Well-Defined Silica Grafted Molybdenum Bis(imido) Catalysts for Imine Metathesis Reactions

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S Supporting Information

ABSTRACT: Novel site-isolated tetracoordinated molybdenum complexes possessing bis(imido) ligands, $[(\equiv Si-O)_2Mo(=NR)_2]$ (R = t-Bu, 2,6-C₆H₃-*i*-Pr₂), were immobilized on partially dehydroxylated silica (SiO₂₋₂₀₀) by a rigorous surface organometallic chemistry protocol. The newly developed materials adorned with bis(imido) functional units, which were previously exploited mainly as spectator ligands on silica-supported olefin metathesis molybdenum catalysts, are found to be efficient heterogeneous catalytic systems for imine cross metathesis under mild conditions.



INTRODUCTION

Over the past decades researchers in the field of chemistry have witnessed an unparalleled impetus from metal–alkylidenemediated olefin metathesis for the formation of new carbon– carbon double bonds.¹ The potential of the reaction has been overwhelmingly exploited in organic synthesis^{1a,b,2} and the synthesis of polymers.^{1c,d,3} Furthermore, efforts have also been made, although to a lesser extent, toward the development of analogous transition-metal-catalyzed methods for selectively metathesizing carbon–nitrogen double bonds (eq 1).⁴ The

$$\mathbf{R}_{1} \qquad \mathbf{N}^{\mathbf{R}_{2}} + \mathbf{R}_{3} \qquad \mathbf{N}^{\mathbf{R}_{4}} \underbrace{\mathbf{Cat.}}_{\mathbf{R}_{1}} \qquad \mathbf{N}^{\mathbf{R}_{4}} + \mathbf{R}_{3} \qquad \mathbf{N}^{\mathbf{R}_{2}} \qquad (1)$$

main advantage associated with the latter process in comparison to the traditional approaches for carbon–heteroatom bond formation, for instance acid-catalyzed imine exchange,⁵ encompasses better selectivity, milder reaction conditions, tolerance to the diverse functional groups, and improved reaction rates.

Furthermore, the study of metal-mediated imine metathesis still has a fundamental interest, as no definite mechanism has yet been identified. In fact, in addition to the Chauvin-type [2 + 2] mechanism, a pathway involving an amide intermediate has been proposed.^{46,6,7} Finally, another fundamental benefit of this study is its potential to obtain a better understanding of the reactivity of transition-metal imido groups that have mainly been used so far as spectator ligands in a number of catalytic reactions, including olefin metathesis. The Meyer group in particular has demonstrated the utility of a number of

hexacoordinated molybdenum based bis(imido) complexes of the general formula Mo(NR)₂Cl₂dme^{4a,b} toward imide/imine cross metathesis under homogeneous catalytic conditions. In our recent research endeavor to this end, we strived to explore the potential of a tetracoordinated bis(imido) molybdenum based system to serve as an intermediate in imido group (= NR) transfer reactions under heterogeneous catalytic conditions. In particular, we sought to immobilize the tetracoordinated bis(imido) molybdenum core structure on the surface of silica by accurate surface organometallic chemistry (SOMC) techniques and investigate their catalytic activities. SOMC has emerged as an unique strategy for the isolation of catalytically relevant organometallic fragments in well-defined sites on the surface of oxide supports,^{8,9} thus allowing access to a myriad of surface complexes that are active for a wide range of catalytic reactions including alkane metathesis, alkene metathesis, methane nonoxidative coupling, etc.^{8b,9} We recently communicated catalytic imine metathesis reactions using SOMCdeveloped silica-supported imido zirconium complexes, which represent the first heterogeneous catalysts active for imido group (=NR) transfer reactions.⁴ Here we disclose the SOMC preparation of two Lewis base free well-defined tetracoordinated bis(imido) molybdenum catalysts, $[(\equiv Si-O-)_2Mo(=$ NR_{2} (R = t-Bu (2a), 2,6-C₆H₃-i-Pr₂ (2b)), and their full characterization using FT-IR and solid state NMR spectroscopy, elemental microanalysis, and X-ray absorption spectroscopy

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(XAS). **2a,b** were both found to be efficient heterogeneous catalysts for imine cross metathesis under mild conditions.

