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Ethene-Induced Temporary Inhibition of Grubbs Metathesis Catalysts

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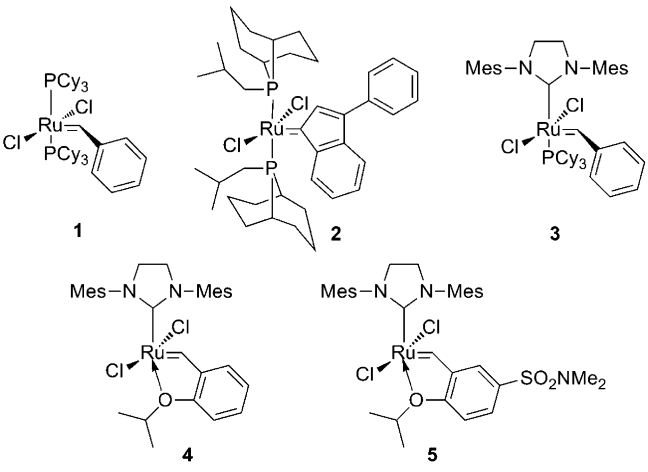
Abstract: Grubbs-type catalysts were immobilized in form of supported ionic liquid phase (SILP) materials and applied in the gas-phase cross-metathesis of various substrates in order to study the effect of ethene on catalyst activity and stability in detail. From our theoretical and experimental findings we suggest that ethene causes temporary inhibition effects due to a reversible shift of ruthenium complexes from the productive catalytic cycle towards unproductive, dormant ruthenium species. By avoiding the presence of ethene, constant catalytic activity and selectivity for more than 20 days of continuous operation could be realized.

Keywords: DFT calculations; ionic liquids; metathesis; ruthenium; SILP catalysis; supported ionic liquid phase (SILP)

Introduction

The development of highly active homogeneous metathesis catalysts that do not require co-catalyst activation has been a major breakthrough for organic synthesis in the past decades.[1] Ruthenium-carbene complexes of the general type [$RuCl_2L_2(=CHR)$], known as Grubbs catalysts, are tolerant towards a variety of functional groups in the substrate molecules and are kinetically stable against water and air.[2] Additionally, the development of modified, phosphine-free Grubbs catalysts by Hoveyda and co-workers has given access to even more reactive and also somewhat more stable metathesis catalysts.[3]

In this contribution, we report kinetic studies dealing with immobilized Grubbs metathesis catalysts in continuous gas-phase cross-metathesis reactions of short-chain, unfunctionalized alkenes under very mild conditions. The study applies the Ru complexes **2**, **4** and **5** (Scheme 1) and focuses on the effect of ethene on catalyst activity and stability. To realize homogeneous catalysis conditions in the continuous gas-phase process, the applied catalyst complexes were immobilized in a thin film of ionic liquid dispersed on a porous support. Such *supported ionic liquid phase*



Scheme 1. Selected Grubbs-type metathesis catalysts. PCy_3 = tricyclohexylphosphine; Mes = 2,4,6-trimethylphenyl.

(SILP) materials have proven to be highly suitable for a variety of gas-phase and batch reactions as demonstrated by us and other groups.[4] Recently, Hagiwara and co-workers reported on the synthesis and application of SILP metathesis catalysts.[5] In Hagiwara's work, SILP catalysts based on complexes **1**, **3** and **4** (Scheme 1) were applied in slurry phase reactions (solid SILP material dispersed in liquid reaction mixture) and the systems proved to be active in a variety of ring-closing metathesis reactions. After reaction, the SILP catalysts were isolated by filtration and could be reused for three times before showing clear signs of deactivation.

Although SILP catalysts are applied in this work, the scope of our contribution goes far beyond demonstrating the SILP technology for a gas-phase metathesis process. Our aim is to apply SILP catalysis to demonstrate the influence of ethene on the activity and stability of immobilized, Ru-based metathesis catalysts in a very general sense. Our surprising experimental findings have been rationalized with the help of density-functional theory (DFT) calculations.

