Cationic Molybdenum Imido Alkylidene N-Heterocyclic Carbene Complexes Confined in Mesoporous Silica: Tuning Transition States Towards Z-Selective Ring-Opening Cross-Metathesis

Elizabeth L. Goldstein,[a] Felix Ziegler,[a] Ann-Katrin Beurer,[b] Yvonne Traa,[b] Johanna R. Bruckner,[c] and Michael R. Buchmeiser*[a, d]

We recently reported a method for selective macro(mono)cyclization of dienes utilizing catalysts confined inside the pores of mesoporous silica, which we believe occurs due to suppression of oligomerization due to pore size. We hypothesized, however, that the system of cationic molybdenum imido alkylidene N-heterocyclic carbene (NHC) catalysts immobilized selectively inside the mesopores of silica materials could address much more subtle selectivity differences, such as E/Z selectivity in ring-opening/cross-metathesis (ROCM). Upon investigation, we observed that surface-bound cationic molybdenum imido alkylidene NHC catalysts indeed display an increased Z-selectivity, especially during the early stages of the reaction. This effect was present when the catalyst was confined inside a pore, as well as when the catalyst was bound to nonporous silica, which led us to conclude it is an effect caused by the catalyst being bound directly to the surface of a silica material where the proximity of the catalyst to the surface governs the transition state. Kinetic investigations revealed that significant post-metathesis olefin isomerization occurs, the amount of which seems to be governed by the rate of diffusion of the product away from the active catalyst, with smaller pore sizes resulting in higher Z-selectivity at higher conversion, attributable to faster diffusion of the product out of the pore than diffusion back into the pore.

Introduction

Surface-supported organometallic catalysts have long been of interest to the scientific community, especially in regard to industrial scale synthesis.[1] There are a number of advantages to using surface-supported catalysts, the most prominent of which is the ease of catalyst separation, limiting the amount of metal in the final product and potentially leading the way to recyclable and reusable catalysts.[2] In the case of olefin metathesis, surface-supported catalysts have been used since the 1960s in the petrochemical industry for the synthesis of longer chain olefins from ethylene utilizing either molybdenum or tungsten oxides on silica or alumina surfaces.[3] These types of catalysts display high productivity but low selectivity.[4] On the other hand, the field of well-defined homogeneous olefin metathesis has led to the development of many highly reactive and highly selective catalysts to create more complex products.[5] Within the last twenty years, it has been demonstrated that well-defined metathesis catalysts can also be immobilized onto surfaces, and display good reactivity.[6] These immobilized olefin metathesis catalysts not only have the advantages of both homogeneous and surface-supported catalysts, but sometimes benefit from additional changes in reactivity due to increased stability[7] and/or selectivity[8] due to changes in the transition state of the reaction.

Our lab has recently become interested in the selective immobilization of organometallic catalysts inside the mesopores of tailored silica materials.[9] We began by investigating the macro(mono)cyclization (MMC) of dienes by olefin metathesis.[10] One of the major challenges to this reaction is the formation of oligomers, and we proposed that by performing the reaction under confinement, oligomer formation would be suppressed. We were very pleased that our hypothesis was correct, and that catalyst confinement can indeed influence the selectivity of metathesis reactions. Throughout the course of these reactions, we learned that smaller pore sizes result in higher macrocyclization selectivity but lower reactivity (productivity), and so a balance in terms of pore size is important, with...
2.5 nm pores proving to result in the best selectivity (up to 98% MMC).[8b] Additionally, we learned that cationic molybdenum imido alkylidene N-heterocyclic carbene (NHC) catalysts immobilized without any tether exhibit better macrocyclization selectivity under confinement than a tethered Grubbs-Hoveyda type catalyst.[8b]

With these results in mind, we wanted to investigate how far this confinement effect could go in influencing selectivity in olefin metathesis reactions. Admittedly, the differences in size between the macro(mono)cyclization and oligomerization products is fairly large, and size alone can explain much of the effect. However, we also observed significant changes in E/Z selectivity for the macrocycles formed under confinement, though post-metathesis isomerization was also observed.[8b] This caused us to wonder whether this effect was observable in other metathesis reactions, most importantly in one that has shown little to no evidence of post-metathesis isomerization. We have previously investigated the ring-opening/cross-metathesis (ROCM) of norbornene derivatives with terminal olefins and determined that most products do not undergo post-metathesis isomerization.[9] Therefore, we decided that this system was ideal to study the effect of confinement on the E/Z selectivity of olefin metathesis. In Figure 1 we show the investigated ROCM reaction, as well as the rationale for increased Z selectivity. We believe that the pore wall/silica surface will act in a way that influences the transition states involved, i.e. the intermediate molybdacyclobutanes, pushing the two substituents to the same side as each other. With smaller pore sizes, this effect would be further enhanced due to the smaller space available for the molybdacyclobutane, ultimately leading to the Z product.

