

# From Box to Bench: Air-Stable Molybdenum Catalyst Tablets for Everyday Use in Olefin Metathesis

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ABSTRACT: Molybdenum- and tungsten-based olefin metathesis catalysts have demonstrated excellent results in the control of cis (Z-) selectivity as well as enantioselectivity. However, their air and moisture sensitivity, which requires the use of a glovebox, has prevented their more widespread use by organic chemists. Now we report on developed, preweighed Mo catalysts formulated in paraffin tablets. The significantly improved air stability, high homogeneity, and uniformity of the pellets allow researchers to carry out reactions on the bench avoiding the need of a glovebox. The two different Mo-based complexes which were packed into tablets are XiMoPac-Mo001 (1) that can be used to achieve endo-selective enyne ring-closing metathesis (RCM) reactions, inter alia; and XiMoPac-Mo003 (2) which was reported among the best catalysts to promote Z-selective cross-metathesis. For the evaluation of the wax-protected catalysts commonly used, highly reproducible robust model reactions were chosen: homo crossmetathesis (HCM) of functionalized (e.g., methyl 9-decenoate) and unfunctionalized (allylbenzene) terminal olefins, and ring closing metathesis (RCM) of diethyl diallylmalonate. The yields and conversions were comparable with those which can be achieved in glovebox with nonformulated catalysts. Exposure to air did not cause any significant reduction in conversion while the product selectivity (targeted product vs homologues derived from double bond isomerization) remained high. In contrast, exposure to air caused a measurable drop in the conversion with the nonprotected catalyst. Furthermore, the formulated catalysts remained unaffected even after 4 h of exposure to air, showing its enhanced air stability. In conclusion, these commercially available air-stable Mo-catalyst tablets allow the reactions to be accomplished using ordinary Schlenk techniques, and hence simplify catalyst handling in pilot laboratories and plants.

## INTRODUCTION

Mo and W metathesis catalysts are useful reagents in organic synthesis.<sup>1-4</sup> The increased interest in the past decade resulted in the synthesis of numerous highly active and tunable catalysts, now available to researchers. Many of these unique complexes enable excellent control of enantioselectivity<sup>5,6</sup> as well as *cis* selectivity.<sup>7</sup> The capability to induce stereoselectivity is a particularly valuable feature of these complexes since several properties of a substance, including reactivity, polarity, mechanical characteristics, and/or biological activity, depend on molecular geometry. To have a well-defined molecular structure is especially important in synthesis of biologically active compounds, such as flavors, fragrances, pheromones, and pharmaceuticals, where usually only the right enantiomer delivers the expected biological activity. To illustrate the advantages and usefulness of these complexes, several applications of enantioselective/Z-selective ring closing metathesis (RCM) to natural products synthesis have been developed by the research groups of Schrock and Hoveyda.<sup>8,</sup> However, their air and moisture sensitivity, which necessitates the handling of these complexes under a strictly controlled, inert atmosphere, using a glovebox, has certainly prevented their widespread use by organic chemists.<sup>10</sup>

A more practical approach is the preparation of an air-stable "dosage form" of the catalyst allowing researchers to carry out reactions on the bench, avoiding the need of a glovebox. In this context Fürstner et al. demonstrated that sensitive Mo-based bisalkoxide metathesis catalysts can be converted into a benchstable but catalytically inactive form through complexation with bidentate N-heterocycles. The active catalyst can be efficiently recovered with the addition of a Lewis acid.<sup>11,12</sup> The suggested solution works well for the given examples since the prepared bidentate complexes can be stored on bench for weeks, without any extra care, however, the applicability of this approach for other, e.g., sterically demanding complexes, might be challenging. Very recently, Buchwald and colleagues reported a more general solution. They prepared several handmade air sensitive reagent "cocktails" sealed in paraffin-wax capsules for important coupling reactions.<sup>13</sup> Such capsules provide a protection for the air and moisture-sensitive reagents to some extent (depending on the nature of the active ingredient), thus, facilitating the work of organic chemists and at the same time diminishing the waste of decomposed reagents.<sup>14</sup> In other historical examples the moisture-sensitive reagents, such as sodium or potassium hydride, were protected by mineral oil or paraffin.<sup>15</sup> The same approach has also been applied for Grubbs' Ru-catalyst to prevent the loss of its catalytic activity during a long-term storage to open air.<sup>16,17</sup> Paraffin wax is particularly attractive as a protective matrix or carrier for reagents since it releases the active ingredients upon melting and/or adding appropriate solvents, while it is generally unreactive, inexpensive, and easy to handle and remove.

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Figure 1. Structure of the active catalyst of XiMoPac-Mo001 (1) and XiMoPac-Mo003 (2).

Table 1. Characteristics of XiMoPac-Mo001 and XiMoPac-Mo0
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				amou	unt of the a vari	ssumed subs ous catalyst	strate <sup>b</sup> /pelle loadings	′pellet [mg] @ gs		
	weight of the pellet [mg]	MW of the catalyst [g/mol]	amount of active catalyst/pellet [wt%]	[mg]	[mmole]	5.0 mol%	1.0 mol%	0.3 mol%		
XiMoPac- Mo001	200	895.03	5	10	0.0112	90	448	1493		
XiMoPac- Mo003	100	1062.98	10	10	0.0094	75	376	1253		

<sup>a</sup>Concentration and the potential substrate use at various catalyst loadings. <sup>b</sup>Molecular weight of the hypothetical substrate: 400 g/mol.