Results and Discussion

All kinetic studies were carried out as continuous gas-phase reactions in classical fixed-bed reactors with direct product analysis *via* online gas chromatography. Details about the reactor set-up and all chemicals applied in this study can be found in the Experimental Section. Figure 1 shows the catalytic performance of the three single-component ruthenium ylidene complexes **2**, **4** and **5** immobilized as SILP systems in the ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$]) on calcined silica 60. The so obtained **2**-SILP, **4**-SILP and **5**-SILP materials were tested in the propene self-metathesis at 40 °C and 1 bar using an average residence time of 32 s in the reactor. Note that propene metathesis affords the products ethene and 2-butene under the applied reaction conditions in a maximum, equilibrium-limited conversion of 34%. Disappointingly, all three SILP catalysts showed a rapid decrease in conversion *versus* time on stream, the **5**-SILP catalyst being the most active representative.

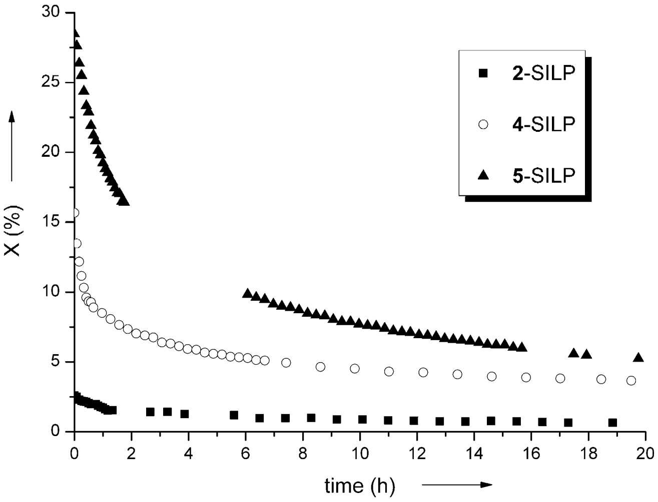


Figure 1. Conversion versus time plots for different SILP metathesis catalysts in propene cross-metathesis at 40 °C, 1 bar, residence time = 32 s, 0.4 g SILP, Ru loading 0.2 wt%, calcined silica gel 100, [BMIM][BF$_4$], IL loading 5 vol%.

In seeking to understand the influence of the immobilizing ionic liquid on the catalyst performance, the **5**-SILP catalyst was prepared by using a number of different ionic liquids, namely [BMIM][BF$_4$], [BMIM][PF$_6$], [BMIM][SbF$_6$], [BMIM][OTf], [BMIM][NTf$_2$], and [Me(C$_2$H$_4$O)$_3$MIM][BF$_4$]. The lowest catalyst stability was obtained in [NTf$_2$]$^-$-based ionic liquids whereas the most stable systems contained the [BF$_4$]$^-$ anion. The experimentally established order of stability was $[BF_4]^- > [CF_3SO_3]^- \geqslant [PF_6]^- > [SbF_6]^- > [NTf_2]^-$. Note that the observed stability order does neither correlate to the IL anion's coordination strength[6] nor to the anion's thermal[7] or hydrolytic stability.[8]

Therefore, a deactivation mechanism based on the coordination of the IL counter-ion or on IL decomposition products is unlikely. In searching for other possible correlations, we realized that the SILP catalyst stability order does indeed match surprisingly well with the order of ethene solubility in the different ionic liquids. While the least stable **5**-SILP catalyst was obtained with [BMIM][NTf$_2$], having the highest solubility of ethene ($k_H = 873$ MPa at 30 °C),[9] the most stable catalyst was based on [BMIM][BF$_4$], exhibiting the lowest solubility of ethene ($k_H = 2065$ MPa at 30 °C).[10] Upon variation of the ionic liquid cation, it was found that the ethylene glycol-modified ionic liquid [Me(C$_2$H$_4$O)$_3$MIM][BF$_4$] and [BMIM][BF$_4$] gave the best results with respect to activity and stability (see the Supporting Information for all details of the IL variation experiments).