Results and Discussion

Catalyst synthesis and immobilization. Our group has long been interested in olefin metathesis catalysts, with a particular focus on cationic molybdenum imido alkylidene NHC complexes since we first reported them in 2014.[10] Due to our long-standing interest, we have developed a library of these catalysts with robust synthetic methods, and also an understanding of the inherent reactivity and selectivity of many of them.[11] Additionally, we have been able to develop a method for the selective immobilization of these catalysts inside the pores of silica materials by adapting a method developed by Crudden and coworkers (Figure 2).[12] For this study, we decided to investigate three different pore sizes using two different silica support materials. These were SBA-15 with an average pore diameter of 5.0 ± 1.0 and 6.8 ± 1.2 nm, referred to as SBA-1550Å and SBA-1568Å, as well as ordered mesoporous silica with an average pore diameter of 2.8 ± 0.75 nm, referred to as OMS28Å (see Supporting Information for more information on the source of these materials). Two different molybdenum

Figure 1. Proposed confinement effect in ring-opening cross metathesis.

Figure 2. Procedure for the selective immobilization of catalysts in pores and catalysts used in this investigation.
complexes Mo1 and Mo2 (Figure 2), were used for immobilization. Briefly, the mesoporous materials were filled with Pluronic® P-123 followed by functionalization of the outer surface with trimethylsilyl groups. Removal of the Pluronic then allowed for immobilizing the catalysts selectively inside the pores via reaction of the surface silanol groups inside the pores with the molecular progenitors under the release of (CF$_3$)$_2$COH. A detailed version of this procedure has been described by our group in previous publications. In order to probe the effect of confinement, we investigated the corresponding ROCM reactions both under homogeneous conditions using Mo1 and Mo2 and their supported versions. Additionally, in order to determine whether the effect was surface-based or due to confinement, we also immobilized the catalyst on unmodified SBA-15 (SBA-15*) catalyst not selectively bound inside the pores and non-porous silica nanospheres (mean diameter 5.0 μm, catalyst cannot be inside a pore).

**Investigations of reactivity and selectivity.** We first investigated the differences in reactivity of the various catalysts under both homogeneous and heterogeneous conditions. We began by studying the ROCM of exo, exo 2,3-dicarbomethoxy-norborn-5-ene (1, DCMNBE) with five different terminal olefins, 1-pentene, allyl benzene, allyl trimethylsilane (allyl TMS), allyl chloride, and allyl benzyl ether (Figure 3). Starting with DCMNBE and 1-pentene, we were very pleased to immediately notice an increase in Z-selectivity with Mo1@SBA-15 in comparison to the homogenous Mo1 (from 14 % to 41 %, Table 1, entries 1–2). Utilizing Mo1@SBA-15, we saw slightly higher Z-selectivity (51 %, Entry 3) than with Mo1@SBA-15*. However, investigations with Mo1@OMS displayed an even more pronounced effect of confinement on Z-selectivity (81 %, Entry 4). As expected, Mo1@OMS had a comparably low molybdenum content of 0.6 μmol/g, necessitating the use of lower catalyst loadings due to stirring considerations and material limitations (see Supporting Information, Table S1). Nevertheless, a moderate yield of 44 % was still observed even with only half of the catalyst loading used for the other catalyst systems. With these promising results in hand, we proceeded to perform some control reactions in order to determine the source of the increase in Z-selectivity. We were very surprised to see that with Mo1@SBA-15* high Z-selectivity was observed, too (63 %, Entry 5), which is actually higher than with Mo1@SBA-15. In order to further investigate if this Z-selectivity was the effect of the silica surface, we prepared Mo1@nanosphere. While due to the extremely low surface area of the material low conversions were observed (Entry 6), we were still able to observe high Z-selectivity with Mo1@nanosphere. Finally, we also investigated the same reaction with Mo3 in order to determine if the selectivity was only governed by the siloxy ligand, or if the surface also played a role. When Mo3 was employed in the reaction we observed a significantly higher Z-selectivity (50 %, Entry 7) than with Mo1 (14 %, Entry 1), though not as high as with Mo1@SBA-15* or Mo1@OMS. With these results in mind, we conclude that the siloxy ligand may be responsible for some of the changes in Z-selectivity, but the observed high Z-selectivity is predominantly a consequence of the catalyst being bound to the silica surface, which indeed favors a transition state that produces predominantly Z-products (Figure 1).

