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Metathesis of Classical and Functionalized Olefins Catalyzed by Silica-Supported Single-Site Well-Defined W and Mo Pre-catalysts

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Abstract: Olefin metathesis of α -olefins (C_6 , C_8 , C_{10}), α , β -unsaturated ester, α , β -unsaturated acetate and cross-metathesis of 1-octene and ethyl 6-heptenoate were carried out using well-defined $[(\equiv Si-O)W(CH_3)_5]$ and $[(\equiv Si-O)Mo(\equiv C^tBu)(CH_2^tBu)_2]$ pre-catalysts. During the reaction, it was observed that irrespective of the chain length, linear α -olefins are almost showing similar TON. We observed that Mo pre-catalyst performs better with TONs between 700 and 1478 as compared to W with TONs between 213 and 962 at room temperature. Both pre-catalysts performed equally at 70 °C, with almost similar activity as well as TON (≈ 1700). We also carried out self-metathesis of functionalized olefins using both silica-supported W and Mo pre-catalysts. It was observed that W pre-catalyst performs much better than Mo pre-catalyst for functionalized olefin metathesis reaction in our conditions. Additionally, we noticed that W pre-catalyst provides selective metathesis product, whereas Mo pre-catalyst gives a range of products due to the isomerization of the olefinic bond.

Introduction

Olefin metathesis is an essential part of catalysis in chemical and petrochemical research.^[1] Since the early discovery of olefin metathesis by Anderson and Merckling in the 1950s^[2] and Banks and Bailey in the 1960s,^[3] significant progress has been achieved in this area.^[4] Predominantly, the progress in understanding the catalytic behavior, came from the homogeneous catalytic system rather than the heterogeneous ones.^[4a, 5] The primary problem encountered in heterogeneous catalytic systems is the fact that the so-called "active sites" are not well-defined.^[1e] Till now, there are not enough tools developed for their characterization to comment precisely on both the nature and number of these active sites. This problem slowed down the development process of heterogeneous catalysts. On the other hand, homogeneous catalytic systems are in principle well-defined in nature, which makes them fully adaptable to develop further new catalysts adapted for various catalytic reactions.^[1f, 6] Though olefin metathesis was discovered in the 1950s, the understanding of the reaction mechanism came in the 1970s by Chauvin et al., which

led him to be awarded the Nobel prize in 2005 along with Grubbs and Schrock.^{[7], [8]}

It is evident from the literature that early transition metal-oxides (WO_3 , MoO_3 , and Re_2O_7) supported on various oxide supports and late transition metals, specifically organometallic ruthenium complexes, are well known for olefin metathesis reaction.^[1e, 9] We believe that surface organometallic chemistry could be a good approach to erase the existing gap between homogeneous and heterogeneous catalysts by grafting the molecular organometallic complex on various oxide surfaces (making them heterogeneous).^[10] This opens up opportunities for easier and better characterization as well as further development of new catalysts.^[11]

In this regard, we disclose here the catalytic application of tungsten hexamethyl and molybdenum tris-neopentyl neopentylidene pre-catalysts on self-metatheses of linear α -olefins as well as functionalized olefins. Apart from the gas-phase olefin metathesis reaction,^[10b] recently, we and other research groups worked on liquid phase olefin metathesis reaction using various W-oxo and Mo-oxo SOMC catalysts.^[4b, 12] To further understand the reaction, we have not only used α -olefins with various lengths of alkyl chains but also the challenging functionalized olefins. Additionally, we also carried out cross olefin metathesis reaction to understand the reactivity of W and Mo SOMC pre-catalysts.

Silica supported tungsten $[(\equiv Si-O)W(CH_3)_5]$ **1**, and molybdenum $[(\equiv Si-O)Mo(\equiv C^tBu)(CH_2^tBu)_2]$ **2** pre-catalysts were previously synthesized and well-characterized by our group (SI Figures S1-S6).^[13] The catalytic properties of **1** were explored extensively in alkane and various metathesis reactions.^[13a, 14] In contrast, the catalytic properties of $[(\equiv Si-O)Mo(\equiv C^tBu)(CH_2^tBu)_2]$ have not been much studied.^[15] In the case of **1**, we have studied in details the molecular transformations occurring when **1** was heated at 70 °C (temperature of our metathesis reactions) or transformed under UV light at RT. **1** is transformed into $[(\equiv Si-O)W(\equiv CH)Me_2]$ which is further giving $[(\equiv Si-O)W(=CH)_2Me]$ upon coordination of