To further test the hypothesis that the propene metathesis product ethene is indeed responsible for the observed catalyst deactivation, a flow of ethene was passed through the **5**-SILP {ionic liquid: [Me(C$_2$H$_4$O)$_3$MIM][BF$_4$]} catalyst bed prior to starting the propene metathesis reaction. Different times of ethene purge (10 mL min^{-1} for 0, 1, 3, 5 and 15 h) were realized in independent experiments, corresponding to an ethene exposure of the catalyst (3.69×10^{-2} mmol) of 0, 23, 69, 115 and 350 mmol of ethene. As shown in Figure 2, after 1 h (23 mmol) ethene exposure, the initial catalyst activity remained nearly the same as for no ethene purge. For longer ethene exposure, however, a direct correlation between ethene exposure time and initial activity was ob-

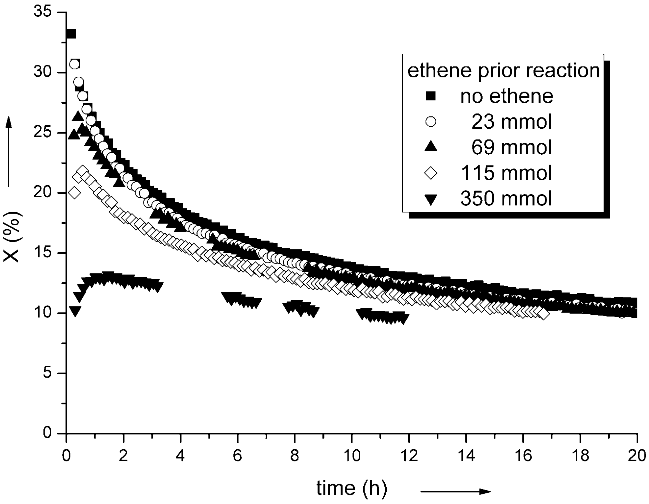
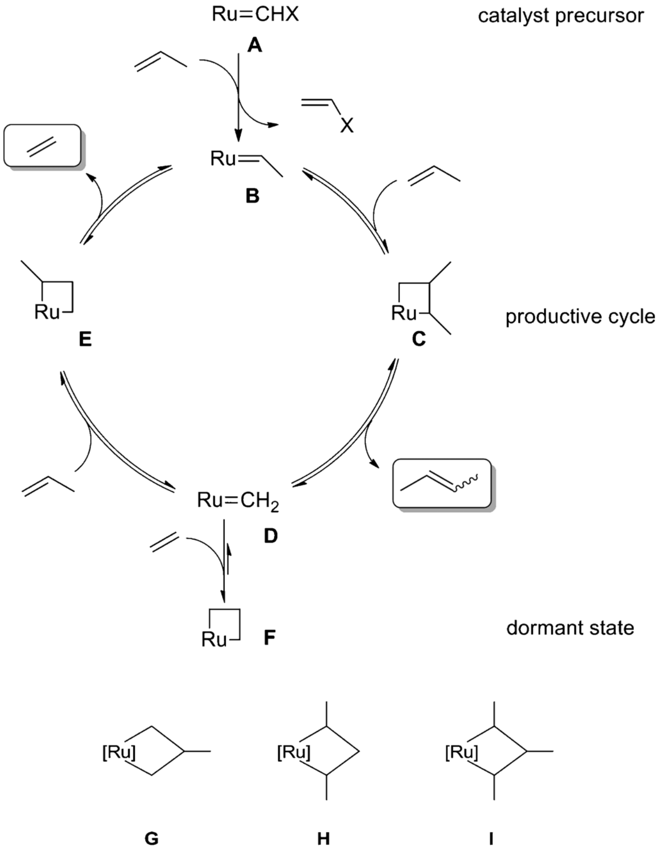


Figure 2. Ethene exposure of **5**-SILP prior to propene metathesis. 40 °C, 1 bar, residence time = 8 s, 0.4 g SILP, Ru loading 1 wt%, silica gel 60, $[Me(C_2H_4O)_3MIM][BF_4]$, IL loading 5 vol%.

served, giving support to the assumption of ethene-induced catalyst deactivation.