### RESULTS AND DISCUSSIONS

We investigated a similar approach and now report a further advancement of the original concept. The new technology can provide a solution for difficulties accompanied by handling of the otherwise particularly sensitive Mo-based metathesis catalysts by making them "air-stable". Our method enables their use outside the glovebox without any risk of deterioration of the catalysts' activity.

Our advanced procedure, in which the metathetically active Mo-complexes are perfectly dissolved or dispersed in melted macrocrystalline paraffin before formulation leads to homogeneous, preweighed paraffin droplets, containing predetermined, constant amount of active ingredient. The process is suitable for automation and to this end we developed an apparatus which can produce pills with very low standard deviation of mass (typically less than 3%). This elaborated formulation technology proved to be a broadly applicable tool for converting air and moisture sensitive reagents, such as triethylaluminum (TEAL), to stable and safe alternatives.

Our earlier studies<sup>18</sup> revealed that the amount of polar impurities, which can irreversibly react with and inactivate Mo/ W-alkylidenes, can be efficiently reduced in various feedstocks prior to metathesis by the addition of an appropriate amount of triethylaluminum. Although this versatile organoaluminum reagent can be purchased as a stock solution in various concentrations working with this highly pyrophoric substance requires much care therefore bench chemists try to avoid it. Moreover, generally only a few mol% of TEAL is needed for an efficient pretreatment therefore further dilution of the commercially available material and safe storage of the prepared manageable stock solution is required, which, once again, is an additional encumbrance. To provide the community with a universal solution for the above hurdle, formulation of neat TEAL into macrocrystalline paraffin was attempted. As a result, preweighed, "air-stable", nonpyrophoric<sup>19</sup> wax droplets of TEAL were obtained. The formulated reagent turned out to be equally efficient as the toluene stock solution for the

pretreatment of commercial grade olefins used later in various metathesis reactions while the handling and storage of the former one were incomparably safer and simpler.

In this study, beside TEAL, the following Mo-complexes were selected for air-stable paraffin formulations:  $Mo(N^{iPr}Ph)-(CHCMe2Ph)(2,5-Me_2Pyrr)(OTPP)$  (1),  $Mo(N^{iPr}Ph)-(CHCMe2Ph)(Me_2Pyrr)(OBitet)$  (2) bearing  $R_{ax}$ -octahydro-BINOL, the so-called  $R_{ax}$ -Bitet ligand (Figure 1.).

The developed formulation technology allowed to generate accurately weighed tablets with high homogeneity. The main characteristics of the tablets are summarized in Table 1 together with an approximation of the potential substrate use/tablet at different catalyst loadings (e.g., 5 mol%, 1 mol%, 0.3 mol%). Due to the high homogeneity and uniformity of the tablets they can readily be cut into smaller portions according to the exact synthesis demand.

The stereogenic-at-Mo monoaryloxide/monoalkoxide (MAP) type of catalysts (including 1) were the first high oxidation state complexes that efficiently catalyze enyne ringclosing metathesis (RCM) reactions, affording the corresponding endo products with high selectivity.<sup>20</sup> The previously reported enyne metathesis catalysts were mostly ruthenium complexes that, in most instances, provided *exo* products.<sup>21</sup> In contrast, the MAP Mo-alkylidenes are the first complexes that allow for selective formation of *endo* products,<sup>20</sup> with a >98:<2 *endo:exo* ratio in the case of (1). According to our experiences<sup>22</sup> catalyst (1) could also be used for performing various crossmetathesis reactions with high conversion.

The active catalyst of XiMoPac-Mo003 (2) was reported to be among the best catalysts to promote catalytic Z-selective cross-metathesis of terminal enol ethers, and allylic amides. It is important to note that thus far the cross metathesis of allylic amides has only been realized in *E*-selective processes. Using the active catalyst of XiMoPac-Mo003, Schrock, Hoveyda, et al. obtained the corresponding disubstituted alkenes in up to >98% Z-selectivity and 82% yield.<sup>23</sup> A close analogue of catalyst 2 (bearing a chlorine instead of bromine in the 3,3'-position of the Bitet ligand) was also successfully applied for enantioselective RCM of natural products' intermediates.<sup>24</sup>

In order to evaluate the applicability of our wax-stabilized catalysts and to compare their efficiencies to that of the parent ones we chose simple, highly reproducible metathesis transformations that apply commercially available substrates. During the design of the model reactions attention was paid to the ease of monitoring conversion as well as product ratio (selectivity). The standardized procedures together with the simple analytical techniques made comparison of the surveyed catalysts very simple and reliable.<sup>25</sup>

As the first model reaction for demonstrating the value of the formulated Mo catalyst tablets homo cross-metathesis (HCM) of 9-decenoic acid methyl ester (9-DAME, **3**) was chosen. The widespread efforts in renewable resources increased the significance of using natural oil derivatives. Unsaturated fatty acid methyl esters (FAME) derived from glycerides can be converted to short fatty acids and then to their derivatives, thus yielding various important intermediates through manipulations via metathesis reaction.<sup>18</sup> Mo- and W-based MAP catalysts can efficiently couple terminal olefins even in a *Z*-selective manner.<sup>26,27</sup> However, up to now, all of these transformations were carried out in an N<sub>2</sub>-filled glovebox. In this study homocoupling of 9-DAME (**3**) (Scheme **1**) was performed out



of a glovebox, in a regular fume hood with 1.0 mol% of XiMoPac-Mo001 using simplified Schlenk techniques. To successfully accomplish these reactions only an inert gas supply and not even Schlenk-type vacuum-inert gas manifold is required (Figure 2).

