Supporting Information

Occlusion of Grubbs' Catalysts in Active Membranes of Polydimethylsiloxane: Catalysis in Water and New Functional Group Selectivities

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Materials. The Grubbs' first and second generation catalysts were purchased from Aldrich, placed in a glove box under N₂, and used as received. All solvents and reagents were purchased at their highest purities from Acros or Aldrich and used as received. Geduran silica gel 60 was purchased from Fisher and used for all purifications. Uncross-linked PDMS (Sylgard 184) was purchased from Essex Brownell.

Characterization. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 300 using CDCl₃ as the solvent and internal standard.

General Considerations. All reactions were carried out using standard Schlenk techniques under an atmosphere of N₂. A Vacuum Atmospheres glove box under an atmosphere of N₂ was used throughout these studies to prepare the samples. All solvents were degassed by three freeze/pump/thaw cycles.

The starting materials **1**, **9**, **11**, **13**, **15**, and **17** were all commercially available. We synthesized starting materials **3**,¹ **5**,² and **7**³ based on literature precedents. The products **2**,⁴ **4**,¹ **6**,⁵ **8**,³ **10**,⁶ **12**,⁷ and **14**⁸ were characterized previously in the literature.

Preparation of Occluded Grubbs' Catalyst. PDMS (Sylgard 184) is sold as two components that are mixed at a 10/1 ratio and heated to fully cure. These components are viscous; hence, thorough mixing is required. No solvent is needed to aid the curing, only heat is required. Typically, two to three hours at 60 °C is sufficient to cure PDMS, we cured PDMS longer to ensure complete reaction.

PDMS was cured by thoroughly mixing the two components at a 10/1 ratio, degassing, and heating to 65 °C for at least 12 h. These PDMS slabs were soaked in a large excess of CH₂Cl₂ for 4 h and removed. This process was repeated two more times and a final soak in a large excess of pentane for 4 h was used to remove most of the uncross-linked PDMS and Pt catalyst used to cross-link PDMS. The PDMS slabs were dried overnight at 65 °C. Each slab was cut into pieces with dimensions from 1 mm to 1 cm. The pieces were not cut evenly, they were cut into small pieces for ease of handling later. These pieces were stored under ambient conditions.

At this stage, Grubbs' catalyst was swelled into the PDMS slabs. In a representative example, we dissolved the Grubbs' second generation catalyst (810 mg, 0.95 mmole) in 15 mL of CH₂Cl₂. This solution was added to a Schlenk flask containing PDMS slabs (19.1 g) and allowed to stand with periodic shaking. After CH₂Cl₂ adsorbed into the PDMS slabs, they were placed under vacuum to remove the CH₂Cl₂. We used less solvent than the maximum that would swell into PDMS so that all of the methylene chloride containing Grubbs' catalyst would adsorb into the slabs. The slabs were briefly rinsed in atmosphere with CH₂Cl₂ to remove any catalyst on the surface and dried again under vacuum. The slabs were stored in a glove box under N₂ at ambient temperatures.

Control Experiments to Reveal if Metathesis Catalysts were Present in the Solvent.
Occluded Grubbs' second generation catalyst was added to a Schlenk flask and removed from

the glove box. A degassed solution of 10% water in methanol was added to the Schlenk flask (5 mL) followed by undecanoic acid (930 μ L, 4.3 mmole). The Schlenk flask was placed in an oil bath at 80 °C under N₂. After 2.5 h half of the solvent was transferred to a new Schlenk flask under N₂ via syringe. This Schlenk flask was heated to 80 °C. A small aliquot was removed from each reaction to check the conversion (30%). After 3 and 5 h small aliquots were removed and the solvent was evaporated. From these aliquots we learned that the reaction with PDMS went to 100% conversion, but the reaction where the solvent was removed from PDMS remained at 30% conversion. This control was repeated several times with the same result each time; the solvent did not contain metathesis active catalyst.