RESULTS AND DISCUSSION

The grafting of bis(imido) molybdenum precursor complexes, $[Mo(=NR)_2(CH_2-t-Bu_2)_2]$ (1a, R = t-Bu; 1b, R = 2,6-C₆H₃-*i*-Pr₂) (see the Supporting Information for experimental details) at room temperature on silica partially dehydroxylated at 200 °C (SiO₂₋₂₀₀), followed by degassing at 80 °C resulted in materials 2a,b (Scheme 1). As we believe, reaction of 1a,b with

Scheme 1. Proposed Reaction Scheme for the Grafting of Bis(imido) Molybdenum Precursor Complexes 1a,b on SiO₂₋₂₀₀



SiO₂₋₂₀₀ presumably occurs via a silanolysis reaction, thereby resulting in a sharp depletion of a part of the isolated ν (SiO–H) at 3747 cm⁻¹ with a concomitant appearance of new bands in the 2990–2870 cm⁻¹ (for 2a) and 3070–2870 cm⁻¹ ranges (for 2b) as well as in the 1600–1360 cm⁻¹ range (Figure 1). These peaks are characteristic of aromatic and aliphatic ν (C–H), ν (C=C), and δ (C–H) vibrations of the ligands of surface-grafted molybdenum complexes. Additionally, a broad band



Figure 1. FT-IR spectra of SiO_{2-200} (bottom), 2a (middle), and 2b (top).

attributable to the remaining silanols, which are likely to be in interactions with the surrounding ligands, extending from 3750 to 3200 cm⁻¹ was observed. The presence of weak infrared signals in the wavelength range of 3290-3250 cm⁻¹ may hint at a partial development of molybdenum amine species (Scheme 1) through a proton transfer reaction.

However, an elemental microanalysis study indicates Mo, C, and N contents of 2.60, 2.88, and 0.66 wt % for **2a** and of 1.55, 4.69, and 0.47 wt % for **2b**, respectively, which corresponds to C/Mo and N/Mo molar ratios of 8.8 and 1.74 for **2a** (theoretical 8.0 and 2.0); for material **2b** these ratios are 24.2 and 2.07 (theoretical 24.0 and 2.0). On the basis of these results it could be inferred that the materials **2a**,**b** are likely to contain mainly the bipodal tetracoordinated molybdenum surface complexes with no significant residual neopentyl ligands at the molybdenum center.

To gain further insights into the aforementioned experimental data, grafting of complexes 1a,b onto SiO_{2-200} and their possible transformation at elevated temperatures were investigated computationally using density functional theory (DFT) a and cluster model of the silica support (see Figure S1 in the Supporting Information). The proposed mechanism for transformations of species 1a,b is given in Scheme 2. For

Scheme 2. Proposed Grafting Pathways for the Molecular Complexes 1a,b onto a Silica Model $(SiO_{2-200})^a$



^{*a*}The numerical values (red for 1a and blue for 1b) noted in parentheses are free energies, in kcal mol⁻¹.

clarity, we will use capital letters A-D to denote all the various minimum-energy species. Transition states are described with the notation exemplified by $[A-B]^{\ddagger}$, referring to the transition state indicating the transformation of A to B. When describing the reaction profile, we concentrate on *t*-Bu complex 1a. The main differences between the reaction profiles of species 1a and 1b are emphasized in the following section.

The grafting of complexes 1a onto $SiO_{2.200}$ support can be initiated via two alternate mechanistic pathways. In the first mechanism, the hydrogen transfer from one of the Si–O–H groups to a CH₂-*t*-Bu group bound to the Mo atom occurs via transition state [1a-A][‡]. The reaction is highly exergonic by 33.9 kcal/mol of Gibbs free energy and results in the formation of monopodal species **A** and liberation of a free CH₃-*t*-Bu molecule. In terms of the activation Gibbs free energy, such a transformation requires 18.3 kcal/mol. As the reverse reaction would require 52.2 kcal/mol of free energy, if it occurs, the

transformation of 1a to A can be considered irreversible. The monopodal species A can further undergo a few subsequent transformations. First, another hydrogen transfer from the vicinal silanol group on silica can occur to the CH₂-t-Bu group bonded to Mo via the transition state $[A-B]^{\ddagger}$. This transformation requires 22.4 kcal/mol of activation free energy and leads to bipodal species B with release of a second CH₃-t-Bu molecule. This step is again found to be highly exergonic by 20.3 kcal/mol and essentially irreversible if it happens. The second transformation the species A can undergo is the transfer of hydrogen from surface silanol to the Mo=N double bond, resulting in bipodal amido species D, in which Mo is pentacoordinated. This reaction is exergonic by 3.1 kcal/mol and requires only 11.1 kcal/mol of activation free energy. In contrast to the processes 1a-A and A-B, the A-D transformation is reversible, as process D-A would require only 14.2 kcal/mol. The transformation of **D** to **B** via α -hydrogen transfer from the NH group bound to Mo and liberation of a CH₃-t-Bu molecule would require 33.8 kcal/mol of Gibbs free activation energy. This process is energetically favorable by 17.2 kcal/mol.

