



GRAFTING OF GROUP 6 IMIDO-ALKYL COMPLEXES ON SILICA: Mo vs. W

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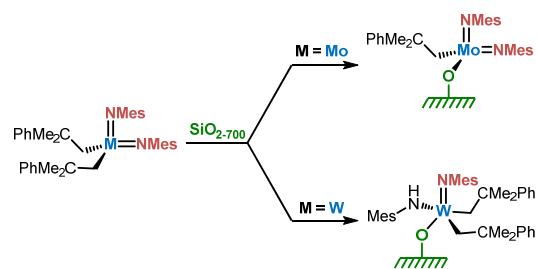
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Abstract

Grafting of the isostructural imido-alkyl complexes $M(=NMe_3)_2(CH_2CMe_2Ph)_2$ ($M = Mo$ (**1**), W (**2**); $Me_3 = 2,4,6-Me_3C_6H_2$) onto the surface of SiO_2 partially dehydroxylated at 700 °C and physicochemical study (mass balance, IR, EA, SSNMR) of resulting materials **1s** and **2s** are presented. While for molybdenum complex, grafting primarily proceeds *via* cleavage of the alkyl group, protonation of the imido ligand becomes a predominant pathway for the tungsten counterpart. The catalytic activity of **1s** and **2s** in oxo/imido heterometathesis is also determined and compared with the previously reported systems.

Key words: imido complexes, heterometathesis, surface organometallic chemistry, tungsten, molybdenum.



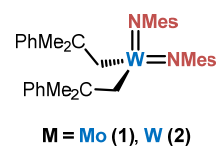
Introduction

Surface organometallic chemistry (SOMC) is a field at the interface between molecular organometallic chemistry and surface science that aims at selective preparation and rigorous characterization of well-defined transition metal complexes on surfaces of solid supports with the ultimate goal to rationalize and facilitate the development of heterogeneous catalysis [1–7]. The key motivation of SOMC is building the well-defined models of classical heterogeneous catalysts (that are often ill-defined and difficult to study) in order to apply the knowledge of molecular transition metal catalysis to investigate the reaction mechanisms and intermediates on surfaces, to develop structure–activity relationships, as well as to design the unusual supported organometallic species that cannot exist in solution (or are too unstable). Due to the rapid improvements of physicochemical techniques in recent decades this approach has led to impressive advances in many areas.

In our studies, we applied SOMC to design well-defined silica-supported imido complexes $(=SiO)M(=NR)(L_n)$ to be used as oxo/imido heterometathesis catalysts [8–12] that mediate a direct imidation of various oxo substrates to afford the corresponding imine derivatives using such imidating agents as *N*-sulfanylamines [13, 14]. The covalent attachment of the active species to the surface and resulting site-isolation was a critical step in the development of such catalysts as it helped to suppress the undesired oligomerization of $[M]=NR$ and especially $[M]=O$ intermediates, which is particularly pronounced in the case of highly reactive imides of such metals as Ta [12], Ti [9, 10], and Zr [11]. The development of these catalysts required careful choice of the molecular precursors that would selectively interact with the surface OH groups leaving the imido ligand intact as protonation of multiply-bonded ligands is a very

common side reaction during grafting of such species. Due to this selectivity issue, the careful characterization of the resulting materials by physicochemical methods is always necessary.

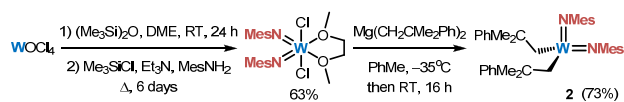
In this report, we investigated and compared the interaction of two isostructural Mo and W imido-alkyl complexes $M(=NMe_3)_2(CH_2CMe_2Ph)_2$ ($M = Mo$ (**1**), W (**2**); $Me_3 = 2,4,6-Me_3C_6H_2$) with the surface of silica partially dehydroxylated at 700 °C (SiO_{2-700}) (Scheme 1). Our interest to group 6 was inspired by a recent discovery that W imides in fact represent a viable alternative to the highly active but also highly sensitive Ti oxo/imido heterometathesis catalysts due to their greater stability combined with fairly good activity [15].