Procedure for Metathesis with Occluded Catalysts. The experimental procedures for each metathesis experiment differed in the temperature of the reaction, the length of time the reaction took to reach 100% conversion, the solvent, and the identity of occluded catalyst. All of these reactions were run under an atmosphere of N₂. We will describe one example and list the reaction conditions for the others in abbreviated form.

Cyclopent-3-ene-1,1-dicarboxylic acid diethyl ester, 2. In a glove box occluded Grubbs' first generation catalyst (2 g PDMS, 60 mg catalyst, 0.073 mmole) was placed in a Schlenk flask. The flask was sealed and removed from the glove box and attached to a Schlenk manifold. Next, 5 mL of MeOH in water (10% MeOH by volume) was added to the flask. Diethyldiallylmalonate (860 μ L, 3.6 mmole) was added, and the flask was placed in an oil bath at 100 °C for 2 h. The reaction was cooled and the solvent was decanted. The PDMS was swelled in 5 mL of CH₂Cl₂ for 4 h and then decanted into the aqueous solvent from the reaction. The solvents were removed under vacuum. The product was cleaned by column chromatography (1/9 ethyl acetate/hexane) to yield a clear liquid (0.64 g, 3.1 mmole, 85% yield). The ¹H and ¹³C NMR matched that reported in the literature.⁴ ¹H NMR (CDCl₃, ppm): δ 1.17 (t, 6H, J = 7.1 Hz),

2.92 (s, 4H), 4.11 (q, 4H, $J = 7.1$ Hz), 5.51 (s, 2H). ^{13}C NMR (CDCl_3 , ppm): δ 13.79, 40.62, 58.60, 61.25, 127.58, 171.92.

2. Reaction with **1** and occluded Grubbs' second generation catalyst was carried out in 100% H_2O at 100 $^\circ\text{C}$ for 2 h to yield the product in 88% yield.

N-Tosyl-2,5-dihydropyrrole, 4: Reaction with **3** and occluded Grubbs' second generation catalyst was carried out in 7 mL of 10% H₂O/90% MeOH (v/v) at 50 °C for 2 h to yield the product in 98% yield. The ¹H and ¹³C NMR spectra agreed with those reported in the literature. ¹H NMR (CDCl₃, ppm): δ 2.44 (s, 3H), 4.12 (s, 4H), 5.64 (s, 2H), 7.32 (d, 2H, *J* = 8.1 Hz), 7.71 (d, 2H, *J* = 8.1 Hz). ¹³C NMR (CDCl₃, ppm): δ 21.42, 54.75, 125.33, 127.29, 129.67, 134.06, 143.37.

4. Reaction with **3** and occluded Grubbs' first generation catalyst was carried out in 5 mL of 10% H₂O/90% MeOH (v/v) at 25 °C for 44 h to yield the product in 61% yield.

6. Reaction with **5** and occluded Grubbs' second generation catalyst was carried out in 5 mL of 10% H₂O/90% MeOH (v/v) at 50 °C for 17 h to yield the product in 79% yield. The ¹H and ¹³C NMR spectra agreed with those reported in the literature. ¹H NMR (CDCl₃, ppm): δ 2.55 (m, 4H), 4.30 (m, 1H), 4.50 (s, 2H), 5.70 (s, 2H), 7.33 (m, 5H). ¹³C NMR (CDCl₃, ppm): δ 39.23, 70.70, 78.64, 127.39, 127.63, 128.29, 128.37, 138.64.

Cyclopent-3-ene-1,1-dicarboxylic acid, 8. Reaction with **7** and occluded Grubbs'

second generation catalyst was carried out in 5 mL of 10% H₂O/90% MeOH (v/v) at 75 °C for 27 h to yield the product in 61% yield. ¹H NMR (CDCl₃, ppm): δ 3.04 (s, 4H), 5.62 (s, 2H). ¹³C NMR (CDCl₃, ppm): δ 40.85, 58.50, 127.66, 174.95. HRMS: Calcd for C₇H₈O₄: 156.0423. Found: 156.0427.