Finally, coming back to the initial species 1a, it can also interact with the surface silanol groups via another mechanism. Thus, hydrogen transfer can occur from the Si-O-H group to the Mo=N bond, leading to monopodal amido species \tilde{C} in which Mo is pentacoordinated. This transformation requires only 13.8 kcal/mol of free energy and is slightly exergonic by 1.5 kcal/mol. In addition, this step is reversible and requires only 15.3 kcal/mol of activation energy for the transformation of C to 1a. Furthermore, C can undergo α -hydrogen transfer from the NH group to the Mo-CH₂-t-Bu moiety and form A with liberation of one molecule of CH3-t-Bu. This process is highly exergonic by 32.4 kcal/mol and requires 36.1 kcal/mol of activation free energy; hence, it is irreversible if it occurs. Finally, C can transform into the bipodal species D with release of a CH₃-t-Bu molecule via hydrogen transfer from the silica OH group to one of the CH₂-t-Bu groups bonded to the Mo atom. Such a transformation is highly favorable by 35.5 kcal/ mol and requires 18.8 kcal/mol.

There are only two substantial differences between reaction profiles for species 1a and 1b. First, the most important for the species 1b, the transformation C-D requires ~10 kcal/mol higher activation free energy. We explain this by taking into consideration the greater steric repulsion of the bulky 2,6-diisopropylphenyl groups, which appears in the compact transition state $[C-D]^{\ddagger}$ derived from the 1b precursor in comparison to the steric repulsion in its 1a-based counterpart. Similarly, transition state $[C-A]^{\ddagger}$ is higher by ~10 kcal/mol for the 1b derivative in comparison to its 1a counterpart. All other differences between the reaction profiles for the 1a and 1b precursors are miniscule and can be neglected.

Overall, the analysis of Scheme 2 clearly suggests species **B** to be the thermodynamic product of the grafting of both 1a and 1b precursors. Identifying the kinetic product is more complicated, however, as all the important reaction barriers might be sensitive to both the silica model and particular DFT functional chosen. However, as it is now, at 80 °C the species **B** is most likely to be the major kinetic product as well at reasonably long (of few days) reaction time. Otherwise, the species **D** is a clear candidate to be the kinetic product as well and perhaps a mixture of species **D** and **B** is formed at short reaction time or with insufficient heating, as the difference [**A**-**B**][‡] – **D** is about 25.5–29.6 kcal/mol and can stabilize **D**. All other species such as **A** and **C** are unlikely to be the kinetic products, as they easily undergo chemical transformations through relatively low free energy barriers.

The ¹H MAS NMR spectrum of 2a (Figure 2a) displayed only one resonance centered at 1.3 ppm that can be readily



Figure 2. NMR characterization: ¹H MAS NMR spectra of (a) 2a and (c) 2b; ¹³C CP MAS NMR spectra of (b) 2a and (d) 2b (11.75 T, spinning rate 10 kHz).

assigned to the protons of tert-butyl groups. The ¹³C CP MAS NMR spectrum (Figure 2b) showed signals at 30.0 and 69.0 ppm corresponding to $=NC(CH_3)_3$ and $=NC(CH_3)_3$ groups, respectively. Two additional weak signals at 43.0 and 51.0 ppm were observed. These peaks are presumably occurring due to the minor formation of molybdenum amido species, as indicated by infrared spectroscopy (Figure 1). On the other hand, the solid-state NMR data (¹H, ¹³C) of **2b** (Figure 2c,d) feature the expected signals of an anchored molybdenum imido aryl species. The broad peak at 3.1 ppm arises from the ¹H of isopropyl – $CH(CH_3)$, and the peak centered at 1.0 ppm can be assigned to the protons of the aliphatic $-CH_3$ group. A weak broad resonance centered at 6.9 ppm originates from the aromatic protons. The intense resonances at 21.0 and 26.8 ppm observed in the ¹³C spectrum are due to the aliphatic $-CH_3$ groups. Aromatic carbons appear in the range of 120–152 ppm.