This led us to wonder why the Z-selectivity with Mo1@SBA-15* and Mo1@SBA-15 was not as high as that seen with Mo1@nanosphere. For this reason, we proceeded to perform some kinetic investigations on the various systems to determine whether this was due to post-metathesis isomerization. With Mo1, we could see no evidence of post-metathesis isomerization, which is consistent with our previous observations (see Supporting Information, Figure S3). However, when we measured the kinetics of Mo1@SBA-15, we did in fact observe a significant amount of post-metathesis isomerization (Figure 4), with 77 % Z at low conversion that shifts overtime to 53 % Z at high conversion.

The same trend was also observed with Mo1@SBA-15* (Supporting Information, Figure S4) and Mo1@SBA-15* (Supporting Information, Table S2). Based on these results, we propose that when Mo1 is bound to silica a highly Z-selective reaction occurs, however, if the product remains close to the catalyst for too long after metathesis, isomerization occurs, resulting in less Z product at high conversion. The amount of post-metathesis isomerization appears to be governed by the pore size when the catalyst is under confinement in that the pore’s size determines the rate of diffusion of the product into and out of the pore. In ROCM the smaller pores limit the time the larger product is in contact with the catalyst compared to the time the smaller substrates are. This is based on the "cork of a bottle of champagne" effect we already observed with macro(mono)cyclization, where the large macrocyclic prod-

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**Figure 3.** Substrates for investigation.

**Table 1.** ROCM results for 1-pentene with Mo1 and Mo1 immobilized on mesoporous silica.

| Entry | Catalyst | Substrate | Conversion [%] | [%] Z |
|-------|----------|-----------|----------------|------|
| 1     | Mo1      | 1-pentene | > 99           | 14   |
| 2     | Mo1@SBA-15* | 1-pentene | > 99           | 41   |
| 3     | Mo1@OMS | 1-pentene | > 99           | 51   |
| 4     | Mo1@OMS | 1-pentene | > 99           | 41   |
| 5     | Mo1@SBA-15* | 1-pentene | 34             | 63   |
| 6     | Mo1@nanosphere | 1-pentene | 10             | 83   |
| 7     | Mo3      | 1-pentene | > 99           | 50   |

Reaction conditions: 25 μmol DCMNBE, 250 μmol 1-pentene, 0.25 μmol (1 mol %) catalyst, 500 μL C$_6$H$_6$, 50 °C, 17 h. $^{i}$12.5 μmol DCMNBE, 125 μmol 1-pentene, 0.0625 μmol (0.5 mol %) catalyst, 500 μL C$_6$H$_6$, 50 °C, 17 h.
products leave a small pore, slightly change their conformation outside the pore and then can hardly return into the pore. As the ROCM products are much smaller than the macro(mono)cyclization products studied earlier, it is logical that this effect is only visible with Mo1@OMS28Å, which explains why the Z product is more abundant with this material.

With a good understanding of the different effects at play, we proceeded to investigate the reaction of DCMNBE with other acyclic substrates. When allyl benzene and allyl TMS were employed in ROCM with DCMNBE we observed the same trend (Table 2, Entry 1–10) as with 1-pentene. Indeed, the reaction of DCMNBE with allyl TMS showed even higher Z-selectivity, and when Mo1@OMS28Å was used for the ROCM of allyl TMS and DCMNBE, an extremely high Z-selectivity of 94% was observed (Table 2, Entry 4). This suggests that the post-metathesis isomerization of this product is not as favorable, resulting in increased Z fractions even at higher conversions. We then proceeded to investigate whether functional groups would be tolerated in the reaction. There are a number of potential issues that could arise from functional groups when investigating these ROCM reactions with surface-bound catalysts. Of the most concern is the free silanols on the surface or in the mesopores, which can have a strong effect on the distribution of substrates, especially those that could react with the silanols or remain stuck inside the pores. Additionally, the reactivity of the catalyst complex with different substrates could also play an important role, both in the selectivity and overall reactivity, and this effect may interfere with the other effects. Nevertheless, we thought it important to investigate at least some functional group compatibility.