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an L ligand (phosphine or olefin) at room temperature.^[10e] In the case of $[(\equiv\text{Si-O})\text{Mo}(\equiv\text{C}^t\text{Bu})(\text{CH}_2^t\text{Bu})]$, we expect a similar behaviour, that would consist of its transformation into $[(\equiv\text{Si-O})\text{Mo}(\equiv\text{CH}^t\text{Bu})_2(\text{CH}_2^t\text{Bu})]$, although not proved so far.

Results and Discussion

In this work, we compare the reactivity of W vs. Mo pre-catalysts in the metathesis reaction of various α -olefins as well as some functionalized olefins (mostly with olefinic esters or acetates). We have shown that with **1** the real coordination sphere of the real catalyst is $[(\equiv\text{Si-O})\text{W}(\equiv\text{CH})_2\text{Me}]$, and we are expecting that with **2** the real coordination sphere at 25 and 70 °C would be $[(\equiv\text{Si-O})\text{Mo}(\equiv\text{CH}^t\text{Bu})_2(\text{CH}_2^t\text{Bu})]$ (Figure 1).

Figure 1. Well-defined silica-supported pre-catalysts $[(\equiv\text{Si-O})\text{W}(\text{CH}_3)_3]$ **1** and $[(\equiv\text{Si-O})\text{Mo}(\equiv\text{C}^t\text{Bu})(\text{CH}_2^t\text{Bu})_2]$ **2** and their expected corresponding active species $[(\equiv\text{Si-O})\text{W}(\equiv\text{CH})_2\text{Me}]$ and $[(\equiv\text{Si-O})\text{Mo}(\equiv\text{CH}^t\text{Bu})_2(\text{CH}_2^t\text{Bu})]$.

Self-metathesis of α -olefins

All the reactions were carried out using a batch reactor. In a typical run, the catalyst precursor (the molar ratio olefin to the metal center M was established at the same value of 1900 regardless of M or the olefin) **1** or **2** were mixed with 1 ml of the α -olefins; C_nH_{2n} , $n = (6, 8, \text{ or } 10)$ inside a glovebox. The reactor tubes were taken out of the glove box, and were frozen using liquid nitrogen, the tubes were sealed under vacuum, then inserted into the oil bath and heated either at 25 or 70 °C to determine conversions and selectivities with respect to time (Figure 2 and SI Figures S7 and S8).

At room temperature, the initial selectivity towards the primary metathesis product (C_{10} , C_{14} , and C_{18} , respectively) is higher as compared to secondary products. With time, various secondary products are observed due to double bond migration, followed by metathesis (SI Figures S9-S20). The primary reason for the formation of secondary products is due to the chain walking process of the olefinic double bond (Scheme 1).^[15-16] We observed similar reactivity in the case of C_6 and C_8 , whereas in the case of C_{10} , the reactivity is slightly lower using **1** and **2** at

room temperature, but almost equal TONs (≈ 1700) are observed at the higher temperature.

Figure 2. The evolution of turnover number (TON) vs. time for C_6 , C_8 , and C_{10} olefins metathesis reactions using **1** (A) and **2** (B) at room temperature in batch conditions.

Scheme 1. Double bond isomerization process by SOMC complex (n = number of carbons, M = transition metal, R = alkyl group)

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To get maximum conversion of the olefins, the reaction was heated to 70 °C, to our expectations, the selectivity towards primary product decreases with simultaneous increase of various secondary products. This is understandable, as at higher temperatures, double bond migration occurs faster than metathesis reaction.

Self-metathesis of functionalized olefins

Furthermore, **1** and **2** were tested for functionalized olefin metathesis reaction. As the literature report says that these early transition metal catalysts are oxophilic in nature; hence they would be poisoned by oxygen-containing components.^[14c] We wanted to understand the behavior of these catalysts towards functionalized and olefin cross-metathesis reactions.