Homocoupling performed in a toluene solution at 40  $^{\circ}$ C, using a distilled, predried ester (3) proceeded to nearly complete conversion within 4 h, affording the targeted C18 diester (9-ODDAME, 4) with perfect selectivity (Table 2, entry



1). Analysis of the reaction mixture indicated that under the applied reaction conditions no detectable double bond isomerization occurred. Isolation and purification of the crude product by a simple flash chromatography, in a single run gave the paraffin-free 4 in 69% yield. It should also be noted that at 1.0 mol% catalyst loading the amount of the expected product and paraffin were practically identical which explains the somewhat lower than expected isolated yield. In contrast to the experiment carried out in toluene, in a "solvent-free" reaction, at 65 °C, and under continuous argon flow (Table 2, entry 2), migration of the double-bond took place and the homologous products formed in ca. 6%. However, this double-bond migration can be considerably suppressed if either a lower catalyst loading or continuous dynamic vacuum is used (Table 2, entries 3, 4). In these cases the amount of double bond migration derived products was less than 3%. Metathesis reactions assisted by Mo- as well as W-based complexes are known to be sensitive to polar impurities, such as water,28 alcohols, or organic hydroperoxides. Removal of the last traces of these catalyst poisons from the feedstock is crucial for a successful transformation, but can be far from trivial when one works in small quantities. To overcome this difficulty we envisioned the use of triethylaluminum as an in situ pretreatment agent<sup>18</sup> When the commercial grade decenoate treated with 3.0 mol% toluene solution of TEAL was submitted to HCM with 1 mol% XiMOPac-Mo001 again close to complete conversion was realized (Table 2, entry 5). To illustrate the positive impact of TEAL on substrate quality and thus on catalyst performance reactions using untreated and in situ purified feedstock at reduced catalyst loading were compared. The obtained conversion values (Table 2, entries 6, 7) clearly showed the utility of this simple pretreatment.

To evaluate the synthetic utility of paraffin formulated catalysts, air stability of XiMoPac-Mo001 was thoroughly investigated and compared to that of the nonformulated metal complex, used as a control sample. In this study both formulated and nonformulated catalyst samples were exposed to air for various time periods before the extent of catalyst's decomposition and the retained catalytic performance were determined (Figure 3). To this end, after the given time of exposure each sample was divided into two parts-pellets were cut in half—and one part was submitted to <sup>1</sup>H NMR study in anhydrous deuterated benzene while the other part was used in HCM of 9-DAME (3), according to Method A. Exposure to air for up to 24 h did not reduce the catalytic performance of XiMoPac-Mo001 at all, in each case the conversion remained close to quantitative (96%). On the contrary, only 5 min "aeration" of the nonformulated control sample resulted in detectable decomposition and measurable drop of its catalytic activity. The attainable conversion using the aforementioned sample did not exceed 79%. The <sup>1</sup>H NMR experiments carried out parallel with the metathesis reactions revealed that up to 4 h no decomposition can be detected in case of the paraffin pellets. However, after 4 h a slow decomposition starts and some decomposition products can appear in 4-6 mol%, after 24 h. Nevertheless the metal complex of XiMoPac-Mo001 is so active that this level of decomposition is not noticeable at the applied 1.0 mol% catalyst loading (Table 3). NMR data collected from the parallel experiment applying nonformulated catalyst suggest that beside detectable decomposition some other factors must have effect on catalysts performance (e.g., moisture can more readily adsorb onto the surface of a

Tabl	e 2.	Homocoupl	ing of	f 9-Decenoic Acid	Methy	l Ester (	<b>9-DAME</b> , 3	3) wit	h XiMoPac-Mo001	(1)	) unde	r Various	Conditions
		1	0				· /	/		· ·			

entry	method <sup>a</sup>	loading [mol %]	solvent	substrate	$T [^{\circ}C]$	reaction time [h]	conv. [%] <sup><i>b</i>,<i>c</i></sup>	sel. [%] <sup>d</sup>
1	А	1.0	dry toluene	purified (distilled, mol. sieves dried)	40	4	93 <sup>e</sup>	99
2	В	1.0	neat	purified (distilled, mol. sieves dried)	65	2	99	94
3	В	0.3	neat	purified (distilled, mol. sieves dried)	65	2	88	99
4	С	1.0	neat	purified (distilled, mol. sieves dried)	65	2	99	97
5	D	1.0	dry toluene	in situ purified with $TEAL^{f}$	40	4	96	97
6	А	0.3	dry toluene	commercial grade	40	4	0-42	> 99
7	D	0.3	dry toluene	<i>in situ</i> purified with TEAL <sup>f</sup>	40	4	89	99

"Method A: Under argon atmosphere, into a predried 10 mL glass vessel equipped with an oil-bubbler and an inert gas inlet (a Schlenk tube or a two-neck round-bottom flask) one tablet of XiMoPac-Mo001 catalyst was placed while a continuous argon flow was maintained. Then, 9-DAME (or allylbenzene or allyltrimethylsilane) and dry toluene were added consecutively via automatic pipet before the reaction mixture was heated to 40 °C and stirred for 4 h. In order to purge out the evolving ethylene the inert gas flow was kept constant during the reaction. Workup/removal of the paraffin: to the reaction mixture wet acetonitrile was added, which led to the precipitation of over 90% of the paraffin. The resulting slurry was intensively mixed before filtered through a short silica column. Method B: Same as Method A, with the exception that the reaction was performed at 65 °C for 2 h with no additional solvent. Method C: Same as Method B, except that after the additions the vessel was closed with a glass stopper, Ar flow was discontinued, and the gas inlet was connected to a membrane pump. The vacuum was set to 25 mbar and the reaction mixture was heated to 65 °C for 2 h. Method D: Under argon atmosphere, into a predried Schlenk tube (equipped with an oil-bubbler) 9-DAME (or allyl-benzene), dry toluene, and a stock solution of triethylaluminum in anhydrous toluene were added successively by automatic pipet and the reaction mixture was stirred for 30 min at room temperature while a continuous slow argon flow was maintained. After the pretreatment the procedure was continued as parallel reactions in entries 2–4 and that of 2 parallel reactions in entries 1, 5–7. The results are based on noncalibrated results (GC peak areas). "Sell: [ area(9-ODDAME)/(area(9-ODDAME) + 2 × area(9-ODDAME)] × 100%. "C18-diseter (4) was isolated by flash chromatography; yield: 69% (132 mg). <sup>f</sup>Addition of 3.0 mol% TEAL to the commercial grade substrate as pretreatment agent makes its prior distillation and drying dispensable.