The structures of 2a,b were also studied by EXAFS spectroscopy (Figures 3 and 4 and Tables 1 and 2). In both cases the XANES part of the absorption spectra presented a pre-edge structure with a maximum at 20004.0 eV (normalized intensity of the peak of ca. 0.4), agreeing with geometries that are not octahedral but probably tetrahedral for Mo(VI) complexes. For material 2a, the results are consistent with the following coordination sphere around Mo, ca. two imido ligands at 1.725(7) Å and ca. two oxygens at 1.958(8) Å, which can be assigned to siloxide ligands. The lengths found for Mo=N and Mo-O bonds are close to those observed by XRD for



Figure 3. Molybdenum K-edge k^3 -weighted EXAFS (left) for **2a** and the corresponding Fourier transform (right; modulus and imaginary part); (solid lines) experimental; (dashed lines) fit using the spherical wave theory.



Figure 4. Molybdenum K-edge k^3 -weighted EXAFS (left) for **2b** and the corresponding Fourier transform (right; modulus and imaginary part): (solid lines) experimental; (dashed lines) fit using the spherical wave theory.

Table 1. EXAFS Parameters for 2a^a

type of neighbor	no. of neighbors	distance (Å)	σ^2 (Å ²)
Mo=N-t-Bu	1.9(2)	1.725(7)	0.0039(9)
Mo− O Si≡	$2.2(2)^{b}$	1.958(8)	0.0036(8)
Mo=N-CMe ₃	1.9^{b}	2.98(3)	0.0020(16)
MS_{31} Mo= $N-CMe_3^c$	3.8 ^b	2.98 ^b	0.025(4)
MS_{41} Mo= $N-CMe_3^c$	1.9^{b}	2.98 ^b	0.025 ^b
MoO($Si\equiv$) ₂	2(1)	2.79(3)	0.0051(32)
(Mo Si≡)	(2.2^{b})	(3.35(32))	(0.29(28))

"Errors generated by the EXAFS fitting program "RoundMidnight" are indicated in parentheses. $\Delta k = [1.9-16.1 \text{ Å}^{-1}] - \Delta R$: [0.5-3.2 Å]([0.5-2.1 Å], when considering only the first coordination sphere). $S_0^2 = 0.85$. $\Delta E_0 = 8.9 \pm 1.0 \text{ eV}$ (the same for all shells). Fit residue: $\rho =$ 7.7%. Quality factor: $(\Delta \chi)^2 / \nu = 2.97$, with $\nu = 14/26$ $([(\Delta \chi)^2 / \nu]_1 =$ 4.32 with $\nu = 10/16$, considering only the first coordination sphere == N and -O). ^bShell constrained to parameters above (in particular 2 N_N + N_O = 6, the same number of neighbors, the same distance, or the same DW factor). ^cMS₃ three-leg multiple scattering path; MS₄ fourleg multiple scattering path.

molecular complexes such as $[Mo(=N-t-Bu)_2(OB(mes)_2)_2]$ (1.726(3) Å for Mo=N and 1.914(2) Å for Mo-O) and $[Mo(=N-Ar)_2(OB(mes)_2)_2]$ (1.707–1.753 Å for Mo=N and 1.86–1.91 Å for Mo-O),¹⁰ though the Mo-O distance is longer but is in the usual range observed, e.g. 1.932–1.945 Å for $[Mo(N-Ar)(L)(=CHCMe_2Ph)]$,¹¹ where L is a pyridine-diolato ligand (1.745(3) Å for Mo=N) and up to 2.048(2) Å for an Mo-O X-type ligand in $[{Mo(NR)_2Me(\mu-OMe)}_2]^{12}$ (1.754(2) Å for Mo=N). Similar parameter values were obtained on fitting the $k^2 \cdot \chi(k)$ spectrum. The fit could be

Table 2. EXAFS Parameters for 2b^a

type of neighbor	no. of neighbors	distance (Å)	σ^2 (Å ²)
Mo=N-Ar	2	1.74(1)	0.0053(12)
Mo− O Si≡	2 ^b	1.955(8)	0.0029(8)
$Mo = N - C_{Ar} <$	2 ^b	2.95(3)	0.0016(12)
$MS_{3l} Mo = N - CMe_3 <^c$	4 ^b	2.95 ^b	0.017(6)
$MS_{41} Mo = N - CMe_3 <^c$	2^{b}	2.95 ^b	0.017 ^b
$Mo-O(Si \equiv)_2$	2	2.76(2)	0.0025(13)
MoC≡	4	3.48(5)	0.0033(28)
Mo <i>Si</i> ≡	2 ^b	3.43(6)	0.008(6)