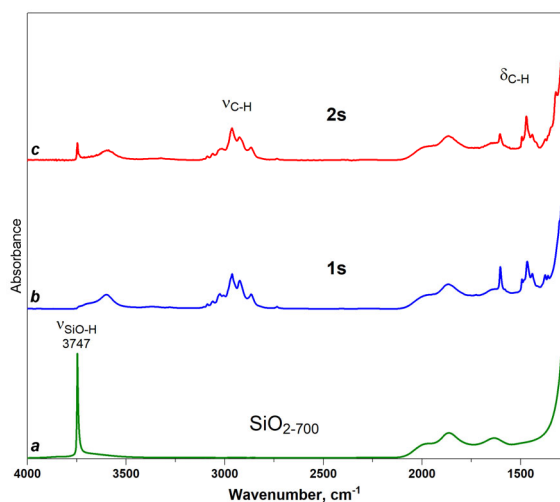
Scheme 1. Complexes studied in this work.

Results and discussion

The application of silica-supported Mo complex $Mo(=NMe_3)_2(CH_2CMe_2Ph)_2$ (**1**) in oxo/imido heterometathesis has been reported previously but the nature of surface species in the material was not investigated by physicochemical methods [16]. We have recently prepared and tested the supported W bis-imide $(=SiO)W(=NMe_3)_2(Me_2Pyr)$ (**3s**; $Me_2Pyr = 2,5$ -dimethylpyrrolyl) [15]; however, for the correct comparison, we wanted to investigate the Mo and W complexes with exactly the same ligand set (Scheme 1) and thus prepared complex $W(=NMe_3)_2(CH_2CMe_2Ph)_2$ (**2**) starting from the reported bis-imido dichloride (Scheme 2) [17].

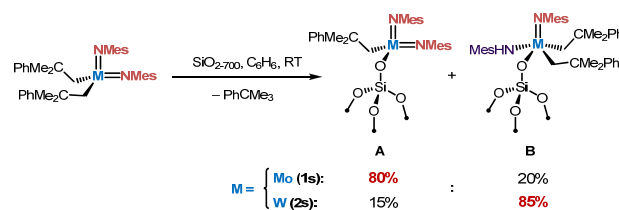


Scheme 2. Synthesis of W complex 2.

Figure 1. IR spectra of SiO₂₋₇₀₀ (a) and materials 1s (b), 2s (c).

The treatment of SiO₂₋₇₀₀ (silica dehydroxylated at 700 °C containing only isolated silanol groups on the surface) with benzene solutions of 1 and 2 gave materials 1s and 2s. The IR spectra of these materials (Fig. 1) confirmed the appearance of ν_{CH} and δ_{CH} bands of the ligands and the consumption of a sharp band of isolated silanols at 3747 cm⁻¹ (complete in the Mo case and almost complete for W), but the presence of broad bands in the region of 3750–3500 cm⁻¹ corresponding to the residual silanols, interacting with the ligands of surface complexes, indicated that in both cases grafting was not quantitative. Indeed, the analysis of the ¹H NMR spectra of the liquid phase confirmed that ca. 10% of 1 and ca. 20% of 2 remained unreacted. It also showed that in the case of Mo ca. 0.7 equiv. of PhCMe₃/Mo evolved in solution during grafting. This indicated the formation of the expected bis-imido complex A as major surface species along with a minor amount of mono-imide B, resulting from the protonation of one of the imido groups (A/B = ca. 80/20 (±10%), Scheme 3). Surprisingly, in the case of W only ca. 0.1 equiv. of PhCMe₃/W was observed in solution, leading to a conclusion that the main grafting pathway for 2 was the protonation of the imido ligand with the predominant formation of surface form B (A/B = ca. 15/85 (±10%)). The elemental analyses of the materials showed the metal content of 0.15–0.16 mmol·g⁻¹ (1.4 wt % of Mo for 1s and 3.0 wt % of W for 2s) and revealed that 1s had a Mo/N/C ratio of 1/2.6/29.8 close to the value of 1/2/28 expected for form A, while 2s had somewhat higher carbon content corresponding to the values intermediate between forms A and B (different measurements showed the value in the range W/N/C = 1/1.9/32–38).

