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Boosting the Metathesis Activity of Molybdenum Oxo Alkylidenes by Tuning the Anionic Ligand σ Donation

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ABSTRACT: The catalytic performances of molecular and silica-supported molybdenum oxo alkylidene species bearing anionic O ligands [OR_{F9}, OTTP, OHMT – where OR_{F9} = OC(CF₃)₃, OTTP = 2,3,5,6-tetraphenylphenoxy, OHMT = hexamethylterphenoxy] with different σ -donation abilities and sizes are evaluated in the metathesis of both internal and terminal olefins. Here, we show that the presence of the anionic nonafluoro-*tert*-butoxy X ligand in Mo(O){=CH-4-(MeO)C₆H₄}(THF)₂{X}₂ (**1**; X = OR_{F9}) significantly increases the catalytic performances in the metathesis of both terminal and internal olefins. Its silica-supported equivalent displays slightly lower activity, albeit with improved stability. In sharp contrast, the molecular complexes with large aryloxy anionic X ligands show little activity, whereas the activity of the corresponding silica-supported systems is greatly improved, illustrating that surface siloxy groups are significantly smaller anionic ligands. Of all of the systems, compound **1** stands out because of its unique high activity for both terminal and internal olefins. Density functional theory modeling indicates that the OR_{F9} ligand is ideal in this series because of its weak σ -donating ability, avoiding overstabilization of the metallacyclobutane intermediates while keeping low barriers for [2 + 2] cycloaddition and turnstile isomerization.

INTRODUCTION

Olefin metathesis has become a key reaction for the synthesis of basic chemicals as well as complex molecular architectures including polymers, growing in importance in both academia and industry.¹ Since its early mechanistic proposal,² continuous efforts have been directed at gaining a detailed understanding of what makes specific metal alkylidenes good for this catalytic reaction.³ For instance, for early-transition-metal (d⁰) metathesis catalysts that share a common structural motif—(X)(Y)M(=CHR)E⁴ (M = Mo or W, E = imido or oxo ligand, and X and Y are anionic ligands)—each ligand has a tremendous influence on the stability of the reaction intermediates and the overall catalytic activity.^{3a,5} In that context, surface organometallic chemistry,^{1e,6} in combination with computational chemistry, has played a key role in the identification and understanding of the effect of each ligand.⁷ In particular, these studies, complemented by molecular chemistry, have shown that (i) the trigonal-bipyramidal (TBP) isomer is a key intermediate in the metathesis pathway while the square-pyramidal (SP) isomer is usually more stable and corresponds to an off-cycle intermediate and (ii) the anionic ligands play a major role in the stability of the TBP and SP metallacyclobutane intermediates and, in turn, drive the overall catalytic performance (Scheme 1A).⁸ In that context, W-based metathesis catalysts display typically poorer activity

toward terminal olefin compared to their Mo analogues, because of the significantly higher stability of the parent metallacyclobutane formed from the ethylene byproduct. Nonetheless, their performance, whether molecular or supported, can in most cases be significantly improved by introducing strong σ -donating ligands like oxo,⁹ thiolate,¹⁰ or N-heterocyclic carbene (NHC).¹¹ Even with molybdenum alkylidenes, which are particularly efficient metathesis catalysts for terminal olefins, their activity can also be dramatically improved by replacing an imido with an oxo ligand (Schemes 1B and 2) or by introducing a NHC ligand in their cationic form.