The primary idea was to test these catalysts with reactants like fatty acid ester, unsaturated acetate, and compare their catalytic activity. In a typical reaction, 1 ml of the reactant was taken in a glass ampoule inside the glovebox, and an amount of pre-catalysts **1** or **2** (fixed reactant to pre-catalyst ratio R/C = 475) were added. The glass ampoules were taken outside, sealed under vacuum, and heated at 80 °C. The catalytic reaction was carried out in neat conditions for 5 days. At the end of the reaction, the evolution of the products was analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

With the ester (ethyl 6-heptenoate) as a reactant, we observed the self-metathesis product exclusively $C_{10}H_{18}(CO_2C_2H_5)_2$ using **1** with a TON of 77 (Figure 3). However, in the case of **2**, we observed the primary self-metathesis product $C_{10}H_{18}(CO_2C_2H_5)_2$ with a TON of 19 (Figure 3), along with secondary metathesis products (Figure 4). These products are explained by the isomerization of the di-ester $C_{10}H_{18}(CO_2C_2H_5)_2$ followed by cross-metathesis reaction either with the ethylene (coming from the self-metathesis reaction of the ester) to give unsaturated mono-esters $C_5H_9(CO_2C_2H_5)$, $C_7H_{13}(CO_2C_2H_5)$, and $C_8H_{15}(CO_2C_2H_5)$ or with the reactant $C_6H_{11}(CO_2C_2H_5)$ resulting in new di-ester molecule $C_{12}H_{22}(CO_2C_2H_5)_2$ (Scheme 2).

Figure 3. Products distribution of the self-metathesis of ethyl 6-heptenoate with **1** and **2**.

Figure 4. Products distribution of the metathesis reaction of ethyl 6-heptenoate with **1** and **2**

Scheme 2. Various pathways (metathesis and isomerization) observed in the metathesis of different olefinic ester.

Surprisingly, we could not observe any isomerization product with pre-catalyst **1** though we experienced with the same pre-catalyst isomerization in the case of non-functionalized olefins metathesis reaction (Figures S9-S20). Likely, the oxygen is coordinated to the oxophilic metal center preventing the isomerization process by insertion of the olefinic ester into the M-H bond.

In the case of pre-catalysts **1** and **2**, the difference of reactivity can have another origin: with **1** the steric effect of the methyl ligands remaining on W is less pronounced than that of the neopentyl ligand on Mo, which is likely coordinated to Mo (Figure 1).

We further moved to explore the catalytic activity of **1** and **2** towards other functional groups. We thought of using acetate as a reactant instead of another ester group. We followed the same reaction conditions as that of the ester with 3-butenyl acetate as a reactant. In this case, we exclusively observed self-metathesis product $C_{10}H_{16}O_4$ using both **1** and **2** with a TON of 39 and 15, respectively. It was surprising that we did not observe any isomerization product (Figure 5A).

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Figure 5. Products distribution of the metathesis of unsaturated acetates; (A) 3-butenyl acetate (B) 4-pentenyl acetate, using **1** and **2**.

At this point, we hypothesized that the chain length is playing a role in the isomerization of the double bond. To further understand the reactivity of the acetate, we extended the chain length by one carbon (4-pentenyl acetate), maintaining all the reaction conditions. At the end of the reaction, only the self-metathesis product $C_{12}H_{20}O_4$ was observed with **1** and **2** with a TON of 193 and 23, respectively. Interestingly, we observed that the TON increases almost five times in the case of **1** as compared to **2** (Figure 5B).

Cross-metathesis between functionalized and α -olefins

At this point, it was very interesting for us to understand the isomerization process. This curiosity led us to carry out the cross-metathesis (CM) reaction, where olefinic ester and olefin are the reactants. We envisioned that we could observe a range of products as α -olefin can isomerize and cross-metathesize with the unsaturated ester.

For the cross-metathesis reaction, we used 2.85 mmol of ethyl 6-heptenoate and 6.37 mmol of 1-octene, maintaining the reaction conditions as before. At the end of the reaction, we could observe the cross-metathesis product with pre-catalysts **1** and **2** where **1**

performed better than **2** (Figure 6). Additionally, we also observed self-metathesis and some isomerization products (Figure 7).

Figure 6. Cross-metathesis reaction between ethyl 6-heptenoate and 1-octene with **1** and **2**.

Figure 7. Products distribution of the cross-metathesis reaction between ethyl 6-heptenoate and 1-octene with **1** and **2**.