The ¹³C CP/MAS solid-state NMR (SSNMR) spectra of materials 1s and 2s are shown in Figs. 2a and 2b, respectively (for the enlarged figures, see the Electronic supplementary information (ESI)). Except for the signals of the CH₂ groups directly attached to the metals (which are often problematic to

Scheme 3. Grafting of complexes 1 and 2 onto SiO₂₋₇₀₀.

observe without isotopic labeling [18–20]), they contain all the characteristic resonances of the Mes and alkyl ligands: *ortho*- and *para*-Me of Mes at ca. 17 ppm, CH₂CMe₂Ph groups at 29–30 ppm, quaternary carbon of neophyl at 38–41 ppm, intense signals in aromatic region, and quaternary *ipso*-carbons of Mes and Ph rings at ca. 150 ppm. However, they unfortunately cannot discriminate the bis-imido and imido–amide forms A and B as there are no distinct characteristic ¹³C resonances that would distinguish =NMe and –NHMe ligands, and thus, on the basis of ¹³C SSNMR data, one could mistakenly assume that the same surface species are formed in both cases. Forms A and B could be unambiguously distinguished by the ¹⁵N SSNMR spectra but this requires ¹⁵N-labeled molecular precursors and thus ¹⁵N NMR characterization of surface imido complexes is still extremely rare [21–23]. The difference between materials 1s and 2s could in fact be suspected based on the comparison of their ¹H SSNMR spectra (Figs. 2c and 2d) that show very different ratios between the resonances of the methyl groups of mesityl (at ca. 1.9 ppm) and neophyl ligands (at ca. 1.1–1.3 ppm; observed as a shoulder in the spectrum of 1s and more distinct for 2s), consistent with the presence of ca. two neophyl ligands in 2s and only one in 1s (whereas all forms have two mesityl groups).

This example provides a convincing illustration of the complications that may arise in seemingly straightforward application of SOMC protocols. It also demonstrates that the characterization of surface species in SOMC should not only rely on one particular method (even so powerful as SSNMR) and should not neglect simple complementary techniques, such as elemental and mass balance analysis. Moreover, it points out a drastic reactivity difference between the isostructural W and Mo imides. In this respect, it is also noteworthy that the attempted immobilization of similar W imide W(=NAr)₂(CH₂CMe₃)₂ (Ar = 2,6-*i*Pr₂C₆H₃) resulted in a recovery of ~50% of unreacted complex and only a very small amount of neopentane, whereas its molybdenum analog was reported to graft smoothly [24].

A great deal of classical studies in SOMC performed by Basset, Marks, Yermakov and others [2, 3, 5–7] relied on the alkyl precursors that react with surface silanol groups *via* irreversible elimination of alkane, and thus grafting *via* the alkyl ligand is often considered a universal strategy. Herein, we showed that this might not always be the case. Anwander was the first to point out the usefulness of amides for grafting early transition metal complexes and systematically reviewed this approach [4]. In our work with Ti and Zr imides, where monomeric alkyl precursors are not available, we found 2,5-dimethylpyrrolyl to be an excellent leaving group, in most cases enabling selective grafting without concomitant protonation of