^{*a*}Errors generated by the EXAFS fitting program "RoundMidnight" are indicated in parentheses. $\Delta k = [1.9-16.1 \text{ Å}^{-1}] - \Delta R [0.5-3.5 \text{ Å}]$ ([0.5-2.1 Å], when considering only the first coordination sphere). $S_0^2 = 0.85$. $\Delta E_0 = 9.0 \pm 1.1$ eV (the same for all shells). Fit residue: $\rho = 10.3\%$. Quality factor: $(\Delta \chi)^2 / \nu = 2.79$, with $\nu = 15/29$. ^{*b*}Shell constrained to parameters above. ^{*c*}MS₃ $_{3}$ three-leg multiple scattering path; MS₄ $_{4}$ four-leg multiple scattering path.

improved by adding a layer of further backscatterers, ca. two oxygen and two carbon atoms at 2.79(3) and 2.98(3) Å, respectively, attributed to surface oxygen atoms from siloxane bridges of the silica support and to the quaternary carbon of the tert-butyl groups of the imido ligands. For this contribution two multiple scattering pathways were added using the same distance, since for this imido ligand Mo, N, and C atoms are close to alignment. The consideration of silicon atoms from the surface was not statistically validated, and associated parameters were obtained within huge uncertainty margins and the Debye-Waller (DW) factor is very important. This last contribution is indicated in parentheses in the last row of Table 1 but is not considered in the fit. This is in particular probably due to a structural disorder due to the variety of the bipodal sites on the surface of silica, which would lead in this case to a variety of Mo---Si configurations,¹³ each site presenting a slightly different EXAFS contribution in the resulting spectrum.

For **2b**, the study was conducted similarly and the fit of the EXAFS spectrum agrees with a structure very close to that of **2a**. The parameters, in particular distances and DW factors, are reported in detail in Table 2. An extra level of carbon backscaterrers at 3.48(5) Å had to be added to improve the fit, which may be due to a contribution of the methyl groups of the isopropyl fragments, and the Mo---Si contribution at 3.43(6) Å could be observed. EXAFS results therefore fully agree with the tetrahedral type structures $[(\equiv Si-O-)_2Mo(\equiv NR)_2]$ (R = *t*-Bu) and $[(\equiv Si-O-)_2Mo(\equiv NR)_2]$ (R = 2,6-C₆H₃-*i*-Pr₂) for the silica-supported complexes **2a,b**, respectively.

We investigated the utility of silica-supported tetracoordinated molybdenum complexes 2a,b as heterogeneous catalysts for catalytic imine metathesis using selected imine substrates (Figure 5). In a typical catalytic experiment an equimolar mixture of two imine substrates was combined with 4 mol % of either catalyst 2a or 2b to react at 80 °C in toluene. After a specific time the reactions were terminated (see Table 3 and the Supporting Information for details) and the products of the catalytic run were analyzed by gas chromatography-mass spectrometry (GC-MS), which shows that the imine products formed after each reaction are consistent with those expected via a cross-metathesis reaction (eq 1). In addition, as expected, the imide/imine metathesis products (see Schemes S2–S4 and Table S1 in the Supporting Information for details) were also found to be present in each of the reaction mixtures, as



Figure 5. Imine substrates 3-6 which are utilized in this study.

Table 3. Catalytic Imine Metathesis Substrate Testing Using Catalysts 2a,b

entry	imine combination	cat.	time (h)	conversn (%) ^a	conversn (%) ^b
1	3 + 4	2a	6/24/-	48/53/-	49/51/-
2	3 + 4	2b	6/24/50	49/51/53	50/51/53
3	3 + 5	2a	6/24/-	47/52/-	48/50/-
4	3 + 5	2b	6/24/50	33/50/52	31/50/54
5	3 + 6	2a	6/-/50	49/-/52	47/-/53
6	3 + 6	2b	6/24/-	48/51/-	50/51/-

^{*a*}Determined by GC-FID after a specific reaction time with respect to the first imine (3) given in column 2. ^{*b*}With respect to the second imine in column 2.