We started with the ROCM of allyl benzyl ether with DCMNBE. Unfortunately, the reactivity of this substrate was low with Mo1, proceeding to only 17% conversion under homogeneous conditions, even with double the usual catalyst loading. This low conversion was also observed when using the immobilized catalysts Mo1@SBA-15SBA and Mo1@SBA-15SBAH, while no observable conversion was found using Mo1@OMS28Å. Nevertheless, again an effect on Z-selectivity, when moving from the homogeneous to immobilized catalysts, was observed (Table 2, Entry 11–14). Interestingly, the reactivity of allyl benzyl ether and DCMNBE was increased when Mo1@SBA-15SBA was employed as catalyst, indicating that the surface may also have a stabilizing effect on the catalyst. When investigating the reaction of allyl chloride and DCMNBE, conversion was good under homogeneous conditions though reactivity dropped significantly when immobilized catalysts were used, potentially due to reaction of allyl chloride with the inner pore walls (Table 2, entries 15–17). As was the case with the other

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**Table 2. Summary of ROCM results with Mo1 and Mo1 immobilized on mesoporous silica.**

| Entry | Catalyst | Substrate | Conversion [%] | [%] Z |
|-------|----------|-----------|----------------|------|
| 1     | Mo1      | allyl trimethylsilane | > 99 | 23 |
| 2     | Mo1@SBA-15SBA | allyl trimethylsilane | 72 | 70 |
| 3     | Mo1@SBA-15SBA | allyl trimethylsilane | 72 | 84 |
| 4     | Mo1@OMS28Å | allyl trimethylsilane | 50 | 94 |
| 5     | Mo1@SBA-15SBA | allyl trimethylsilane | 65 | 76 |
| 6     | Mo1      | allyl benzene | > 99 | 16 |
| 7     | Mo1@SBA-15SBA | allyl benzene | > 99 | 30 |
| 8     | Mo1@SBA-15SBA | allyl benzene | 84 | 43 |
| 9     | Mo1@OMS28Å | allyl benzene | 49 | 77 |
| 10    | Mo1@SBA-15SBA | allyl benzene | 59 | 40 |
| 11    | Mo1      | allyl benzyl ether | 17 | 16 |
| 12    | Mo1@SBA-15SBA | allyl benzyl ether | 32 | 31 |
| 13    | Mo1@SBA-15SBA | allyl benzyl ether | 29 | 35 |
| 14    | Mo1@SBA-15SBA | allyl benzyl ether | 72 | 42 |
| 15    | Mo1      | allyl chloride | > 99 | 17 |
| 16    | Mo1@SBA-15SBA | allyl chloride | 20 | 35 |
| 17    | Mo1@SBA-15SBA | allyl chloride | 12 | 41 |

Reaction conditions: 25 μmol DCMNBE, 250 μmol substrate, 0.25 μmol (1 mol %) catalyst, 500 μL C6H6, 50 °C, 17 h. 12.5 μmol DCMNBE, 125 μmol substrate, 0.0625 μmol (0.5 mol %) catalyst, 500 μL C6H6, 50 °C, 17 h. **25 μmol DCMNBE, 250 μmol substrate, 0.5 μmol (2 mol %) catalyst, 500 μL C6H6, 50 °C, 17 h.**
substrates, however, a significant increase in Z-selectivity up to 41 % was observed when the catalyst was immobilized.

Next, we investigated the reactivity and selectivity with Mo2 immobilized on the same silica materials (Table 3). Based on our investigations with macro(mono)cyclization reactions,[14,15] we surmised that Mo2 would show slightly higher Z selectivity than Mo1, which did turn out to be the case. Indeed, the reaction of 1-pentene and DCMNBE as an example, Mo1@SBA-15 showed 41 % Z-selectivity (Table 1, entry 2) while with Mo2@SBA-15 it showed 64 % Z-selectivity (Table 2, Entry 2) was observed, accounting for a 20 % increase in Z-selectivity. A similar increase in Z-selectivity was observed in all cases for Mo2@SBA-15 vs. Mo1@SBA-15, and most cases with Mo2@SBA-15 except in the case of allyl TMS with DCMNBE, perhaps due to the already very high selectivity (84 % for Mo1@SBA-15 vs. 87 % for Mo2@SBA-15). In line with that, little or no difference in Z-selectivity was observed when comparing Mo1@OMS and Mo2@OMS (i.e. for 1-pentene and DCMNBE the Z-selectivity was 81 and 82 %, respectively).