Interestingly, although we observed earlier isomerization of α -olefins and their metathesis product with **1** (SI Figures S9-S20), in the cross-metathesis reaction between olefin and unsaturated ester, we could not observe any isomerization of olefins (Figures 6 and 7). Instead, we observed the self-metathesis products of each of the olefin ($C_{14}H_{28}$) and ester ($C_{10}H_{18}(CO_2C_2H_5)_2$) and cross-metathesis product between both of them ($C_{12}H_{23}(CO_2C_2H_5)_2$). However, in the case of **2**, we observed both self and cross-metathesis of 1-octene and ethyl 6-heptenoate ($C_{14}H_{28}$, $C_{10}H_{18}(CO_2C_2H_5)_2$ and $C_{12}H_{23}(CO_2C_2H_5)_2$) as well as isomerization products; C_7H_{14} , C_9H_{18} , $C_5H_9(CO_2C_2H_5)_2$, $C_7H_{13}(CO_2C_2H_5)_2$, $C_8H_{15}(CO_2C_2H_5)_2$, $C_{11}H_{21}(CO_2C_2H_5)_2$, $C_{14}H_{27}(CO_2C_2H_5)_2$ and $C_{12}H_{22}(CO_2C_2H_5)_2$ (Figures 6 and 7). These isomerization products come from the double bond migration (isomerization) of the self and cross-metathesis products of 1-octene and ethyl 6-heptenoate, followed by cross-metathesis

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between the newly formed olefin and olefinic-esters. During our study of olefin metathesis and cross-metathesis reactions, we understood that Mo based catalysts are prone to isomerize the double bond in olefinic esters. In contrast, W catalysts can only isomerize the α -olefins.

In the olefin metathesis reaction, especially when early-transition metals are involved, one could observe both metathesis and isomerization of the reactant. To be precise, from our previous experiments as well as in this paper, we observed that isomerization and metathesis both depend on temperature and time of reaction.^[14a] At a shorter time with SOMC catalysts, we observed exclusively the primary product, which is the metathesis product, followed by isomerization (as soon as we mix the catalyst with the reactant, it first converts olefin to its primary product, and with time it isomerizes the olefin to various other olefins).^[14a]

The main reason for the formation of isomeric products is due to the formation of the metal-hydride bond (M-H) during the course of the reaction. As metal methyl/neopentyl catalysts are used in the catalytic reaction, it takes time for the catalyst to form metal hydride and then isomerization.

We only observed isomerization of the ester in the case of pre-catalyst **2**, whereas with pre-catalyst **1** we do not observe isomerization, but with both pre-catalysts, we observed metathesis product. Because we believe the bulky Mo group inhibits the coordination of the oxygen of the ester group, whereas W has a comparatively less bulky surrounding allowing the coordination of the oxygen moiety hence inhibits the isomerization.^[14c]

Mechanistic insights by DFT calculations

To verify the role of the nature of the ester and acetate substrates, we took advantage of the DFT calculations (Figure 8). The better performance of **1** as compared to **2** in functionalized olefin self-metathesis of ester (ethyl 6-heptenoate) can be rationalized by the kinetic cost of 23.5 kcal/mol for **1** in comparison with 29.3 kcal/mol for **2**, for the catalytic cycle. On the other hand, for the acetate (4-pentyl acetate), the trend is the same. Actually, calculations confirmed a huge preference for pre-catalyst **1** with an upper energy barrier of 25.6 kcal/mol, whereas for **2** it goes up till 34.8 kcal/mol. This explains the much better performance of **1** for this substrate.

Figure 8. Free energy profile (in kcal/mol) using **1** and **2** for self-metathesis reaction of methyl 6-heptenoate (in black, R = (CH₂)₄COOCH₂CH₃) and 4-pentyl acetate (in blue, R = (CH₂)₃OCOCH₃).

Bearing the results with ester, cross-metathesis reaction with 1-octene worsened the performance of both catalysts. Actually, this is right according to the upper energy barriers (step IV→V) that increase by 5.7 and 4.3 kcal/mol for **1** and **2**, respectively. Comparing with 1-octene energy profiles (see Tables 1 and 2), the ester is kinetically 3.7 and 3.9 kcal/mol favored for **1** and **2**, respectively. This explains why in the mixture, the self-metathesis of the olefinic ester is preferred with respect to the 1-octene one despite the excess of the latter olefin.