confirmed again by GC-MS analysis, thus suggesting a direct involvement of the metal center in the metathesis reaction.⁴ When these results were taken into consideration, a hypothetical catalytic cycle (Scheme S1 in the Supporting Information) for the imine metathesis by catalyst 2a or 2b, possessing a tetracoordinated molybdenum center, could be proposed. When imines 3 and 4 were combined with catalyst 2a or 2b, the metathesis products 7 and 8 (Scheme S2) together with the imide/imine metathesis products 9 and 10 (for 2a) or 11 and 12 (for 2b) were formed. Interestingly, both of these catalysts equilibrate imines 3 and 4 in just about 6 h (Table 2) and at this stage the imines were present in approximately a stoichiometric ratio. Similarly, a combination of imines 3 and 5 in the presence of catalyst 2a or 2b also undergoes metathetical exchange of the imido groups to produce 13 and 14 (Scheme S3) and reaches equilibrium approximately again after 6 h for 2a, although this takes longer in the case of 2b. Furthermore, a mixture of imines 3 and 6 was also found to undergo cross metathesis, at approximately a similar reaction rate, in the presence of either catalyst 2a or 2b to yield 7 and 17 as metathesis products (Scheme S4) and reaches equilibrium within a time frame similar to that required for other substrate combinations.

From these above catalytic results it appears that the activation of a given set of imine substrates, with the exception of a combination of 3 and 5, is similar for both catalysts 2a and 2b: i.e., independent of the imido substituents bearing different electronic and steric properties. This is in variance with the previously reported results obtained under homogeneous catalytic conditions for hexacoordinated molybdenum complexes bearing a bis(imido) core structure,^{4d} where the rate of the reactions were hypothesized to significantly depend on the steric properties of the imide nitrogen substituents.

CONCLUSIONS

In summary, a rigorous SOMC protocol was adopted to decorate the surface of silica with novel types of Lewis base

(e.g., DME) free molybdenum complexes possessing bis-(imido) functionalities, giving two unique well-defined bipodal tetracoordinated molybdenum surface complexes. X-ray absorption spectroscopic studies, complemented by the FT-IR, SS NMR spectroscopy, and elemental microanalysis, were undertaken to unequivocally elucidate the molecular level structure of the surface-grafted molybdenum complexes. Furthermore, the grafting of four-coordinated molybdenum complexes onto the surface of silica and their probable transformation at elevated temperatures were also investigated computationally using density functional theory and a cluster model of the silica support. Finally we explored the utility of our newly developed well-defined molybdenum surface complexes as heterogeneous catalytic media, which exhibited efficient metal-mediated carbon-nitrogen double-bond metathesis under mild conditions.

EXPERIMENTAL SECTION

Materials and General Procedures. All experiments were carried out by using standard Schlenk techniques. Air- and moisture-sensitive materials were stored and handled in a glovebox. Solvents were purified and dried according to standard procedures. Mo(N-t- $Bu_2)_2Cl_2(DME)$ and Mo(N-2,6-C₆H₃-*i*-Pr₂)₂Cl₂(DME) were synthesized following the literature procedures.¹⁴ Gas-phase analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector and an Al₂O₃/KCl on fused silica column (50 m \times 0.32 mm). Elemental analyses were performed at the Pascher Mikroanalytisches Labor at Remagen-Bandorf, Germany. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer in either transmission or DRIFT mode in an airtight cell equipped with CaF₂ windows. The samples were prepared under argon within a glovebox. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm⁻¹). For NMR characterization, solution NMR spectra were recorded on an Avance-300 Bruker spectrometer. All chemical shifts were measured relative to residual ¹H or ¹³C resonances in the deuterated solvent: $C_6 D_{64} \delta$ 7.16 ppm for ¹H, 128.06 ppm for ¹³C. ¹H and ¹³C solid-state NMR spectra were recorded on Bruker Avance-500 and Bruker Avance-300 spectrometers with a conventional double-resonance 4 mm CP MAS probe at the Laboratoire de Chimie Organométallique de Surface. The samples were introduced under argon into a zirconia rotor (4 mm), which was then tightly closed. The rotation frequency was set to 10 kHz unless otherwise specified. Chemical shifts were given with respect to TMS as external reference for ¹H and ¹³C NMR.

GC measurements were performed with an Agilent 7890A Series (FID detection). Method for GC analyses: column HP-5, 30 m length \times 0.32 mm ID \times 0.25 μ m film thickness; flow rate, 1 mL/min (N₂); split ratio, 50/1; inlet temperature, 250 °C; detector temperature, 250 °C; temperature program, 40 °C (1 min), 40–250 °C (15 °C/min), 250 °C (1 min), 250–300 °C (10 °C/min), 300 °C (30 min). GC-MS measurements were performed with an Agilent 7890A Series coupled with Agilent 5975C Series instruments.