Although the initial activity of the **5**-SILP catalyst decreased upon exposure to ethene, it is a very interesting observation that the catalyst regained part of its activity when the substrate was switched to propene (as monitored by the 2-butene formed in the reaction; note that the situation regarding unproductive ethene + propene metathesis is independent on the duration of ethylene exposure). In fact, a maximum in activity was observed shortly after the substrate change. Remarkably, the **5**-SILP catalysts with higher ethene exposure required longer times to reach its maximum activity and a direct correlation between the amount of ethene and the lag time to t_{max} was observed. Based on this finding, it appeared highly unlikely to us that the observed maximum stems from reactor instationarities. Instead, we assumed a kind of catalyst re-activation process going along with the substrate change.

To provide a possible explanation for the ethene influence on the ruthenium alkylidene catalysts, we performed DFT calculations on the possible reaction intermediates shown in Scheme 2. For the intermediates **C** and **E** all the different regio- and stereoisomers were calculated which originate from catalyst **4** (see the Supporting Information for details). The mechanism of ligand effects in olefin metathesis using Grubbs-type catalysts has been studied theoretically in great detail before[11] (including certain aspects of propene cross-metathesis[12]) and a dissociative pathway has been found to be favorable compared to an associative pathway in the gas-phase. In this study, we considered the lowest energy metallacyclobutane intermediates as possible resting states along both the favored dissociative pathway and a hypothetical associative pathway (see the Supporting Information for details on the calculated species). In the latter case, the *O*-donor ligand in **4** or **5** remains coordinated to the Ru center, while in the former case it is not. We take both pathways into account here because it is unclear to what extent dissociation occurs in an ionic liquid environment. Test calculations have shown that the gas-phase dissociation energies of the *O*-coordinated moiety in **4** or **5** can be substantial (50–100 $kJ\,mol^{-1}$) at the present dispersion-corrected DFT level. In agreement with previous investigations, we consider the metallacycle in a *cis* position with respect to the NHC ligand in the associative path, while it was found to be more favorable in the *trans* position in the dissociative pathway.[11c,e,l,n,s] Among the possible isomers, we here discuss only the lowest-energy metallacyclobutane intermediates as predicted by the present DFT method (details on the other intermediates will be published elsewhere). In the associative pathway, the highest formation energy (lowest relative energy) of all intermediates was found for the RuC_4H_8 metallacycle **G** (see Table 1, Scheme 2, and the Supporting Information) with one methyl sub-



Scheme 2. Catalytic cycle of the Ru-catalyzed metathesis reaction displaying the calculated intermediates of Table 1; species **G**, **H**, **I** are unproductive in propene cross-metathesis.

Table 1. Formation energies in kJ mol^{-1} of the lowest energy isomers of the various metallacyclobutane intermediates shown in Scheme 2 according to DFT calculations (see the Supporting Information for further information).