Table 1. Relative energies (in kcal/mol) of the reaction pathway bearing **1** as a catalyst with 1-hexene and 1-octene substrates.

	I	I-II	II	II-III	III	III-IV	IV	IV-I	I
ethylene	0.0	14.5	-3.2	22.5	0.0	22.6	-4.1	15.0	0.0
1-hexene	0.0	16.6	-1.6	22.5	0.4	24.5	0.0	17.4	0.9
1-octene	0.0	16.1	-2.8	22.1	1.4	24.4	-1.9	17.8	1.1

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Table 2. Relative energies (in kcal/mol) of the reaction pathway bearing **2** as a catalyst with 1-hexene and 1-octene substrates.

	I	I-II	II	II-III	III	III-IV	IV	IV-V	V	V-VI	VI	VI-VII	VII
ethylene	0.0	27.6	4.1	21.5	2.9	16.5	-0.3	27.6	4.1	29.0	-0.2	18.4	3.4
1-propene	0.0	32.0	10.7	27.2	0.5	14.7	4.6	35.5	4.7	32.3	8.7	16.8	3.9
1-hexene	0.0	29.4	10.5	25.9	1.4	11.8	7.5	32.9	5.0	29.2	14.6	16.3	2.3
1-octene	0.0	31.0	9.0	27.1	0.0	17.4	5.1	33.2	5.2	29.7	15.2	16.4	1.0

Screening the results for pre-catalyst **1** in table 1, the conducted calculations agree with the kinetic cost of the rate-determining transition state (III-IV), with respect to intermediate II, of 26.1 and 27.2 kcal/mol for 1-hexene and 1-octene, respectively. Then, the energy barrier was further evaluated for ethylene, 1-propene, and also 1-decene with values of 25.8, 24.4, and 26.6 kcal/mol, respectively. Overall, for this W based pre-catalyst, the reaction might seem quite independent of the type of olefin, being worse the performance when increasing the length of the alkyl chain of the alkene. However, 1-decene does not allow to confirm this trend. For **2**, knowing that experimentally the performance increases when elongating the alkyl chain of the olefin substrate, but worse for 1-decene, computationally the upper energy barriers range from 32.9 kcal/mol for 1-hexene to 33.2 kcal/mol for 1-octene, being 1-decene in between (32.3 kcal/mol). Even though the trend that claims that the TON increases together with the length of the alkyl chain from 6 to 8 carbon centers is in perfect agreement with experiments (Figure 2), the experimental poorer performance for 1-decene could not be computationally rationalized here. However, the analyses of the computed transition states that define the rds confirmed that the elongation of the olefin length goes beyond the available space in the silica model. Thus, in the real supported system, this will be not feasible, increasing the corresponding energy barriers, hence affecting significantly the reactivity for 1-decene and longer olefins. Apart from the silica support used to simulate the silica surface, to support this hypothesis, another larger model of silica was used. For pre-catalyst **1**, increasing slightly the silica surface,^[17] the energy barriers for the rds of C₆, C₈ and C₁₀ were still rather similar, whereas increasing significantly the silica surface the energy barrier ranged from 17.5 and 17.9 kcal/mol for C₆ and C₈, respectively, to 22.1 kcal/mol for C₁₀. Figure 9 confirms the collision with the silica suffered by C₁₀, whereas it is absent

for C₆. This was further corroborated for **2**, with values of 30.4, 29.7, and 32.1 kcal/mol for C₆, C₈, and C₁₀, respectively. Thus, the collisions with the surface negatively affect the activity in olefin metathesis of 1-decene or longer olefins.

Figure 9. Transition state that defines the rate-determining step for 1-hexene (left) and 1-decene (right) with the extended silica model, main distances are shown in Å.

Bearing the low covalent character displayed by the interactions between the substrates and the silica support, we computed the NCI plots using the NCIPLOT package by Contreras-García et al., to describe the non-covalent interactions.^[18] Figure 10 uses NCI plots to unveil how the chain of the acetate and the ester substrates interact with the pre-catalyst **2**. The isocontour obtained for a value of 0.4 on the reduced density gradient was plotted for the three substrates. While for the oxygen-containing substrates, *i.e.*, 6-heptenoate and 4-pentenyl acetate, there are stronger H-bonds with favorable red color; this latter interaction is less important for the apolar 1-octene substrate, with particular blue regions due to the repulsion between CH moieties. Since the model for the silica support is rather small here, it was extended for the larger model in Figure S21 to validate that the nature between the substrate and the silica support is qualitatively similar.^[17a]

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Figure 10. NCI plots of the absorption of the TS that defines the rate-determining step for the reaction pathway bearing pre-catalyst **2** with (a) ethyl 6-heptenoate; (b) 4-pentenyl acetate; and (c) 1-octene. The iso-surface represents a value of 0.4 with a color scale for the reduced density gradient from -0.05 (red) to 0.05 (blue).