XAS. X-ray absorption spectra were acquired at the ESRF, using beamline BM23, at room temperature at the molybdenum K-edge, with a double crystal Si(111) monochromator detuned 70% to reduce the higher harmonics of the beam. The spectra were recorded in the transmission mode between 19.66 and 21.53 keV. Airtight sample holders equipped with Kapton windows were filled with the Mo samples within an argon-filled glovebox, and these sample holders were placed within airtight containers also equipped with Kapton windows in order to ensure a double air protection. Once they were extracted from the glovebox, these containers were positioned on the beamline in order to record the spectra. The spectrum of a Mo(0)metal foil was recorded simultaneously in each case, and its E_0 edge value (annulation of the second derivative of the signal) was set at 19999.5 eV,¹⁵ in order to standardize the energy of the sample spectra. Two or three spectra were averaged for each sample. The data analyses were carried out using standard procedures ("Athena"16 and

"RoundMidnight"¹⁷ programs). The program FEFF8 was used to calculate theoretical files for phases and amplitudes on the basis of model clusters of atoms.¹⁸ The S_0^2 factor was evaluated using the crystallized molecular complexes Mo(O)(CH₂-*t*-Bu)₃Cl and Mo(O)-(CH₂SiMe₃)₂(OCH₂-*t*-Bu)₂, also characterized by XRD. These were studied diluted in BN and conditioned as wafers, and the average value of S_0^2 found from the fit of the EXAFS of these two reference samples, $S_0^2 = 0.85$, was chosen. The refinements were performed by fitting the structural parameters $N_{i\nu} R_{i\nu}$ and σ_i and the energy shift ΔE_0 (the same for all shells). The fit residue, ρ (%), was calculated by the formula

$$\rho = \frac{\sum_{k} \left[k^{3} \chi_{\exp}(k) - k^{3} \chi_{cal}(k)\right]^{2}}{\sum_{k} \left[k^{3} \chi_{\exp}(k)\right]^{2}} \times 100$$

As recommended by the Standards and Criteria Committee of the International XAFS Society,¹⁹ the quality factor, $(\Delta \chi)^2 / \nu$, where ν is the number of degrees of freedom in the signal, was calculated and its minimization considered in order to control the number of variable parameters used in the fits.

Preparation of Mo(N-t-Bu₂)₂(CH₂-t-Bu)₂ (1a). 1a was synthesized following a synthesis procedure identical with that reported by Osborn et al.,²⁰ with the exception that the precursor complex used in this study was $Mo(N-t-Bu_2)_2Cl_2(DME)$. In brief, $Mo(N-t-Bu)_2Cl_2(DME)$ (0.20 g, 0.5009 mmol) was dissolved in pentane (ca. 10 mL) and added to a pentane solution of LiCH₂-t-Bu (0.07823 g, 1.0019 mmol) at 23 °C and stirred for another 1.2 h at this temperature. After the completion of the reaction the volatiles were removed to leave a brown liquid product (yield 98%). The spectroscopic data are consistent with those reported elsewhere.²⁰

Preparation of Mo(N-2,6-C₆H₃-*i***-Pr₂)₂(CH₂-***t***-Bu)₂ (1b). For the synthesis of 1b, a slightly modified procedure reported in the literature was followed.²¹ Mo(N-2,6-C₆H₃-***i***-Pr₂)₂Cl₂(DME) (1.0 g, 1.646 mmol) was dissolved in diethyl ether (ca. 15 mL) and slowly added to a solution of LiCH₂-***t***-Bu (0.257 g, 3.292 mmol) in 5 mL of diethyl ether at -78 °C. Then the reaction mixture was warmed to 23 °C and stirred for another 7.5 h. After this time the solvent content of the reaction was thoroughly washed with cold pentane and finally dried under vacuum to give a bright orange solid product (yield 80%). The spectroscopic data are consistent with those reported elsewhere.²¹**

Grafting of Molecular Precursor 1a onto the Surface of SiO₂₋₂₀₀ To Yield Material 2a. $Mo(N-t-Bu_2)_2(CH_2-t-Bu)_2$ (1a; 0.18 g, 0.473 mmol) was dissolved in 5 mL of dry pentane and was slowly added to a slurry of SiO₂₋₂₀₀ (1.0 g, around ~0.8 mmol of -OH) in pentane (ca. 7 mL) and stirred at room temperature for 12 h. The solvent was then removed by filtration, and the solid residue was thoroughly washed with pentane (5 × 5 mL) followed by drying under dynamic vacuum for 12 h. The light gray-brown solid obtained was further degassed at 80 °C (under dynamic vacuum; <10⁻⁵ Torr) for another 16 h to yield material 2a. Anal. Calcd for 2a: Mo, 2.60; C, 2.88; N, 0.66. ¹H MAS NMR (500 MHz): δ 1.3 ppm. ¹³C CP MAS NMR (125 MHz): δ 69.0, 51.0, 43.0, and 30.0 ppm.