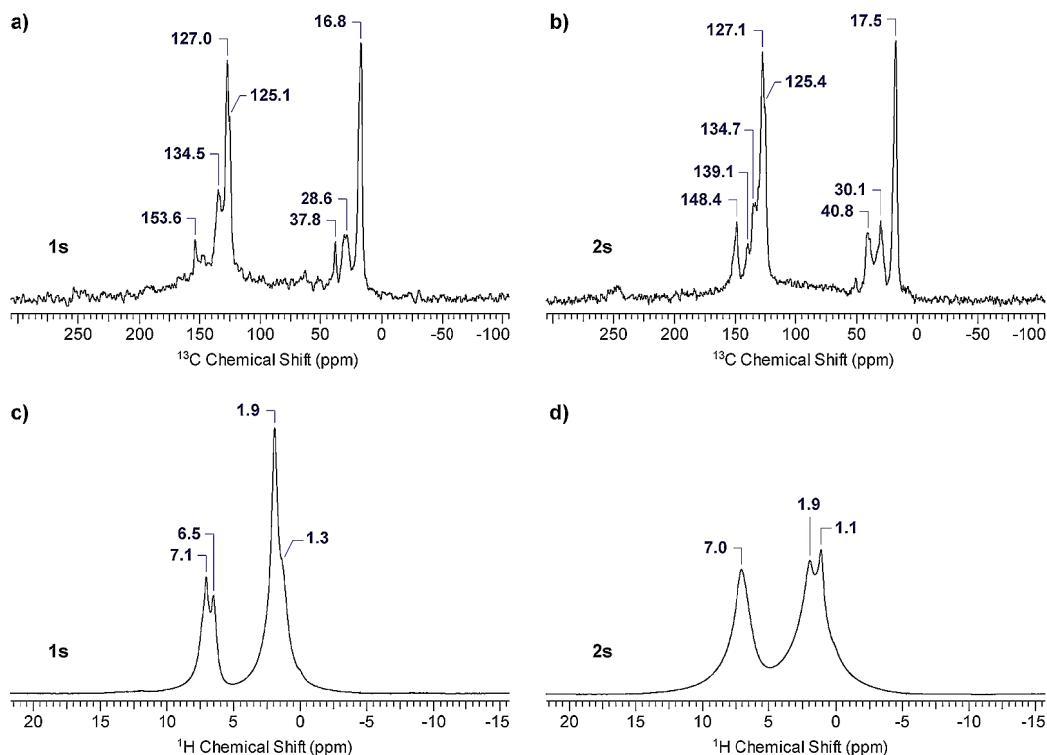
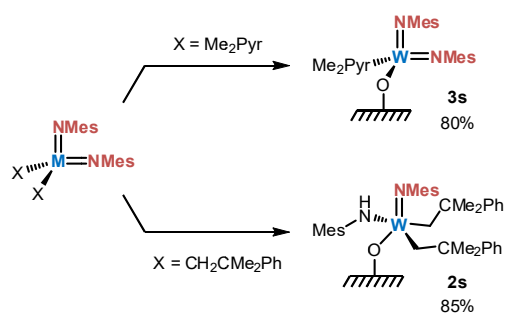


Figure 2. ^{13}C CP/MAS SSNMR spectra of materials **1s** (a) and **2s** (b); ^1H MAS SSNMR spectra of **1s** (c) and **2s** (d).

the imido ligand [8–11]. Now, the comparison between isostructural W alkyl (**2s**) and pyrrolyl (**3s** [15]) bis-imides (Scheme 4) showed even more convincingly that, for early transition metals, the more ionic amides/pyrrolides may in fact be a better option for grafting of the molecular precursors containing highly reactive moieties than the more covalent alkyls. This case is an instructive example demonstrating that alkyl is not a 'by default' leaving group and that careful choice of a molecular precursor is very important to direct the preparation of supported species in a desired way.



Scheme 4. Predominant grafting pathways for W pyrrolyl and alkyl imides.

The activity of catalysts **1s** and **2s** in the oxo/imido metathesis was evaluated by the previously developed model reaction of benzophenone imidation with *N*-sulfinyl-*p*-toluidine in boiling heptane (98 °C) at 1 mol % loading with respect to the metal (Fig. 3). Both materials demonstrated quite similar performances, with $\text{TOF}_{15\text{min}} = 18 \text{ h}^{-1}$ and $\tau_{1/2} \sim 2 \text{ h}$ for **1s** vs. $\text{TOF}_{15\text{min}} = 25 \text{ h}^{-1}$ and $\tau_{1/2} < 2 \text{ h}$ for **2s** (Table 1). In both cases, the moderate induction behavior was observed, which is likely to be associated with bulky mesityl substituents on the imido nitro-