Figure 3. Isolated catalysts and their air-stable "successors".

nonformulated catalyst), however, these still have to be investigated more thoroughly.

In another model study, the HCM reactions of allylbenzene (5; Scheme 2) were carried out using XiMoPac-Mo001 tablets at various loadings and conditions (Table 4).



In this series of experiments the conversion and selectivity of the HCM reaction was comparable when applying triethylaluminum (TEAL) pretreatments, either in toluene stock solution (conv.: 80%, Table 4, entry 2) or in preformulated paraffin tablets (conv.: 78%, Table 4, entry 3). Moreover, using the paraffin formulated TEAL is a safer and more practical method for this transformation. Isolation and purification of the highly apolar 1,4-diphenylbut-2-ene (6) was accomplished by a reverse phase flash chromatography.

RCM of diethyl diallylmalonate (DEDAM, 7)<sup>16</sup> (Scheme 3.) was carried out under constant argon flow (Method A, 40  $^{\circ}$ C, 4 h) using XiMoPac-Mo001 and XiMoPac-Mo003 tablets. GC-

			HCM of 9-DAME			
entry <sup>a</sup>	exposure to air [h]	observation	2,3,5,6-Ph <sub>4</sub> PhOH [n/n%]	2,5-Me2-pyrrole [n/n%]	conv. (GC%) <sup>b</sup>	sel. (GC%) <sup>c</sup>
1	0 (control)	no detectable decomp.—high			99	97
2	2	conv.			98	99
3	4				99	96
4	8	detectable decomp.—high conv.	4	3	98	97
5	24		8	2	97	> 99
6	nonformulate catalyst (ca. 5 min)	detectable decomp.—decreased conv.	2	3	79	99

Table 3. Air-Stability Study of XiMoPac-Mo001 (1)

<sup>*a*</sup>The reactions were accomplished according to Method A. The results are based on noncalibrated results (GC peak areas). <sup>*b*</sup>Conv. =  $[2 \times area(9-ODDAME)/(area(9-DAME) + 2 \times area(9-ODDAME))] \times 100\%$ . <sup>*c*</sup>Sel.=  $[area(9-ODDAME)/(area(9-ODDAME) + area(9-ODDAME))] \times 100\%$ .

Table 4. Homocoupling of 5 with XiMoPac-Mo001 with and without TEAL Pretreatments

entry <sup>a</sup>	method <sup>b</sup>	loading [mol%]	solvent	substrate	TEAL pretreatment	$T [^{\circ}C]$	reaction time [h]	conv. [%] <sup>c</sup>	sel. [%] <sup>d</sup>
1	А	1.0	dry toluene	commercial grade		40	4	22-31	> 99
2	D	1.0	dry toluene	in situ purified with TEAL	3.0 mol% in toluene	40	4	80	> 99
3	Е	1.0	dry toluene		3.0 mol% in paraffin	40	4	78 <sup>e</sup>	> 99

<sup>*a*</sup>The results based on 2 parallel reactions in entries 1–3. The given conversion and selectivity based on noncalibrated results (GC peak areas). <sup>*b*</sup>Method E: Method D, except a preformulated 5 wt% triethylaluminum (TEAL) paraffin tablet (3.42 mg, 0.03 mmol, triethylaluminum in 64 mg macrocrystalline paraffin) was applied instead of a toluene stock solution. <sup>*c*</sup>Conv. =  $[2 \times area(product)/(area(allylbenzene) + 2 x area(product))] \times 100\%$ . <sup>*d*</sup>Sel. =  $[area(1,4-diphenylbut-2-ene)/(area(1,4-diphenylbut-2-ene) + area(1,4-diphenylbut-2-ene homologues + isomers))] \times 100\%$ . <sup>*e*</sup>Scaleup experiment at ca. 8.0 mmol scale gave 99% conv.; 1,4-diphenylbut-2-ene (648 mg) was isolated with 79% yield.

# Scheme 3. RCM of 7 with XiMoPac-Mo001 and XiMoPac-Mo003



MS analysis confirmed the high conversion (XiMoPac-Mo001:86%; XiMoPac-Mo003:99%) even at 1.0 mol% catalyst loading.

In the RCM reaction of 7, XiMoPac-Mo003 yielded higher conversions compared to XiMoPac-Mo001, although in the former cases untreated, commercial grade substrate was used (Table 5). This observation highlights that metathesis catalysts are strongly substrate- and reaction-specific,<sup>29</sup> which also means that their activity and sensitivity toward impurities might vary a lot. Once again, addition of TEAL pellets to the untreated substrate resulted in higher conversion, highlighting the advantage of this additive.