With the recent development of synthetic routes for several molybdenum oxo *p*-methoxybenzylidene complexes Mo(O){=CH-4-(MeO)C₆H₄}(THF)₂(OR_{F9})₂ [**1**; OR_{F9} = OC(CF₃)₃] and Mo(O){=CH-4-(MeO)C₆H₄}(OTTP)₂ (**2**; OTTP = 2,3,5,6-tetraphenylphenoxy) (Scheme 1),¹² we investigate here the role of the X anionic ligand in metathesis

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Scheme 1. (A) Proposed Olefin Metathesis Mechanism for d^0 Transition-Metal Catalysts and (B) General Structures of (a) Molybdenum and Tungsten Imido Alkylidene Catalysts, (b) Tungsten Oxo Alkylidene with a Thiolate Ancillary Ligand, and (c) Tungsten Oxo and Molybdenum Imido Alkylidenes with Strong σ -Donor NHC Ligands

A) General Mechanism of Olefin Metathesis for d^0 Transition Metal Catalysts

B) State-of-the-Art Metathesis Catalysts

Scheme 2. Grafting Procedures of 1–3, Leading to 1@SiO₂, 2@SiO₂, and 3@SiO₂

This work

Previously reported (2019)

for molecular and silica-supported neutral molybdenum oxo alkylidene complexes. We show that introducing a poor σ -donating and less sterically demanding ligand, namely, $\text{OR}_{\text{F}9}$, boosts the activity for the metathesis of both terminal and internal olefins, surpassing previously reported systems.

RESULTS AND DISCUSSION

Synthesis and Characterization of Silica-Supported Catalysts. First, the silica-supported catalysts 1@SiO₂ and 2@

SiO₂ were prepared under an inert atmosphere by grafting onto silica partially dehydroxylated at 700 °C (SiO_{2-700}) 1 and 2 with $\text{OR}_{\text{F}9}$ and OTPP anionic ligands, respectively (Scheme 2).

Quantification by elemental analysis showed a Mo loading of 0.24 and 0.17 mmol of Mo/g for 1@SiO₂ and 2@SiO₂, respectively, in agreement with solution NMR quantification of the released alcohol/phenol after reaction with silica. In both cases, IR spectroscopy shows that after grafting a large amount of isolated silanols associated with the band at 3747 cm^{-1} are consumed, in accordance with surface anchoring via protonolysis (Figures S11 and S14). For 2@SiO₂, a broad absorption band around 3500 cm^{-1} can be observed, corresponding to interaction of the bulky phenoxy ligand with residual OH groups that are no longer accessible for grafting.¹³ For 1@SiO₂, this band is less prominent, in line with the smaller footprint of complex 1, hence the observed difference of metal loadings in the respective cases. Furthermore, the band at 2842 cm^{-1} indicates the presence of at least one coordinated tetrahydrofuran (THF). ¹H magic-angle-spinning (MAS) NMR spectra of the silica-supported complexes show the alkylidene proton resonances at 14 and 13 ppm for 1@SiO₂ and 2@SiO₂, respectively, slightly downfield with respect to the molecular precursor signals in solution (13.7 and 11.8 ppm; Figures S8 and S12). The signal at 7.4 ppm can be assigned to protons of the phenyl moieties, and the resonances at 2.6, 1.9, and 1.4 ppm for 2@SiO₂ can be attributed to the interaction of organometallic fragments with adjacent OH groups.¹³ Similar signals can be seen for 1@SiO₂ at 2.9 and 1.9 ppm. The ¹³C cross-polarization (CP) MAS NMR spectrum of 1@SiO₂ shows the presence of aromatics, the methoxy at 54 ppm as well as resonances at 25 and 75 ppm associated with coordinated THF (Figure S9). Because the solid-state ¹³C NMR spectrum did not show any signals from the natural abundance, the ¹³C-enriched supported species of the metathetically more active catalyst 1@SiO₂, 1*@SiO₂, was prepared through metathesis of 1 with ¹³C-labeled 4-vinylanisole followed by grafting on silica. As shown by ¹H and ¹³C NMR (Figures S6 and S7), the labeled complex 1* is obtained as a mixture of syn and anti isomers and corresponds to the mono-THF adduct, as confirmed by X-ray crystallography (see the Supporting Information for more details). Subsequent grafting of 1* on SiO₂₋₇₀₀ was performed. The ¹³C CP MAS spectrum of 1*@SiO₂ shows the same signals as those detected in 1@SiO₂ with an additional ¹³C resonance at 293 ppm from the labeled alkylidene carbon, which exhibits several prominent spinning sidebands consistent with a large chemical shift anisotropy that is typical of molybdenum alkylidenes (Figure S16).¹⁴ Solid-state ¹⁹F NMR was also measured for 1@SiO₂, showing a single peak at −76.5 ppm associated with the pendant $\text{OR}_{\text{F}9}$ ligand (Figure S10).