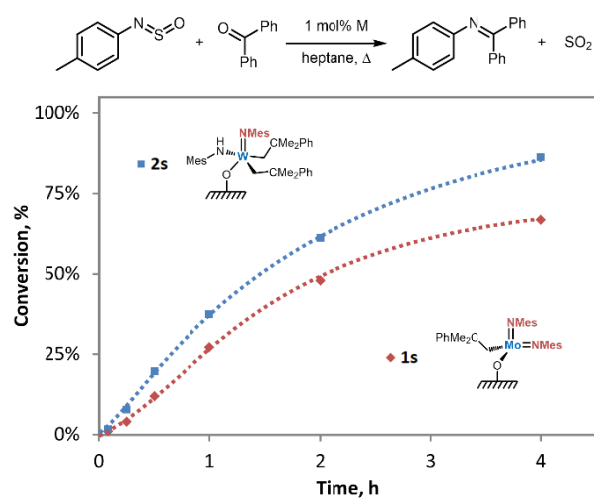


Figure 3. Catalytic performance of materials **1s** and **2s** in the oxo/imido heterometathesis.

gens that may impede initiation of the catalytic cycle (the initial replacement of =NMe₂ for =NTol).

Interestingly, the comparison of **2s** with **3s** showed that bis-imide **3s** revealed drastically higher initial activity ($\text{TOF}_{15\text{min}} \sim 100 \text{ h}^{-1}$; $\tau_{1/2} = 1 \text{ h}$ [15]), which is in line with bis-imido complexes being generally more reactive than their mono-imido counterparts due to the π -loading effect [25–28]. After 4 h of the reaction, both of the W catalysts actually converge to the same conversion (Fig. S9 in the ESI), but at such a late stage of the reaction, the performance may be already affected by the catalyst degradation. It is also interesting to compare the supported Mo and W catalysts with the corresponding oxides dispersed on silica *via* wet impregnation (Table 1) [15]. Noteworthy, the activity of WO₃/SiO₂ is in fact higher than that

of grafted catalyst **2s** and falls in between **2s** and **3s**, correlating with the well-known presence on its surface of both mono- and dioxo species, $(\equiv\text{SiO})_4\text{W}(\text{=O})$ and $(\equiv\text{SiO})_2\text{W}(\text{=O})_2$, isostructural to **2s** and **3s**, respectively [29].

It should also be noted that molecular precursors **1** and **2** used as homogeneous catalysts under the same conditions (but replacing heptane with toluene to ensure solubility) displayed negligible activities, producing *ca.* 16% and 6% of the imine product after 24 h for **1** and **2**, respectively.

Table 1. Activity of different Mo and W oxo/imido heterometathesis catalysts^a

Catalyst	TOF _{15min} ^b	$\tau_{1/2}$ ^c
$(\equiv\text{SiO})\text{Mo}(\text{=NMes})_2(\text{CH}_2\text{CMe}_2\text{Ph})$ (1s)	18 (3)	2 h
MoO ₃ /SiO ₂ [15]	8 (2)	6–8 h
$(\equiv\text{SiO})\text{W}(\text{=NMes})_2(\text{CH}_2\text{CMe}_2\text{Ph})$ (2s)	25 (8)	1.5–2 h
WO ₃ /SiO ₂ [15]	58 (12)	1–2 h
$(\equiv\text{SiO})\text{W}(\text{=NMes})_2(\text{Me}_2\text{Pyr})$ (3s) [15]	99 (14)	1 h

^a the reaction is shown in Fig. 3;

^b TOF averaged over the first 15 min of the reaction (average of several runs, SD given in parentheses);

^c half-conversion time.

Conclusions

In search for a direct comparison between Mo and W imides in catalytic oxo/imido heterometathesis, we prepared and characterized silica-supported complexes of these metals *via* SOMC approach starting from the isostructural imido-alkyl precursors. However, it was found that these compounds demonstrated very different behavior upon grafting. Whereas the Mo complex gave the expected surface bis-imido species, for W analog, the interaction with the surface $\equiv\text{SiOH}$ groups proceeded mainly as 1,2-addition of O–H across one of the W=N bonds and not as a desired cleavage of the W-alkyl bond. This is also in stark contrast to the previously reported similar W imido-pyrrolyl complex which grafts selectively to give a surface bis-imide. We consider this case a representative example that, for the immobilization of compounds with reactive metal–ligand multiple bonds, leaving groups other than alkyls could sometimes be more efficient and thus should not be disregarded.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the experimental procedures and spectra. For ESI, see DOI: 10.32931/io2445a.

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