An additional HCM example of allyltrimethylsilane (9) (Scheme 4) was carried out under constant argon flow (Method A, 40  $^{\circ}$ C, 4 h) using XiMoPac-Mo001 and XiMoPac-Mo003 tablets. GC-MS analysis confirmed the high conversion of the starting material to the desired product (XiMoPac-Mo001:99%; XiMoPac-Mo003:98%). However, isolation of the paraffin-free bis(trimetlysilyl)but-2-ene having polarity akin to paraffin was not feasible at such a scale.

### CONCLUSIONS

In the present article we are reporting a new approach to Mobased alkylidene assisted olefin metathesis and giving a hand to scientists who would like to use this versatile transformation but have no access to an expensive glovebox in which sensitive





reagents can be readily handled. By encapsulation of the otherwise air and moisture sensitive molybdenum monoalkoxid-monopyrrolides (MAP) catalysts to macrocrystalline wax we generated "air-stable", easy-to-handle metathesis pills (XiMo-Pac-Mo001/-Mo003) which can be used outside the glovebox. To demonstrate the practical importance of our solution the stabilized reagents were tested on the bench, in various, wellknown metathetic transformations. The achieved high conversions, good yields, and excellent selectivities show clearly the utility of our method. We proved that a catalyst which lasts only minutes under air without any extra protection can be readily rendered to preweighed pills which remain unaffected for up to 4 h. We also showed that homogeneity of the tablets provides users with the possibility to cut it into pieces and adjust the catalyst/substrate ratio accordingly. The designed encapsulation method turned out to be broadly applicable which allows the conversion of various air sensitive reagents into stable alternatives as it is demonstrated by the formulation of the highly reactive and pyrophoric triethylaluminum.

Our preweighed homogeneous tablets have the following advantageous characteristics: (a) their uniformity and homogeneity assures a robustness and resistance to any mechanical impacts; (b) their homogeneity and accurate active ingredient content allows the user to cut them into smaller pieces, thus adjusting the loading according to their needs; (c) the

Table 5. Ring Closing Metathesis of 7 with XiMoPac-Mo001,-Mo003

entry	XiMoPac-	method	loading [mol%]	solvent	substrate	T [°C]	reaction time [h]	conv. [%] <sup><i>a,b</i></sup>
1	Mo001 (1)	Α	5.0	dry toluene	purified (distilled, molecular sieves dried)	40	4	> 99
2	Mo001 (1)	Α	1.0			40	4	86
3	Mo001 (1)	Α	0.3			40	4	9
4	Mo003 (2)	Α	5.0	dry toluene	commercial grade	40	4	> 99
5	Mo003 (2)	Α	1.0			40	4	> 99
6	Mo003 (2)	Α	0.3			40	4	33
7	Mo003 (2)	E	0.3		in situ purified with TEAL <sup>c</sup>	40	4	57

"Conv.:  $[area(8)/ \{area(DEDAM, 7) + area(8)\}] \times 100\%$ ." The conversion values are the average of 3 parallel reactions. The results are based on noncalibrated results (GC peak areas). "Addition of 3.0 mol% TEAL to the commercial grade substrate as pretreatment agent makes its prior distillation and drying dispensable.

automatized mass-production guarantees high reproducibility for weight and loading accuracy.

In summary, our commercially available air-stable Mocatalyst tablets prepared by a well-controlled formulation technology has many practical advantages (uniformity, accurately preweighed units), facilitating not only the experimental process in laboratory, but can simplify the everyday work with highly sensitive reagents in pilot laboratories and plants. (Note: See a very recent successful application of this new approach: Nguyen, T. T., Koh, M. J.; Shen, X.; Romiti, F.; Schrock, R. R.; Hoveyda, A. H. *Science* **2016**, 352, 369.) A more comprehensive analysis of the utility of Mo-, W-, and certain Ru-based complexes that are part of the portfolio of XiMo AG is planned for publication in the near future.

### EXPERIMENTAL SECTION

**Materials and Methods.** All reactions were carried out in oven-dried (140 °C, for 4 h) or flame-dried glassware under an inert atmosphere of dry argon unless otherwise stated.

Molecular sieve (3 Å) was purchased from Merck and activated at 300 °C, under <1 mbar vacuum for 18 h.

Allylbenzene (5), diethyl diallylmalonate (DEDAM, 7), and triethylaluminum were purchased from Sigma-Aldrich.  $C_6D_6$  (99.98%) and  $CDCl_3$  (99.8%) were purchased from Euriso-top, and 9-decenoic acid methyl ester (9-DAME, 3) from Elevance Renewable Science.

Each substrate was purified by atmospheric (for 5) or vacuum distillation (3, 7) under inert atmosphere before they were stored on 10 wt% activated 3 Å molecular sieves for 24 h in an ordinary Schlenk tube. Toluene was distilled from potassium under dry nitrogen, and stored over activated 3 Å molecular sieves in a Schlenk tube.

Prior to use, all substrates (purified and commercial grade), the triethylaluminum stock solution (TEAL, 5.18 wt % in toluene), and abs. toluene were stored in Schlenk tube on the bench.

The applied formulated catalysts (XiMoPac-Mo001 and -Mo003) are already available while the paraffin formulated triethylaluminum will be accessible in January 2017 at Aspira Scientific (www.aspirasci.com). They are sold in airtight, sealed sachets and must be stored at 4  $^{\circ}$ C in a normal refrigerator.

Analysis of metathesis reactions was performed by GC-MS-FID (Shimadzu GCMS QP2010Plus) or Agilent DB-23 (30 m  $\times$  I.D.: 0.25 mm); the results of the reactions are given as ratio of area of the corresponding GC-FID peaks.