Complex	Associative pathway	Dissociative pathway
C [Ru]$C_3H_4Me_2$	−38[a]/−73[b]	−109[a]/−131[b]
E [Ru]C_3H_5Me	−31[c]/−65[d]	−114[c]/−135[d]
F [Ru]C_3H_6[e]	−87	−130
G [Ru]C_3H_5Me[e]	−90	−124
H [Ru]$C_3H_4Me_2$[e]	−16	−119
I [Ru]$C_3H_3Me_3$[e]	−18	−115

[a] Formation from **B** and propene.
[b] Formation from **D** and *trans*-2-butene.
[c] Formation from **B** and ethene.
[d] Formation from **D** and propene.
[e] Metallacycles **F**–**I** are unproductive in propene metathesis, *cf.* Scheme 2.

stituent in the 2-position. This intermediate would undergo an unproductive cycle to yield propene and complex **B**. The second lowest energy was found for the non-substituted RuC_3H_6 metallacycle **F** which is formed by addition of ethene to complex **D**. In the dissociative pathway, metallacycles **E**, **C**, and **F** are lowest in energy, i.e., a significant amount of catalyst can be trapped in the low-energy species **F** also here, although the energetic differences in metallacycles are less pronounced (Table 1). The other possible intermediates have lower formation energies as summarized in Table 1.

The difference in energy of the metallacycle intermediates can help to understand our experimental observations. The initial activity of the **5**-SILP catalyst system is high and propene is converted with the equilibrium conversion of 34% at 40 °C. The formed ethene will then shift the equilibrium between **D** and **F** towards the low energy complex **F**.

This complex is not part of the productive metathesis cycle and overall lowers the effective concentration of productive ruthenium complexes.

The observation that the [BMIM][NTf_2] containing **5**-SILP catalysts deactivated faster than the [BMIM][BF_4] based system can now be explained, since the two different ionic liquids act as ethene reservoirs of different efficiency, thus creating different ethene concentrations at the catalyst center.

Assuming that the presence of ethene primarily shifts the equilibrium between complexes **D** and **F**, the effective concentration of the active catalyst is merely lowered without deactivating the ruthenium species irreversibly. Deactivation of ruthenium based metathesis catalysts by ethene had been proposed by several authors in the past.[13,14] In contrast, we concluded from our experiments and calculations that replacing propene by another alkene feed that would hardly produce any ethene as a product of metathesis should be able to shift the equilibrium back to the active species **B**–**E**. As a consequence such a shift should re-activate the metathesis system as more Ru catalyst species would become part of the productive cycle again.

To check this hypothesis we performed the following experiment. Our fixed-bed reactor was filled with 2 g of **5**-SILP (IL: [$Me(C_2H_4O)_3MIM$][BF_4], support: silanized silica gel 60) and contacted at 40 °C first with a pre-mixed, highly diluted gas mixture of 1-butene and 2-butenes in butanes (2.5% 1-butene, 39.0% 2-butenes, 58.5% butanes; residence time 8 s). Under the applied conditions, **5**-SILP promoted almost complete 1-butene conversion ($X_{1\text{-butene}} = 96\%$, note that the equilibrium of 1-butene/2-butene cross-metathesis under the applied conditions is 96%) in the 1-butene/2-butene cross-metathesis leading to propene and 2-pentene formation. Due to the high dilution of the feed consecutive metathesis of the primary product propene was insignificant during the residence time of 8 s as demonstrated by our GC product analysis (ethene concentrations in the product gas mixture were always below 0.2%). The very high conversion of 1-butene found in this experiment is very remarkable given its low concentration in the feed (low feedstock concentration should slow down the reaction rate) and the fact that unproductive 2-butene self-metathesis is proceeding in parallel to the productive 1-butene/2-butene reaction. Most important in the context of our catalyst stability study is, however, the finding, that the immobilized Grubbs catalyst showed no deactivation over 20 h time-on-stream in this 1-butene/2-butene cross-metathesis reaction (Figure 3).