Catalytic Testing. The metathesis activity of both molecular and supported complexes was evaluated in a nitrogen filled glovebox using *cis*-4-nonene and 1-nonene as prototypical substrates. The data, including these for $\text{Mo}(\text{O})\text{=CH-4-(MeO)C}_6\text{H}_4\text{-(OHMT)}_2$ (3; OHMT = hexamethylterphenyl) and its supported analogue 3@SiO₂ that were previously reported,¹⁵ are summarized in Table 1. Detailed kinetic profiles can be found in the Supporting Information.

For *cis*-4-nonene, the molecular complex 1 reaches equilibrium conversion within the first 3 min at 0.02 mol % loading with an (under)estimated turnover frequency of 870 min^{-1} . As the catalyst loading is further lowered to 0.014 mol

Table 1. Homometathesis of *cis*-4-Nonene and 1-Nonene (Toluene, 30 °C)

catalyst	mol %	TOF _{3 min} ^a min ⁻¹ (conversion, %) ^a		time to equilibrium/maximum conversion ^b	
		<i>cis</i> -4-nonene	1-nonene	<i>cis</i> -4-nonene	1-nonene
1	0.1	170 (52) ^c	210 (62)	3 min	97% after 4 h
1	0.02	870 (52) ^c	940 (58)	3 min	97% after 4 h
1	0.014	250 (11)		11% after 1 h	
1	0.01		1270 (38)		50% after 4 h
2	0.1	1 (<1)	30 (9)	4% after 1 h	62% after 4 h
3 ^d	0.1	5 (1)	<1	3% after 24 h	45% after 8 h
1@SiO ₂	0.1	170 (51) ^c	70 (22)	3 min	97% after 4 h
1@SiO ₂	0.02	725 (42–46) ^{c,e}	170 (10)	5–10 min ^e	73% after 8 h
1@SiO ₂	0.014	680 (29)		10 min	
1@SiO ₂	0.005	100 (1)		41% after 9 h	
2@SiO ₂	0.1	170 (52) ^c	40 (12)	3 min	98% after 6 h
2@SiO ₂	0.02	350 (24)	70 (5)	30 min	95% after 8 h
3@SiO ₂ ^d	0.1	120 (40) ^c	75 (13)	10 min	98% after 8 h
3@SiO ₂ ^d	0.02	300 (17)		1 h	
3@SiO ₂ ^d	0.014	410 (18)	70 (4)	1 h	97% after 24 h
3@SiO ₂ ^d	0.005	520 (8)	45 (1)	28% after 24 h	63% after 24 h

^aTOF at 3 min, given in min⁻¹, with the corresponding conversions given in parentheses. Equilibrium conversion is 50%. ^bMaximum conversion is 100%. When full conversion was not reached, the maximum conversion measured after a given time is provided. ^cThe TOF value is underestimated given that the conversion is close to equilibrium. ^dPreviously reported results in ref 15. ^ePerformed in duplicate and averaged.