Flash chromatography was performed by a Teledyne Isco Combiflash Rf apparatus. Stationary phase: LiChroprep RP-18 (25, 40  $\mu$ m, Merck) or silica gel 60 (0.063–0.2 mm, spheric, Molar Chemicals Ltd.).

Characterization of the isolated compound was performed by NMR measured on a Bruker Avance 300 spectrometer. Chemical shifts are reported in ppm using the residual peak of the CDCl<sub>3</sub> or  $C_6D_6$  as an internal reference.

**Reactions.** HCM of Purified 9-DAME (**3**) with 1.0 mol% XiMoPac-Mo001, According to Method A (Table 2, Entry 1). Under argon atmosphere, into a dry 10 mL Schlenk tube (equipped with an oil-bubbler) purified 9-DAME (**3**; 234  $\mu$ L, 206 mg, 1.12 mmol) and anhydr. toluene (1776  $\mu$ L) were measured by automatic pipettes. One piece of XiMoPac-Mo001catalyst pellet (200 mg tablet containing 10 mg, 0.011 mmol **1** in 190 mg macrocrystalline wax; 1.0 mol%) was added, the reaction mixture was heated up to 40 °C, and it stirred for 4

h while a continuous slow argon flow was applied. After 4 h the reaction mixture was diluted to 25 mL with acetonitrile (of technical grade, containing some water to decompose catalyst). At this step, the majority of the paraffin precipitated. The obtained slurry was thoroughly stirred, then filtered through a short silica column (2.0 mL), finally the silica pad was washed with further 15 mL acetonitrile. The combined elute was analyzed by GC-MS-FID (column: Phenomenex Zebron-Inferno 35HT (30 m x I.D.:0.25 mm); method: 100 °C for 5 min, 50 °C/min until 250 °C, 250 °C for 10 min, 50 °C/min until 340 °C, 340 °C for 5 min). Conversion: 93%; selectivity: > 99%; E/Z-ratio: 85/15.

Isolation of Product 4. The volatiles were removed in vacuum, the obtained crude product was purified by flash (silica gel) column chromatography (heptane:EtOAc = 50:1) to afford the product as a colorless oil. (TLC visualization reagent: potassium permanganate.)

*Isolated Yield:* 132 mg (69%) of Pure 4. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 5.44–5.27 (2H, m, CH=), 3.66 (6H, s, CH<sub>3</sub>), 2.29 (4H, t, J = 7.5 Hz, CH<sub>2</sub>), 1.81 (4H, m, CH<sub>2</sub>) 1.68–1.52 (4H, m, CH<sub>2</sub>), 1.39–1.16 (16H, m, CH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): 174.5 (C1), 130.5 (C9), 51.6 (O–CH<sub>3</sub>), 34.2 (C2), 29.7 (C8), 29.2, 29.1, 25.1 (C3); MS (m/z): 340, 308, 276.

HCM of Commercial Grade 9-DAME (**3**) with 0.3 mol% XiMoPac-Mo001, According to Method A (Table 2, Entry 6). Analogously to the above procedure but used commercial grade 9-DAME (**3**; 776  $\mu$ L, 686 mg, 3.72 mmol), anhydr. toluene (1224  $\mu$ L), and one piece of XiMoPac-Mo001catalyst (200 mg pellet: 10 mg, 0.011 mmol **1** in 190 mg macrocrystalline wax; 0.3 mol%). Workup as described above. Conversion: 42%; selectivity: > 99%; *E*/*Z*-ratio: 87/13.

HCM of Purified 9-DAME (**3**) with 1.0 mol% XiMoPac-Mo001, According to Method B (Table 2, Entry 2). Similar to Method A, with the following modifications: purified 9-DAME (**5**; 234  $\mu$ L, 206 mg, 1.12 mmol) and one piece (200 mg) of XiMoPac-Mo001catalyst (10 mg, 0.011 mmol **1** in 190 mg macrocrystalline wax; 1.0 mol%) were placed in a Schlenk tube and the neat reaction mixture was heated to 65 °C for 2 h in a continuous dry argon stream before the reaction was quenched. The workup was analogous to the one described above. Conversion: 99%; selectivity: 94%; E/Z-ratio: 83/17.

HCM of Purified 9-DAME (3) with 0.3 mol% XiMoPac-Mo001, According to Method B (Table 2, Entry 3). Analogously to Method B but used purified 9-DAME (5; 776  $\mu$ L, 686 mg, 3.72 mmol) and one piece of XiMoPac-Mo001catalyst (200 mg pellet:10 mg, 0.011 mmol 1 in 190 mg macrocrystalline wax; 0.3 mol%). Workup was the same as for Method A with 0.3 mol% catalyst loading. Conversion: 88%; selectivity: > 99%; E/Z-ratio: 84/16.

HCM of Purified 9-DAME (3) with 1.0 mol% XiMoPac-Mo001, According to Method C (Table 2, Entry 4.). Analogously to Method B described for 1.0 mol% catalyst loading, except that after addition of the substrate and the catalyst the reaction vessel was closed with a glass stopper, its gas inlet was connected to a membrane vacuum pump set to 25 mbar, and the reaction was heated to 65 °C. Workup was the same as for Method B at 0.3 mol% catalyst loading. Conversion: 99%; selectivity: 97%; E/Z-ratio: 83/17.

HCM of Commercial Grade 9-DAME (3) with 1.0 mol% XiMoPac-Mo001, According to Method D (Table 2, Entry 5). Analogously to Method A applying 1 mol% catalyst loading, but using commercial grade substrate which was treated with 3.0 mol% TEAL in toluene ( $85.9 \ \mu$ L,  $5.18 \ w/w$ %, containing 3.83

mg, 0.033 mmol, TEAL) at 30 °C for 30 min prior to the addition of the catalyst pellet. Conversion: 96%; selectivity: 97%; E/Z-ratio: 86/14.