The overall higher Z-selectivity of the immobilized Mo2 complexes is a result of the lower reactivity of Mo2 compared to Mo1, which in turn is a consequence of the lower Tolman electronic parameter (TEP) of 1,3-dimesityl-4,5-dichlorimidazol-2-yldiene (IMesCl, TEP = 2054 cm⁻¹) compared to 1,3-dimesitylimidazol-2-yldiene (IMes, TEP = 2050 cm⁻¹).[15] This allows the products to diffuse out of the pore, thereby avoiding post-metathesis isomerization.[16] Indeed, the reactivity of Mo2 was lower than that of Mo1, especially with the OMS immobilized complexes and in the reactions of DCMNBE with allyl chloride and allyl benzyl ether. In the interest of completeness, we also performed a kinetic study with Mo2@SBA-15 and observed very minimal post-metathesis isomerization (see Supporting Information, Figure S5), indicating that our proposal is consistent with the experiment. Additionally, we probed the Z-selectivity of Mo2@SBA-15 after 3 minutes and overnight, and observed a drop from 87 to 73 % Z (see Supporting Information, Table S2) indicating that post-metathesis isomerization is happening but to a significant lesser extent than with Mo1. Finally, it is again interesting to observe a higher reactivity of allyl benzyl ether with Mo2@SBA-15 compared to all other catalysts, again indicating a positive effect on stability for the surface-bound catalyst.

In order to probe the scope of the reaction further, we proceeded to investigate whether other cyclic olefins would also be tolerated (Figure 5), in particular 2,3-eno, exo-bis(acetoxyethyl)-7-oxabicyclo[2.2.1]hept-5-ene (3a, 7-oxa-NBE), and endo, endo-2,3-dimethoxymethyl-norborn-5-ene (3b, DMMNBE).

We decided to use allyl TMS as the terminal olefin in these investigations, as that substrate provided some of the best reactivity across all investigated substrates. We were very pleased to observe similar trends with these cyclic olefins as we had observed with DCMNBE (Table 4). In both cases, an increase in Z-selectivity was observed when the reaction was performed with immobilized catalysts, with the highest selectivity observed with the OMS immobilized complexes, and with a slightly higher selectivity again in the case of Mo2 in comparison to Mo1. This demonstrates that the immobilization of cationic molybdenum imido alkylidene NHC complexes on silica surfaces leads to higher Z-selectivity across a variety of different ROCM reactions.

### Table 3: ROCM results with Mo2.

| Entry | Catalyst | Substrate | Conversion [%] | [%] Z |
|-------|----------|-----------|----------------|-------|
| 1     | Mo2      | 1-pentene | > 99           | 13    |
| 2     | Mo2@SBA-15 | 1-pentene | > 99           | 64    |
| 3     | Mo2@SBA-15 | 1-pentene | > 99           | 70    |
| 4     | Mo2@OMS  | 1-pentene | 27             | 82    |
| 5     | Mo2@SBA-15 | 1-pentene | 82             | 73    |
| 6     | Mo2@nanosphere | 1-pentene | 17             | 84    |
| 7     | Mo2@SBA-15 | allyl trimethylsilyl | 74 | 21 |
| 8     | Mo2@SBA-15 | allyl trimethylsilyl | 84 | 73 |
| 9     | Mo2@SBA-15 | allyl trimethylsilyl | 96 | 73 |
| 10    | Mo2@OMS   | allyl trimethylsilyl | 96 | 87 |
| 11    | Mo2@SBA-15 | allyl trimethylsilyl | 64 | 94 |
| 12    | Mo2       | allyl benzene | > 99 | 16 |
| 13    | Mo2@SBA-15 | allyl benzene | 73 | 55 |
| 14    | Mo2@SBA-15 | allyl benzene | 76 | 68 |
| 15    | Mo2@OMS   | allyl benzene | 23 | 72 |
| 16    | Mo2@SBA-15 | allyl benzene | 72 | 75 |
| 17    | Mo2       | allyl benzyl ether | 6 | 15 |
| 18    | Mo2@SBA-15 | allyl benzyl ether | 4 | 45 |
| 19    | Mo2@OMS   | allyl benzyl ether | 7 | 65 |
| 20    | Mo2@SBA-15 | allyl benzyl ether | 88 | 76 |
| 21    | Mo2       | allyl chloride | 14 | 12 |
| 22    | Mo2@SBA-15 | allyl chloride | 9 | 65 |
| 23    | Mo2@SBA-15 | allyl chloride | 5 | 66 |