Table 2. Relative Gibbs Free Energies and Reaction Enthalpies (kcal/mol) of Molecular and Grafted Oxo Alkylidene Complexes with Respect to Separate Reactants (Methylidene and Ethylene)

catalyst	TOF _{3 min} (0.1 mol %) for 1-nonene	$\Delta G^\ddagger_{[2+2]}$ ($\Delta H^\ddagger_{[2+2]}$)	ΔG_{TBP} (ΔH_{TBP})	$\Delta G^\ddagger_{\text{turnstile}}$ ($\Delta H^\ddagger_{\text{turnstile}}$)	ΔG_{SP} (ΔH_{SP})
1	210	8.12 (−6.25)	−2.60 (−16.66)	8.38 (−6.45)	−8.46 (−22.54)
2	30	<i>a</i>	2.06 (−11.40)	<i>a</i>	−11.23 (−22.67)
3	<1	<i>a</i>	3.42 (−12.81)	<i>a</i>	−6.57 (−20.42)
1@SiO ₂	70	<i>a</i>	axial siloxy −0.08 (−15.47) equatorial siloxy −1.96 (−16.60)	<i>a</i>	−10.39 (−24.44)
2@SiO ₂	40	<i>a</i>	−1.70 (−14.87)	<i>a</i>	−14.36 (−26.71)
3@SiO ₂	75	<i>a</i>	−0.37 (−15.21)	<i>a</i>	−9.74 (−24.53)

^aNot calculated.

%, the conversion is fast but stagnates at 11% because of deactivation, as indicated by the substantially lower TOF_{3 min} of 250 min⁻¹. This sharply contrasts with the catalyst performance of the molecular complex 2, which shows very low activity at 0.1 mol % loading, reaching only 4% conversion after 1 h. This parallels the low activity of the previously reported dimesitylphenoxy analogue 3, which only reaches 3% conversion after 24 h under the same conditions. This lack of reactivity is likely associated with the presence of a large aryloxy ligand that prevents the necessary distortion of the metal complex to a trigonal prism to accommodate the incoming olefin.¹⁵ In fact, the corresponding silica-supported systems 2@SiO₂ and 3@SiO₂ are far more active, reaching full conversion and high TOF_{3 min} at 0.02 mol % (equilibrium conversion after 30 min and 1 h and TOF_{3 min} = 350 and 300 min⁻¹, respectively). 1@SiO₂ displays unprecedented high activity toward internal olefins for Mo, reaching TOF_{3 min} of 725 min⁻¹ at 0.02 mol % loading and thereby surpassing even the highest value previously reported for grafted molybdenum oxo complexes at significantly lower loading (TOF_{3 min} = 520 min⁻¹, 0.005 mol %).¹⁵ In comparison to the molecular counterpart 1, the stability of 1@SiO₂ is also increased as the catalyst remained active even at 50 ppm loading (41% conversion after 9 h).

For 1-nonene, the activity of the molecular complex 1 exceeds the activity toward internal olefins, reaching TOF_{3 min}

of 1270 min⁻¹ at a low loading of 0.01 mol %. Here again, deactivation is observed as the conversion stagnates at 50% after 4 h. Compared to the results of the homometathesis of *cis*-4-nonene, the molecular complex 2 at 0.1 mol % loading is more active toward the terminal olefin with TOF_{3 min} of 30 min⁻¹ but suffers from deactivation as well, as seen by a conversion reaching only 62% after 4 h. The supported catalysts 1@SiO₂ and 2@SiO₂ are both active at 0.02 mol % loading, reaching TOF_{3 min} values of 170 and 80 min⁻¹, respectively. 1@SiO₂ does not reach full conversion within 8 h (73% conversion) because of deactivation. This parallels the results observed for 3@SiO₂, showing an activity similar to that of 1@SiO₂ at high catalyst loadings (0.1 mol %, 75 vs 70 min⁻¹); the catalyst also deactivates at lower loadings (0.014 mol %, TOF_{3 min} = 70 min⁻¹), reaching equilibrium conversion only after 24 h.

