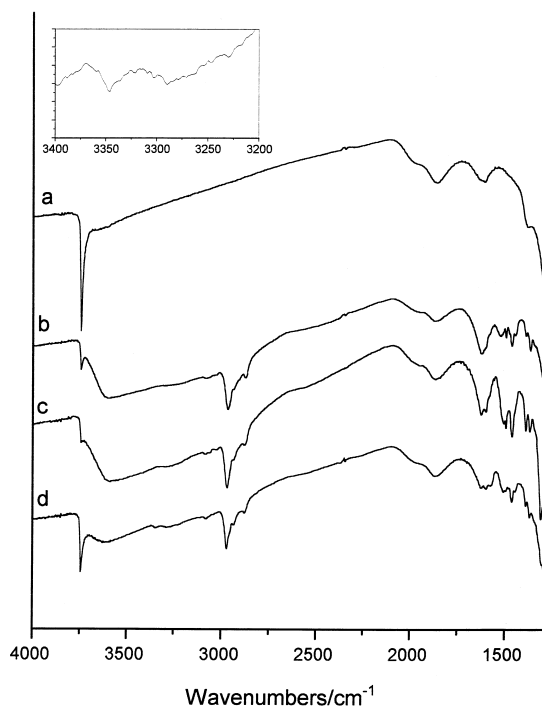If the alkylidene fragment had remained intact when I or II were attached to the surface of

Fig. 2. Infrared spectra of (a) SiO$_2$–Al$_2$O$_3$(500); (b) I/SiO$_2$–Al$_2$O$_3$(500) after heating at 120°C; (c) II/SiO$_2$–Al$_2$O$_3$(500) after heating at 120°C; and (d) II/SiO$_2$–Al$_2$O$_3$(500) after evacuation at 120°C; inset: magnification of the 3400–3200 cm^{-1} region of (d).

the inorganic oxide, it should be possible to identify it in a ROMP polymer started by I (or II)/SiO$_2$(500). In order to verify this possibility, a polymerization was carried out using only 10 equivalents of norbornene. The ^{13}C NMR spectrum (CDCl$_3$) of the resulting polymer showed a group of resonances at δ 129.1, 128.3, and 125.4, assigned to the carbons of the phenyl group, and a single peak at δ 29.6, corresponding to the methyl groups of the neophylidene ligand.[3] This result confirms that the surface reaction did not affect the alkylidene ligand.

On the other hand, if I and II were indeed attached to the silica surface via a Lewis acid–base interaction, it should be possible to extract them using a stronger Lewis base. Therefore,

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[2] These would be the species present on the silica surface when higher amounts of I or II/silica were prepared in a toluene suspension to be used in the catalytic experiments.

[3] The signal at δ 29.6 might also be due to the methyl groups from acetone, used to terminate the polymerization.

I/SiO$_2$(500) was allowed to react with 2,2′-bi-pyridine under reflux in a THF suspension. After 1 h, the beige solid turned orange but the complex could not be extracted from the surface. After removal of the THF, the orange solid was tested in a polymerization reaction with norbornene, showing no activity at all. Moreover, after addition of acetone, the solid remained orange, in contrast with the behavior displayed by all other systems in the same conditions, whose colors turned green. This result suggests that, via coordination to the molybdenum center, bipyridine/THF had promoted an addition of the surface OH groups on the Mo=C bond.

3.3. Catalytic experiments

All solids were tested in metathesis of *cis*-2-pentene (Table 1). Although grafting of **II** caused a decrease in its intrinsic catalytic activity [23], as it was already reported when **II** was complexed with dimethoxyethane [22], I and II supported on silica–alumina are far more active than when supported on silica. This difference may be due to the different kind of interaction operating in each case. In order to check whether the attachment to a surface had any effect on the stereoselectivity of these systems, they were also tested in ROMP of norbornene (Table 1). Although benzaldehyde was used to quench the polymerization, GC analyses of the reaction media showed 100% consumption of the monomer in 5 min in all cases. Nevertheless, yields were usually around 80%, probably due to problems found when trying to separate the polymer from the support and/or to the formation of low molecular weight oligomers. It was also observed that the ratio Mn$_{found}$/Mn$_{theor.}$ for all supported systems was ca. 21, suggesting that no more than 5% of the molybdenum sites were acting as initiators. It can be seen that although grafting of **II** causes a great decrease in the *cis/trans* ratio of the resulting polymer, in the case of **I** this effect was not observed. Polydispersities, however, were increased. A high PDI

value for polynorbornene (∼ 1.63) obtained with W(CH^{t}Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ as the initiator has been attributed to slow initiation followed by very rapid propagation [25]. In our case, a decrease in the polymerization initiation rate might be due to the steric hindrance caused by the solid ligand and/or to the lack of a vacant site in the coordination sphere of the supported complex. Once this site is created via decoordination of an ≡SiOH ligand and metathesis is initiated, propagation can easily take place.

4. Conclusions

Complexes I and II react with the surface of inorganic oxides in different ways, depending on the Brönsted acid strength of the surface OH groups. With silica, which presents a very weak Brönsted acidity, I and II appear to form Lewis acid–base adducts even at room temperature; with silica–alumina, the highly acidic bridging OH groups seem to add to the Mo=N bond; and, in the case of niobia, there appears to be an addition of the OH groups to the Mo=C bond, thus completely deactivating the catalyst.

For **II**/silica or silica–alumina, a change on both the stereoselectivity and polydispersities in ROMP of norbornene was observed, probably due to the steric hindrance of the solid ligand.

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