Reaction conditions: 25 μmol DCMNBE, 250 μmol substrate, 0.25 μmol (1 mol %) catalyst, 500 μL C₆H₆, 50 °C, 17 h. 12.5 μmol DCMNBE, 125 μmol substrate, 0.0625 μmol (0.5 mol %) catalyst, 500 μL C₆H₆, 50 °C, 17 h. 25 μmol DCMNBE, 250 μmol substrate, 0.5 μmol (2 mol %) catalyst, 500 μL C₆H₆, 50 °C, 17 h.

**Figure 5. Reactions with different cyclic olefins.**

**Conclusion.**

We had previously demonstrated the applicability of confinement to macro(mono)cyclization reactions, resulting in an increase of macro(mono)cyclization via suppression of oligomerization. During the course of that investigation, it became clear that confinement also affects the E/Z selectivity of the reaction.
negligible size differences, as found in currently existing synthetic challenges in other areas. Ongoing to determine how the effect of catalyst confinement displays significantly higher selectivity of various reactions and how this could be applied to the exclusion of air and moisture in a N₂-filled glove box. Equipment and chemicals: All reactions were performed under -filled glove box conditions for almost all of the investigated substrates. In case the reaction products undergo post-metathesis isomerization, its extent is determined by the diffusion of the products into and out of the pore. By tuning the environment surrounding the catalyst, we were able to identify highly Z-selective conditions for almost all of the investigated substrates. Investigations in our lab are currently ongoing to determine how the effect of catalyst confinement on diffusion of substrates/products can be used to affect the selectivity of various reactions and how this could be applied to currently existing synthetic challenges in other areas.

**Experimental Section**

**Equipment and chemicals:** All reactions were performed under the exclusion of air and moisture in a N₂-filled glove box (MBraun Labmaster) unless noted otherwise. Chemicals were purchased from ACR, Acros Organics, Alfa Aesar, Sigma Aldrich, Fluka and TCI. Mesoporous silica SBA-15 was purchased from Glantreo: SBA-15 (50 Å, hexagonal pore morphology). Silica Nanospheres were purchased from Bangs Laboratories, Inc (Dry Silica, nonporous, 5.01 μm mean particle size). Poly(ethylene glycol)-b-poly(propylene glycol)-b-poly(ethylene glycol) (PEG-PPG-PEG, Pluronic® P-123), dodecylethyldimethylammonium bromide (> 98%), tetramethyl orthosilicate (98%, TMOS) and 1,2-dichlorobenzene (anhydrous) were purchased from Sigma Aldrich. CH₃Cl, diethyl ether, n-pentane and toluene were dried using an MBraun SPS-800 solvent purification system and stored over 4 Å molecular sieves. Deuterated solvents were stored over activated alumina and 4 Å molecular sieves for a minimum of 24 h prior to use. NMR spectra were recorded on a Bruker Avance III 400 spectrometer. NMR spectra were internally calibrated to solvent signals. Abbreviations for multiplicities: s (singlet), bs (broad singlet), d (dublet), t (triplet), q (quartet), hept (heptet), m (multiplet). GC-MS analyses were performed on an Agilent Technologies 5975 C inert MSD device consisting of a triple-axis detector, a 7693 autosampler and a 7890 A GC system equipped with an SPB-5 fused silica column (34.13 mÄ~0.25 mmÄ~0.25 μm film thickness). GC data were plotted in Excel (Microsoft). Nitrogen adsorption analyses were performed at 87 K on a Quantachrome Instruments Autosorb iQ MP automatic volumetric instrument. SBA-15 samples were degassed for 16 h at 110 °C under vacuum prior to the gas adsorption studies. Surface areas were evaluated using the Brunauer-Emmett-Teller (BET) model applied between p/p° values of 9.1.10-6 and 0.9 for microporous/ mesoporous SBA-15. Pore size distributions were calculated using the non-local Density Functional Theory (NLDFT) cylindrical adsorption pores for zeolites/silica implemented in the ASiQwin software version 3.01. The powder samples were filled into mark capillaries with a diameter of 1 mm (Hilgenberg, glass no. 14) and flame-sealed. For measurements, a SAXSess mc2 diffractometer (Anton Panar) in the line collimation geometry was used for which the sample to detector distance was calibrated with cholesteryl palmitate. X-ray radiation with a wavelength of λ(Cu-Kα) = 0.1542 nm was generated by an ID 3003 X-ray generator (Seifert) operated at 40 kV and 40 mA. To ensure a uniform irradiation of all lattice planes, samples were rotated during the measurement using a RotorCell placed in a TCS 120 hot stage (both Anton Panar). The sample housing was evacuated prior to measurements, which were carried out at 25 °C and averaged over 60 individual measurements. The scattered X-ray intensity was detected with a one-dimensional CMOS Mythen 2 K detector (Dectris). Using the software SAXSquantTM, the measured scattering profiles were background corrected with a measurement of an empty mark capillary and deconvoluted. The obtained Bragg-like diffraction maxima were fitted with Lorentzian functions to extract the exact peak positions.