Conclusion

Olefin metathesis reaction with various substrates was carried out using W and Mo pre-catalysts; we understood that both of them are active in α -olefin, functionalized olefin, and olefin cross-metathesis reactions. **1** and **2** perform equally in α -olefin metathesis reaction with a TON of ≈ 1700 . However, in the case of the functionalized olefin metathesis reaction of acetate (4-pentenyl acetate) and ester (ethyl 6-heptenoate), **1** performs better with TONs of 193 and 77, respectively as compared to **2**, which possesses TONs of 23 and 19, respectively for the same reactions. This activity difference was further analyzed by DFT, which shows that with **2** the energy barrier is slightly higher than that with **1**. Additionally, we also observed that **2** could isomerize α -olefins and di-ester, whereas **1** only isomerizes α -olefins, and both pre-catalysts do not isomerize mono-esters or acetates. We are currently trying to understand the isomerization process of certain olefins towards pre-catalyst **2**.

Experimental Section

General considerations

All experiments were carried out by using standard Schlenk and glovebox techniques under an inert argon atmosphere. The synthesis and the treatments of the surface species were carried out using a high vacuum line ($< 10^{-5}$ mbar) and glovebox techniques. Pentane was distilled from a

Na/K alloy under Ar and dichloromethane from CaH_2 . Both solvents were degassed through freeze-pump-thaw cycles. All the reactants were purchased from Aldrich; ethyl 6-heptenoate, 4-pentenyl acetate, and 3-butenyl acetate were filtered over activated molecular sieves ($3\text{\AA}$) and stored under argon. Linear Olefins (C_6 , C_8 and, C_{10}) were distilled from Na, degassed through freeze-pump-thaw cycles, and stored under argon. $\text{SiO}_2\text{-700}$ prepared from Aerosil silica from Degussa (specific area of $200\text{ m}^2/\text{g}$), which was partly de-hydroxylated at 700°C under high vacuum ($< 10^{-5}$ mbar) for 24 h to give a white solid having a specific surface area of $190\text{ m}^2/\text{g}$ and containing around $0.3\text{ OH}/\text{nm}^2$. $\text{W}(\text{CH}_3)_6$, and $[\text{Mo}(\equiv\text{C}t\text{Bu})(\text{CH}_2t\text{Bu})_3]$ (SI Figures S1–S4) and supported pre-catalyst $[(\equiv\text{Si-O})\text{W}(\text{CH}_3)_5]$ **1** and $[(\equiv\text{Si-O})\text{Mo}(\equiv\text{C}t\text{Bu})(\text{CH}_2t\text{Bu})_2]$ **2** were prepared according to literature procedures (SI Figures S5–S6).^{27, 28}

Gas chromatography (GC)

GC measurements were performed with an Agilent 7890A Series (FID detection). Method for GC analysis: Column HP-5; 30m length x 0.32mm ID x 0.25 μm film thickness; Flow rate: 1 mL/min (N_2); split ratio: 50/1; Inlet temperature: 250°C ; Detector temperature: 250°C ; Temperature program: 40°C (3 min), $40\text{--}250^\circ\text{C}$ ($12^\circ\text{C}/\text{min}$), 250°C (3 min), $250\text{--}300^\circ\text{C}$ ($10^\circ\text{C}/\text{min}$), 300°C (3 min); 1-hexene retention time: $t_R = 3.75\text{ min}$ / 1-octene retention time: $t_R = 6.48\text{ min}$ / 1-decene retention time: $t_R = 9.5\text{ min}$ / ethyl 6-heptenoate retention time: $t_R = 10.75\text{ min}$ / 4-pentenyl acetate retention time: $t_R = 8.16\text{ min}$ / 3-butenyl acetate retention time: $t_R = 6.55\text{ min}$. GC response factors of the functionalized olefins and available $\text{C}_5\text{--C}_{10}$ linear olefins standards were calculated as an average of three independent runs. The plot of response factor versus olefins carbon

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number was determined, and a linear correlation was found, then we extrapolated the response factors for other olefins.