HCM of Commercial Grade 9-DAME (**3**) with 0.3 mol% XiMoPac-Mo001, According to Method D (Table 2, Entry 7). Analogously to Method A applying 0.3 mol% catalyst loading, but used commercial grade substrate which was treated with 3.0 mol% TEAL in toluene (285  $\mu$ L, 5.18 w/w%, containing 12.8 mg, 0.11 mmol, TEAL) at 30 °C for 30 min. Conversion: 89%; selectivity: > 99%; E/Z-ratio: 90/10.

HCM of Commercial Grade Allylbenzene (5) with 1.0 mol % XiMoPac-Mo001, According to Method A (Table 4, Entry 1). The reaction was performed according to Method A: commercial grade allylbenzene (5, 148  $\mu$ L, 132 mg, 1.12 mmol), anhydr. toluene (1776  $\mu$ L), and one piece of XiMoPac-Mo001 catalyst (200 mg pellet: 10 mg, 0.011 mmol 1 in 190 mg macrocrystalline wax; ca. 1.0 mol%). Workup: the reaction mixture was diluted to 25 mL with further amount of wet acetonitrile. At this step majority of the paraffin (90-95%) precipitated. The obtained slurry was thoroughly stirred before it was filtered through a short silica column (2.0 mL), which was eluted with further 15 mL of acetonitrile. The combined elute was diluted and analyzed by GC-MS-FID (column: Phenomenex Zebron-Inferno 35HT (30 m × I.D.: 0.25 mm); method details: 50 °C for 5 min, 18 °C/min until 275 °C, 20 °C/min until 340 °C, 340 °C for 6.4 min). Conversion: 31%; selectivity: > 99%; *E*/*Z*-ratio: 69/31.

HCM of Commercial Grade Allylbenzene (5) with 1.0 mol % XiMoPac-Mo001, According to Method D (Table 4, Entry 2). The reaction was performed according to Method D: commercial grade allylbenzene (5, 148  $\mu$ L, 132 mg, 1.12 mmol) and anhydr. toluene (1776  $\mu$ L). The toluene solution of the substrate was pretreated with 3.0 mol% TEAL in toluene (85.9  $\mu$ L, 5.18 w/w%, containing 3.83 mg, 0.033 mmol, TEAL) before one piece of XiMoPac-Mo001 catalyst (200 mg pellet: 10 mg, 0.011 mmol 1 in 190 mg macrocrystalline wax; 1.0 mol%) was added and the reaction mixture was heated to 40 °C for 4 h. The workup was carried out analogously to the one described above (8.). Conversion: 80%; selectivity: > 99%; *E*/*Z*-ratio: 84/16.

HCM of Commercial Grade Allylbenzene (5) with 1.0 mol % XiMoPac-Mo001, According to Method E (Table 4, Entry 3). Analogous to Method D, but instead of a toluene stock solution TEAL was added in 5 wt% paraffin formulated pellet (3.4 mg, 0.03 mmol, triethylaluminum in 64 mg macrocrystalline wax). Conversion: 78%; selectivity: > 99%; E/Z-ratio: 85/ 15.

HCM of Commercial Grade Allylbenzene (5) with 1.0 mol % XiMoPac-Mo001, According to Method E (Scale-up). Similarly, 5 wt% TEAL in paraffin pellet (16 mg, 0.24 mmol triethylaluminum; 3.0 mol% in 540 mg macrocrystalline wax) was added to allylbenzene (5, 1040  $\mu$ L, 927 mg, 7.84 mmol) in toluene (13 mL) at 30 °C, 30 min later 7 pieces of XiMoPac-Mo001 (7\*200 mg, 70 mg, 0.078 mmol 1 in 1330 mg macrocrystalline wax; 1.0 mol%). After 4 h the reaction was quenched with aq. MeOH. A sample was diluted with dichloromethane for GC-MS-FID analysis. Conversion: 99%; selectivity: 95%; E/Z-ratio: 86/14.

*Isolation of Product* **6**. The volatiles were removed in vacuum, the obtained crude product was purified by flash (RP silica gel) column chromatography (methanol:water =  $7:3 \rightarrow 8:2$ ). The combined fractions containing product **6** were partly

evaporated, then extracted with dichloromethane, giving the product as colorless oil after concentration.

Isolated Yield: 648 mg (79%) of Pure **6**. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.39–7.32 (m, 4H), 7.31–7.22 (m, 6H), 5.72 (m, 2H), 3.50 (m, 4H). 13C NMR (75 MHz, CDCl3)  $\delta$  140.7, 130.4, 128.5, 128.4, 125.9, 38.9. MS (*m*/*z*): 208, 117, 91, 65.

RCM of DEDAM (7) with 1.0 mol% XiMoPac-Mo001, According to Method A (Table 5, Entry 2). Analogous to Method A but used purified DEDAM (7; 271  $\mu$ L, 269 mg, 1.12 mmol), anhydr. toluene (1729  $\mu$ L), and one piece of XiMoPac-Mo001 catalyst (200 mg pellet: 10 mg, 0.11 mmol 1 in 190 mg macrocrystalline wax; 1.0 mol%). After 4 h the reaction mixture was diluted to 25 mL with wet acetonitrile. At that point the majority of the paraffin (90–95%) precipitated. The obtained slurry was thoroughly stirred before it was filtered through a short silica column (2.0 mL), which was then washed with further 15 mL of acetonitrile. From the combined elute 200  $\mu$ L was diluted to 1 mL with acetonitrile from which 1  $\mu$ L was injected and analyzed by GC-MS-FID (column: Phenomenex Zebron-Inferno 5HT ( $30 \text{ m} \times \text{I.D.}$ : 0.25 mm); method details: 50 °C for 5 min, 25 °C/min until 340 °C, 340 °C for 8.4 min). Conversion: 86%.