After 20 h time-on-stream we added ethene to the feedstock entering the reactor so that the molar ratio of ethene and 2-butene in the feedstock was equal to 1. As expected from our previous results (e.g., Figure 1) an immediate deactivation of the immobilized Grubbs catalyst took place when ethene entered the reactor. After 140 h time-on-stream the 2-butene conversion had decreased to a value below 10% start-

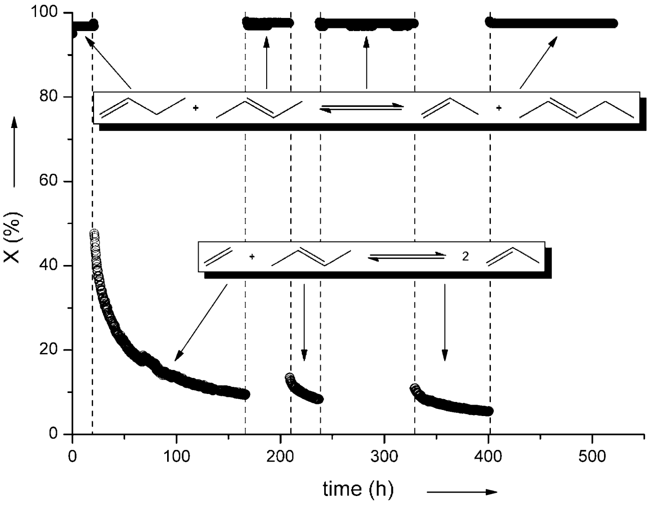


Figure 3. Conversion *vs.* time plot for the investigation of substrate influence on catalyst stability of **5**-SILP at 40 °C, 1 bar, residence time = 8 s, 2 g SILP, Ru loading 0.1 wt%, silanized silica gel 60, $[Me(C_2H_4O)_3MIM][BF_4]$, IL loading 5 vol%, full points: 1-butene metathesis in a diluted C_4 mixture; open points: ethene/2-butene (molar 1:1) metathesis; for TOF information see Supporting Information.

ing from 48% at the moment of the feedstock switch (note that the thermodynamic equilibrium for the formation of propene from ethene and 2-butene is 66% under the applied conditions). Then we changed the feedstock entering the reactor back to the same diluted C_4 feed that was used for the first 20 h time-on-stream. With this switch in feedstock the system returned quickly to the same high 1-butene conversion as observed during the first 20 h indicating the catalyst deactivation observed with ethene feed to be perfectly reversible and feedstock-dependent. To be absolutely sure about this finding we repeated the feedstock switch back to ethene and diluted C_4, and then to the diluted C_4 another two times with different reaction periods leading to a total operation time of the immobilized Grubbs catalyst of more than 500 h time-on-stream. During this prolonged operation time no sign of catalyst deactivation was observed with the diluted C_4 feed while clearly each period using ethene and diluted C_4 feed showed repeatedly an apparent catalyst deactivation. Although the catalyst obviously maintained its full initial conversion for the diluted C_4 feed over 20 days of operation with full recovery of the activity after ethene-rich operation (*cf.* Figure S4 in the Supporting Information), our results also indicate a slow irreversible transformation of the catalyst over time that exclusively affects the metathesis of ethene and 2-butene. While the system provides up to 48% 2-butene conversion at the beginning of the first ethene-rich operation phase, the system has significantly lower initial conversions in ethene/2-butene metathesis for the later slots. The nature of this irreversible catalyst modification is still under investigation in our groups.

Thus, our work provides strong evidence for the conclusion that active Grubbs-type metathesis catalysts suffer from temporary inhibition caused by the presence of large amounts of ethene. Our theoretical work suggests that the observed ethene-induced inhibition effect is due to a reversible shift of Ru complexes from the productive catalytic cycle towards unproductive, dormant Ru species. This shift is reversible, equilibrium driven and thus dependent on the actual ethene concentration at the catalyst. By replacing ethene in the feedstock and by largely avoiding the catalytic formation of ethene, the described Grubbs-type SILP-metathesis catalyst showed constant catalytic activity and selectivity for more than 20 days of continuous gas-phase operation reacting a small concentration of 1-butene (2.5%) in a very short residence time (8 s) to equilibrium concentrations of 1-butene, propene and 2-pentenes. Apart from these specific conclusions on Ru-catalyzed cross-metathesis, our work clearly demonstrates the potential of continuous gas-phase reactions using SILP catalyst systems for systematic mechanistic studies of complex, transition metal complex-catalyzed reactions.