Grafting of Molecular Precursor 1b onto the Surface of SiO₂₋₂₀₀ To Yield Material 2b. $Mo(N-2,6-C_6H_3-i-Pr_2)_2(CH_2-t-Bu)_2$ (1b; 0.148 g, 0.251 mmol) was dissolved in 5 mL of dry pentane and was slowly added to a slurry of SiO₂₋₂₀₀ (1.0 g, around ~0.8 mmol of -OH) in pentane (ca. 7 mL) and stirred at room temperature for 12 h. The solvent was then removed by filtration, and the solid residue was thoroughly washed with pentane (5 × 5 mL) followed by drying under dynamic vacuum for 12 h. The light orange solid obtained was further degassed at 80 °C (under dynamic vacuum; <10⁻⁵ Torr) for another 16 h to yield material 2b. Anal. Calcd for 2b: Mo, 1.55; C, 4.69; N, 0.47. ¹H MAS NMR (500 MHz): δ 6.9, 3.1, and 1.0 ppm. ¹³C CP MAS NMR (125 MHz): δ 152.0, 141.0, 123.0, 120.0, 26.8, and 21.0 ppm.

General Procedure for Imine Metathesis. A clean oven-dried ampule was charged, in a glovebox, sequentially with the catalyst **2a** (or **2b**) (0.04 equiv), toluene (500 μ L), 1.0 equiv of each of the imines **3** and **4** (or **3** and **5** or **3** and **6**), and a Teflon-coated stir bar. The ampule was then removed from the glovebox and placed on a high-

vacuum line. The reaction mixture was condensed by cooling with liquid nitrogen, and the ampules were evacuated ($<10^{-5}$ mbar). After they were sealed, the ampules were placed in an oil bath (80 °C). The reaction mixture was heated for a specific reaction time of 6, 24, or 50 h, and each time after reaction it was cooled to 22 °C. The product solution was filtered to remove the catalyst, and the remaining liquid product was analyzed by GC-FID and GC-MS.

Computational Details. Geometry Optimizations and Calculations of Thermochemical Corrections. All geometry optimizations were performed using the PBE GGA²² functional as implemented in the PRIRODA 13 DFT code.²³ All electron basis sets $(\lambda 1)^{24}$ comparable in quality to the correlation consistent valence double- ζ plus polarization (cc-PVDZ) basis sets of Dunning were used. All stationary geometries were characterized by an analytically calculated Hessian matrix. Possible relativistic effects (for molybdenum) were taken into account via the Dyall Hamiltonian.²⁵

The default, adaptively generated PRIRODA grid, corresponding to an accuracy of the exchange-correlation energy per atom $(1 \times 10^{-8}$ hartree) was decreased by a factor of 100 for more accurate evaluation of the exchange-correlation energy. Default values were used for the self-consistent-field (SCF) convergence and the maximum gradient for geometry optimization criterion $(1 \times 10^{-4} \text{ au})$, whereas the maximum displacement geometry convergence criterion was decreased to 0.0018 au.

Translational, rotational, and vibrational partition functions for thermal corrections to arrive at total Gibbs free energies were computed within the ideal-gas, rigid-rotor, and harmonic oscillator approximations. The temperature used in the calculations of thermochemical corrections was set to 298.15 K in all the cases.

Single-Point (SP) Energy Evaluations. The energies were reevaluated at optimized geometries by means of the $M06^{26}$ functional as implemented in Gaussian 09^{27} code. The all-electron def2-tzvpp basis set of Ahlrichs²⁸ was used on the main elements. For the molybdenum atom the Stuttgart ECP²⁹ was used with the corresponding valence def2-tzvpp basis set. The "Integral(grid = ultrafine)" option was used for evaluation of the exchange-correlation term. The default value for the SP SCF convergence was adopted.

Silica Model. A relatively large cluster model cut out from the β cristobalite-based SiO₂ surface (model 001-4 in the paper published by Rozanska et al.³⁰) has been chosen to simulate a silica surface (see Figure S1 in the Supporting Information).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00115.

Further details on materials and general procedures, synthesis of precursor molybdenum complexes, grafting of tetracoordinated molybdenum complexes onto the silica surface, catalytic results, and computational details (PDF)

Cartesian coordinates of the calculated structures (XYZ)

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Notes

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