**Synthesis of SBA-15:** For the synthesis of SBA-15, 16 g of the triblock copolymer Pluronic P123 (average molecular weight ~5800 g mol⁻¹, Sigma Aldrich) was dissolved in a mixture of 520 ml demineralized water and 80 ml hydrochloric acid (37 wt %) at room temperature overnight while stirring with 100 rpm. Before the addition of 37 ml of tetraethyl orthosilicate (TEOS, 98%, reagent grade, Sigma Aldrich), the solution was heated to 45 °C. The mixture was stirred for 7.5 h with a stirring speed of 150 rpm. The subsequent hydrothermal treatment was carried out under static conditions at 80 °C for 15 h. Afterwards, the as-synthesized SBA-15 was separated under vacuum, washed with demineralized water and then dried in an oven at 80 °C. To open the pores, the as-synthesized SBA-15 was calcined for 6 h at 550 °C in an air flow of 150 l h⁻¹ with a heating rate of 1 K min⁻¹. The N₂-sorption isotherms (Supporting information, Table 4. ROMC results using different cyclic olefins.

| Entry | Catalyst | Substrate | Conversion [%] | [%] Z |
|-------|----------|-----------|----------------|-------|
| 01    | Mo1      | 3a        | > 99           | 36    |
| 02    | Mo1@SBA-15| 3a        | 99             | 62    |
| 03    | Mo1@SBA-15| 3a        | 98             | 57    |
| 04    | Mo1@OMS| 3a        | 18             | 88    |
| 05    | Mo1@SBA-15| 3a        | 61             | 58    |
| 06    | Mo2      | 3a        | > 99           | 64    |
| 07    | Mo2@SBA-15| 3a        | 7              | 99    |
| 08    | Mo2@SBA-15| 3a        | 97             | 81    |
| 09    | Mo2@OMS| 3a        | 55             | 90    |
| 10    | Mo2@SBA-15| 3a        | 78             | 63    |
| 11    | Mo1      | 3b        | > 99           | 37    |
| 12    | Mo1@SBA-15| 3b        | > 99           | 75    |
| 13    | Mo1@OMS| 3b        | > 99           | 90    |
| 14    | Mo1@OMS| 3b        | 99             | 37    |
| 15    | Mo2      | 3b        | > 99           | 77    |
| 16    | Mo2@OMS| 3b        | > 99           | 77    |
| 17    | Mo2@SBA-15| 3b        | > 99           | 89    |
| 18    | Mo2@OMS| 3b        | 72             | 89    |

Reaction conditions: 25 μmol substrate, 250 μmol allyl TMS, 0.25 μmol (1 mol %) catalyst, 500 μL C₂H₆, 50 °C, 17 h. 12.5 μmol substrate, 125 μmol allyl TMS, 0.0625 μmol (0.5 mol %) catalyst, 500 μL C₂H₆, 50 °C, 17 h.
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Figure S1) and pore distributions (Supporting Information, Figure S2) were then measured.