Experimental Section

Chemicals

All syntheses were carried out using standard Schlenk techniques under argon (99.999%, Linde AG). The applied catalysts **2**, **4** and **5** were purchased from STREM Chemicals. Silica gel 100 (Merck KgaA) was partly dehydroxylated at a temperature of 370 °C in air for 12 h followed by storage under vacuum prior to use. Silanized silica gel 60 and dichloromethane were purchased from Merck KgaA and stored under argon prior to use. The ionic liquids [BMIM][BF_4] (99.9%), [BMIM][PF_6] (99.8%) and [BMIM][CF_3SO_3] (99,7%) were purchased from Merck KGaA. The syntheses of [BMIM][SbF_6],[15] [BMIM][NTf_2],[16] $[Me(C_2H_4O)_3MIM][BF4]$[17] were carried out according to the literature.

SILP Catalyst Preparation

The applied SILP materials were prepared by impregnation of the silica support with a solution of dichloromethane and the respective ionic liquid containing the relevant metathesis catalyst under an argon atmosphere using standard Schlenk techniques, followed by subsequent removal of dichloromethane under vacuum to obtain a free flowing SILP catalyst.

Continuous-Flow Gas-Phase Metathesis Experiments

The continuous-flow gas-phase metathesis experiments were performed in a screening-rig consisting of ten parallel, independently operating reactor lines. The solid SILP catalysts were used as a fixed-bed in a stainless-steel tubular reactor at atmospheric pressure and a temperature of 40 °C. Before filling the catalyst into the reactor, the rig was flushed with nitrogen to generate an inert atmosphere. As soon as the reaction temperature was reached the respective gas was fed into the rig by means of mass flow controllers (Brooks Instruments, Brockhorst) for starting the reaction. The reactor lines were connected to the FID-gas chromatograph (Agilent 6890 N) in a switchable manner *via* a multi-port valve. Gaps in the data acquisition (see Figure 1 and Figure 2 as well as Figures S2 and S3 in the Supporting Information) originate from analysis of parallel operated reactors during the continuous experiment.

Computational Details

All DFT calculations were performed using the Turbomole program package.[18] The exchange-correlation functional according to Becke[19] and Perdew[20] augmented with Grimme's dispersion correction[21] (BP-D) has been used throughout in combination with the SV(P) basis set.[22] The multipole-accelerated resolution of the identity (MARIJ) technique[23] has been employed. In addition, test calculations using the same functional (BP-D) but the TZVP basis set[22] as well as the B3LYP-D functional and the SV(P) basis set have been performed, which all resulted in the same qualitative trends as the BP-D/SV(P) method in the present case. Geometry optimizations were performed without symmetry constraints, and the identity of minima was confirmed by frequency calculations.

The theoretical calculations in this study focus on the formation energies of the metallacyclobutane intermediates as possible resting species in propene metathesis to yield *cis*/*trans*-2-butene and ethene. No activation barriers have been considered. For both the dissociative and the associative pathways (cf. Supporting Information, Scheme S1), all possible regio- and stereoisomers for the metallacyclobutane species with 0–3 methyl substituents that can potentially occur in the metathesis reaction have been calculated. In the paper, we discuss only those metallacycles according to Scheme 2 which are lowest in energy as compared to their isomers (see Scheme 2 and the Supporting Information for further information). Table 1 lists the formation energies of these lowest-energy isomers from **B**, **D**, ethene, propene, and *cis*/*trans*-2-butene, see Scheme S4 in the Supporting Information for an example). Note that species **E** in principle can be formed by reaction of **D** with propene or (alternatively) by reaction of **B** with ethene. Likewise, species **C** can either be formed by **B** with 2-butene (*cis* or *trans*) or by reaction of **B** with propene.

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