Gas chromatography-mass spectrometry (GC-MS)

GC-MS measurements were performed with an Agilent 7890A Series coupled with Agilent 5975C Series. GC/MS equipped with a capillary column coated with none polar stationary phase HP-5MS was used for molecular weight determination and identification that allowed the separation of compounds according to their boiling points differences. The used method is the same as that for GC.

Liquid-state nuclear magnetic resonance spectroscopy (NMR)

Liquid state NMR spectra were recorded on Bruker Avance 600 MHz spectrometers. All chemical shifts were measured relative to the residual ^1H or ^{13}C resonance in the deuterated solvent: CD_2Cl_2 , 5.32 ppm for ^1H , 53.5 ppm for ^{13}C .

Fourier-transform infrared spectroscopy (FTIR)

IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer by using a DRIFT cell equipped with CaF_2 windows (SI Figures S5-S6). The IR samples were prepared under argon within a glove box. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm^{-1}).

Elemental analyses

Elemental analyses were performed at KAUST ACL Core Lab.

Catalytic procedure

All the catalytic reactions were carried out following this procedure: an ampoule is filled with a mixture of catalyst and olefin (1-hexene, 1-octene or 1-decene, 1 mL) or functionalized olefin (ethyl 6-heptenoate, 4-pentenyl acetate, and 3-butenyl acetate, 0.5 mL) in a glovebox (The molar ratio between classical olefin to the pre-catalyst, and functionalized olefin to catalyst are equal to 1900 and 475 respectively, they are kept constant for all the reactions). At the end of the reaction, the ampoules were frozen under liquid nitrogen. Then, the catalytic run was quenched by the addition of a fixed amount of CH_2Cl_2 , after filtration, the resulting solution was analyzed by GC and GC/MS.

DFT calculations

All DFT calculations were conducted with the Gaussian09 set of programs.^[19] For geometry optimizations, the well-established and computationally GGA functional BP86 functional of Becke and Perdew was used,^[20] adding the Grimme D3 dispersion term.^[21] Geometry optimizations were performed without symmetry constraints and the located stationary points were characterized by analytical frequency calculations. The complete reaction pathways for all the mechanisms discussed in this study were verified using intrinsic reaction coordinate (IRC) analysis for all transition states. Structures at the last IRC points were optimized to positively identify the reactants and products to which each transition state is connected. The electronic configuration of the systems was described with the split-valence Def2SVP basis set for the main group atoms,^[22] while for molybdenum and tungsten we adopted the quasi-relativistic Stuttgart/Dresden effective core potential with an associated valence contracted basis set (standard SDD keywords in Gaussian 09).^[23] Single-point energy calculations in solution were performed at the M06 functional level,^[24] with the triple- ζ basis set (Def2TZVP keyword in Gaussian) basis set for main group atoms, and again the same SDD pseudopotential for Mo and W. Solvent effects were

included with the Solvation Model based on Density (SMD) using 1-pentene as a solvent (for the sake of consistency, 1-pentene was used as a reference).^[25] Reported energies are M06/Def2TZVP~SDD/BP86-d3/Def2SVP~SDD electronic energies corrected with ZPEs, thermal energies, and entropy effects calculated at 353.15 K using the BP86-d3/Def2SVP~SDD method.

The noncovalent interactions (NCI) were calculated using the NCIPLOT program developed by Contreras-García,^[26] via NCI plots.

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Well-defined SOMC precatalysts $[(\equiv\text{Si-O})\text{W}(\text{CH}_3)_5]$ and $[(\equiv\text{Si-O})\text{Mo}(\equiv\text{C}^t\text{Bu})(\text{CH}_2^t\text{Bu})_2]$ were prepared and used for the metathesis reaction of α and functionalized olefins (ester and acetates). The complexes perform almost equally in α -olefin metathesis reaction, whereas W is better than Mo in the functionalized olefin metathesis reaction due to its lower energy barrier calculated by DFT. Besides, Mo could isomerize α -olefins and di-esters, whereas W only isomerizes α -olefins, and both of them do not isomerize mono-esters and acetates.