**Synthesis of OMS:** In general, the synthesis followed the procedure described in the literature with slight adaptions necessary due to the changed surfactant. 30.46 g of TMOS was added to 21.76 g of an aqueous 0.1 N HCl solution and stirred at room temperature for approximately 10 min while a low vacuum of 120 mbar was applied to remove most of the formed methanol. This colloidal silica mixture was added to 14.995 g of dodecylethyldimethylammonium bromide and homogenized. The clear liquid was poured into a PTFE dish and was left at 80°C for 48 hours to complete the polycondensation process. The now solid material was milled for 1 min with a ball mill (Spex 8000 Mixer/Mill, vial and balls made from stainless steel). Afterwards the powder was calcined by heating it to 550°C with 1°C/min in the presence of an air flow of 14.5 L·h⁻¹ and kept at this temperature for 6 h to remove all surfactant molecules. The N₂ sorption isotherms (Supporting Information, Figure S1) and pore distributions (Supporting Information, Figure S2) were then measured.

**Catalyst synthesis and immobilization:** [Mo(N-2,6-Me₂-C₆H₄)(CH₂CH₂Ph)₂(IMes)(OC(CF₃)₃)] [B(ArF)₃] (Mo1) and [Mo(N-2,6-Me₂-C₆H₄)(CH₂CH₂Ph)₂(IMesCl)(OC(CF₃)₃)] [B(Ar²F)₃]-MeCN (Mo2) were synthesized according to the literature. The various mesoporous silica materials were modified and the catalysts selectively immobilized as described. The Mo-content of the immobilized catalysts was then determined by ICP-OES (Table S1). ICP-OES data were recorded on a Spectro Acros 160 CCD equipped with a Cetec ASX-260 autosampler. Analysis of the samples was carried out with the Software Smart Analyzer Vision 4.02.0834. Quantitative analysis of the Mo-loading of each silica sample was determined by ICP-OES. For analysis, the corresponding silica (30–50 mg, Table S1) was mixed with KOH (0.38 g, 6.77 mmol) and KNO₃ (0.65 g, 6.42 mmol). The mixture was heated to 450°C and the temperature was held for 3 hours. After cooling to room temperature, K₂S₂O₆ (50.0 mg, 0.18 mmol) was added. The colorless solid was dissolved in a minimum amount of deionized water and 1 M KOH (2 mL) was added. The suspension was filtered, transferred into a 10 mL volumetric flask and filled to the mark with deionized water. The colorless solution was added to a 25 mL volumetric flask with concentrated HCl (5 mL) and filled to the mark with deionized water. Mo was measured at 203.97 nm–203.99 nm and λ = 203.97 nm–204.02 nm, respectively. The limit of detection (LOD) was 0.0001 mg L⁻¹. For calibration, aqueous Mo-standards with Mo concentration of 0.000, 0.500, 2.500, 5.000 and 10.000 mg L⁻¹ were used.

**Representative procedure for homogenous reaction:** A solution of DCMNBE (1, 15 μL, 1 M in C₂H₆, 15 μmol, dodecane as internal standard), 1-pentene (10.5 μL, 150 μmol, 10 equiv) and C₂H₆ (250 μL) were added to a vial charged with a stir bar. A solution of Mo1 (10 μL, 0.015 M in DCE, 0.15 μmol, 1 mol%) was added, and the reaction was heated to 50°C and allowed to stir over night. An aliquot for GC-MS was then taken and the conversion and E/Z ratio were quantified using dodecane as an internal standard. Full characterization of the previously unknown compounds is available in the Supporting Information.

**Representative procedure with immobilized catalyst:** A solution of DCMNBE (1, 25 μL, 1 M in C₂H₆, 25 μmol, dodecane as internal standard), 1-pentene (17.5 μL, 250 μmol, 10 equiv) and C₂H₆ (450 μL) were added to a vial charged with a stir bar and 11 mg of Mo1@SBA-15 (1 mol%). The reaction was heated to 50°C and allowed to stir overnight. The reaction mixture was filtered, an aliquot for GC-MS was taken and the conversion and E/Z ratio were quantified using dodecane as an internal standard.

**Supporting Information**

The following files are available free of charge: catalyst synthesis, substrate synthesis, silica surface modification, ROCM reactions, experimental procedures, analysis, full characterization (PDF).

**Notes**

The authors declare no competing financial interest.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** molybdenum · N-heterocyclic carbene · confinement · ring-opening cross metathesis · diastereoselectivity

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