Computational Analysis. Density functional theory calculations (PBE/def2-TZVP//PBE0/def2-TZVP with SDD effective core potential for Mo, ultrafine integration grid, and GD3BJ empirical dispersion) were performed to gain further insight into the origin of the molybdenum oxo alkylidene metathesis catalytic activity. The relative stabilities of TBP and SP unsubstituted metallacycles were assessed for all systems because these key intermediates typically control the turnover rates, in particular for the metathesis of terminal olefins where ethylene is formed. The energies were calculated for both

molecular and silica-supported molybdenum oxo alkylidenes 1–3 and 1–3@SiO₂ (see Table 2 and Figure S17 for details); calculations for the silica-supported systems were carried out by using (MeO)₃SiO as a simple model to interrogate the electronic effects associated with a surface siloxy ligand. From these data, it appears that the SP metallacycle, recognized as the resting state intermediate of olefin metathesis, is always the lower-energy metallacycle for all calculated complexes. Regarding the TBP intermediates, their free energies are also significantly lower than the energies of the separated reactants for all calculated complexes with the exception of the molecular complexes 2 and 3, where formation of the TBP metallacycle is endergonic by ca. 2 or 3.5 kcal/mol, respectively.

An ideal metathesis catalyst would have a close-to-neutral free energy of formation for the TBP isomer ($\Delta G_{\text{TBP}} \approx 0$ kcal/mol) and a destabilized SP isomer, favoring metathesis over formation of the off-cycle intermediate. The data presented in Table 2 clearly indicate that compound 1 allows the formation of not too stable TBP and SP metallacyclobutanes, while 2 and 3 are associated with the positive free energies of formation of the key TBP intermediate, likely associated with a higher barrier for [2 + 2] cycloaddition. In addition, while not calculated, olefin coordination/cycloaddition in complexes 2 and 3 is likely not favorable because of the bulky aryloxide ligands. In contrast, the silica-supported systems with the significantly smaller and weak σ -donating surface siloxy ligand^{13a,16} are associated with the formation of slightly more stable TBP and SP metallacycles.

This could explain their higher activity with respect to the corresponding molecular complexes 2 and 3. These calculations also highlight the specificity of compound 1, containing two very weak σ -donating OR_{F9} ligands that do not stabilize the metallacycles too much. For 1@SiO₂, two TBP isomers can be formed with the siloxy ligand in either the axial or equatorial position. The free energy of the siloxy equatorial isomer is 2 kcal/mol lower compared to the siloxy axial isomer, highlighting the weak σ -donor ability of OR_{F9} that ends up trans to the very strong σ -donor oxo ligand. This may explain the lower activity of 1@SiO₂ compared to 1. To better understand the high activity of 1, we also evaluated the metathesis pathway. While the olefin complex and associated transition state for coordination could not be located, the [2 + 2] cycloaddition and turnstile isomerization transition states have very similar and quite low energies: $\Delta G^{\ddagger}_{[2+2]}$ ($\Delta H^{\ddagger}_{[2+2]}$) = 8.12 (−6.25) kcal/mol and $\Delta G^{\ddagger}_{\text{turnstile}}$ ($\Delta H^{\ddagger}_{\text{turnstile}}$) = 8.38 (−6.45) kcal/mol. The combination of facile [2 + 2] cycloaddition/cycloreversion and formation of not too stable metallacyclobutanes is consistent with the high catalytic activity of compound 1.

CONCLUSIONS

Overall, this study further illustrates how subtle differences in ligand substitution in Schrock alkylidenes can greatly influence their metathesis activity, pointing out to the need to explore this family of complexes in a more systematic fashion toward the development of detailed structure–activity relationships. This study also illustrates the uniqueness of silica, that enables generated isolated metal sites bound to a weak σ -donating and rather small siloxy ligand.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03173>.

Details on the reagents used, experimental setups, synthetic procedures, and corresponding characterizations, computational details including atomic coordinates for all calculated structures, experimental procedures for the metathesis tests and corresponding catalytic data, and crystallographic data (PDF)

xyz files for all computed structures (ZIP)

Accession Codes

CCDC 2053831 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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