RCM of Commercial Grade DEDAM (7) with 1.0 mol% XiMoPac-Mo003, According to Method A (Table 5, Entry 5). Analogous to Method A described above but used commercial grade DEDAM (7; 455  $\mu$ L, 452 mg, 1.88 mmol) and using two pellets of XiMoPac-Mo003 catalyst (2 × 100 mg pellet: 20 mg, 1.88 mmol 2 in 180 mg macrocrystalline wax; 1.0 mol%) as catalyst. Conversion: > 99%.

Isolation of Product 8. The volatiles were removed in vacuum, the obtained crude product was purified by flash (RP silica gel) column chromatography (methanol:water =  $7:3 \rightarrow$  1:0). The combined fractions were extracted with dichloromethane, dried over MgSO<sub>4</sub> and evaporated under vacuum giving product 8 as colorless oil.

Isolated Yield: 337 mg (84%) of Pure **8**. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 5.60 (pseudo s, 2H), 4.19 (q, J = 7.2 Hz, 4H), 3.01 (pseudo s, 4H), 1.22 ppm (t, J = 6.6 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl3):  $\delta$  = 172.4, 127.9, 61.6, 59.0, 41.0, 14.1 ppm; MS (*m*/*z*): 212, 166, 138, 111.

*RCM* of Commercial Grade DEDAM (7) with 0.3 mol% XiMoPac-Mo003, According to Method E (Table 5, Entry 7). According to Method E: commercial grade DEDAM (7; 758  $\mu$ L, 753 mg, 3.13 mmol) in anhydrous toluene (3242  $\mu$ L) was pretreated with 3.0 mol% TEAL in paraffin (10 × 22.8 mg; each of them containing 1.14 mg, 0.01 mmol, triethylaluminum in 21.7 mg macrocrystalline wax) at 30 °C for 30 min before one piece of XiMoPac-Mo003 catalyst (100 mg pellet: 10 mg, 0.094 mmol 2 in 90 mg macrocrystalline wax; 0.3 mol%) was added and the reaction mixture was heated to 40 °C for 4 h. Workup as described above (13). Conversion: 57%; selectivity: > 99%.

HCM of Purified Allyltrimethylsilane (9) with 1.0 mol% XiMoPac-Mo001, According to Method A. Into a dry Schlenk tube the following compounds were transferred: dry toluene (2 mL) via cannula, purified allyltrimethylsilane (180  $\mu$ L, 129 mg, 1.13 mmol, 9) via syringe. An aliquot was taken for GCMS, one piece of XiMoPac-Mo001 (200 mg pellet: 10 mg, 0.011 mmol 1 in 190 mg macrocrystalline wax; 1.0 mol%) was added, and the mixture was stirred for 4 h at 40 °C under a slow constant argon flow. Then, 8 mL of wet acetonitrile was stirred for 20 min. The suspension was filtered over a pipet filled with glass fiber filter and silica and a sample for GC was taken (column:

Agilent DB-23 (30 m × I.D.:0.25 mm); method: 35 °C for 5 min, 35 °C/min until 100 °C, 7 °C/min until 130 °C, 35 °C/min until 240 °C, 240 °C for 5.17 min). Conversion: 99%.

Isolation and purification of the product 10 was attempted on a double scale reaction by means of reverse phase flash chromatography (MeOH: water =  $8:2\rightarrow1:0$ ), but remain unsuccessful.

<sup>1</sup>H NMR (300 MHz,  $C_6D_6$ )  $\delta$  5.41 and 5.28 (m, 2H), 1.4– 1.6 (m, 4H), 0.03 and 0.00 (s, J = 0.8 Hz, 18H).

HCM of Purified Allyltrimethylsilane (9) with 1.0 mol% XiMoPac-Mo003, According to Method A. Similar to the above-described procedure, 153  $\mu$ L of allyltrimethylsilane and one piece of XiMoPac-Mo003 (100 mg pellet: 10 mg, 0.0094 mmol 2 in 90 mg macrocrystalline wax; 1 mol%) was used. Conversion: 98%.

Air Stability of XimoPac-Mo001 (Table 3, Entry 5). A piece of XiMoPac-Mo001 pellet (200 mg tablet containing 10 mg, 0.011 mmol 1 in 190 mg macrocrystalline wax; 5.0 wt%) was stored on the bench without any protection for 2 h. Then it was cut in half. One of the halves (75.3 mg) was dissolved at 45 °C in 600  $\mu$ L benzene-*d*6, an internal standard, 100  $\mu$ L ferrocene (0.0531 mol/L solution in benzene-*d*<sub>6</sub>) was added to it, and the sample was measured by <sup>1</sup>H NMR.

The other half (126 mg) was submitted to HCM (Scheme 1), according to Method A using purified 9-DAME (3; 147  $\mu$ L, 130 mg, 0.705 mmol), in anhydr. toluene (323  $\mu$ L). XiMoPac-Mo001 (after 24 h): conversion: 97%; selectivity: > 99%; *E*/*Z*-ratio: 84/16.

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#### Notes

The authors declare no competing financial interest.

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#### DEDICATION

To our boss and great mentor, Georg E. Frater. On the occasion of his 75th birthday.

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