10. Reaction with **9** and occluded Grubbs' second generation catalyst was carried out in 5 mL of 90% H₂O/10% MeOH (v/v) at 100 °C for 3 h to yield the product in 63% yield. The ¹H and ¹³C NMR spectra agreed with those reported in the literature. ¹H NMR (CDCl₃, ppm): δ 1.41 (m, 4H), 1.56 (m, 4H), 2.01 (m, 4H), 2.21 (s, 2H), 3.62 (t, 4H, *J* = 6.4 Hz), 5.41 (m, 2H). ¹³C NMR (CDCl₃, ppm): δ 25.54, 32.04, 32.18, 62.67, 130.32.

10. Reaction with **9** and occluded Grubbs' first generation catalyst was carried out in 7 mL of 90% H₂O/10% MeOH (v/v) at 100 °C for 12 h to yield the product in 64% yield.

12. Reaction with **11** and occluded Grubbs' second generation catalyst was carried out in 6 mL of 90% H₂O/10% MeOH (v/v) at 100 °C for 4 h to yield the product in 87% yield. The ¹H and ¹³C NMR spectra agreed with those reported in the literature. ¹H NMR (CDCl₃, ppm): δ 1.29 (m, 20H), 1.64 (m, 4H), 1.97 (m, 4H), 2.35 (t, 4H, *J* = 7.4 Hz), 5.38 (m, 2H). ¹³C NMR (CDCl₃, ppm) δ: 22.78, 24.79, 29.13, 29.28, 29.36, 29.67, 31.73, 32.67, 34.20, 130.47, 180.40.

12. Reaction with **11** and occluded Grubbs' first generation catalyst was carried out in 5 mL of 90% H₂O/10% MeOH (v/v) at 90 °C for 3 h to yield the product in 83% yield.

14. Reaction with **13** and occluded Grubbs' second generation catalyst was carried out in 4 mL of 90% H₂O/10% MeOH (v/v) at 25 °C for 48 h to yield the product in 87% yield. The ¹H and ¹³C NMR spectra agreed with those reported in the literature. ¹H NMR (CDCl₃, ppm):

δ 1.68 (m, 4H), 2.05 (m, 4H), 2.30 (m, 4H), 5.42 (m, 2H). ^{13}C NMR (CDCl_3 , ppm) δ : 24.41, 24.60, 26.24, 31.64, 33.39, 129.41 (cis) 129.95 (trans), 177.03.

16. Reaction with **15** and occluded Grubbs' second generation catalyst was carried out in 7 mL of 10% H_2O /90% MeOH (v/v) at 25 °C for 19 h to yield the product in 74% yield. ^1H NMR (CDCl_3 , ppm): δ 1.26 (t, 12H, $J = 7.1$ Hz), 2.62 (m, 4H), 3.33 (m, 2H), 4.19 (m, 2H), 5.48 (m, 2H). ^{13}C NMR (CDCl_3 , ppm) δ : 25.70, 25.72, 29.00, 29.06, 29.38, 29.39, 29.41, 29.42, 29.54, 29.56, 32.53, 32.74, 62.96, 130.31, 130.34. HRMS: Calcd for $\text{C}_{20}\text{H}_{40}\text{O}_2$: 312.3028. Found: 312.3026

18. Reaction with **17** and occluded Grubbs' second generation catalyst was carried out in 8 mL of 10% H₂O/90% MeOH (v/v) at 50 °C for 2 h to yield the product in 67% yield. ¹H NMR (CDCl₃, ppm): δ 1.26 (t, 12H, J=7.1 Hz), 2.62 (m, 4H), 3.33 (m, 2H), 4.19 (m, 2H), 5.48 (m, 2H). ¹³C NMR (CDCl₃, ppm) δ: 13.96, 26.47, 31.52, 51.66, 51.85, 61.27, 61.32, 127.78, 128.76, 168.70, 168.78. HRMS: Calcd for C₁₈H₂₈O₈: 372.1784. Found: 372.1766.

Functional Group Selective Olefin Metathesis. *Reaction with p-toluenesulfonic acid.*

occluded Grubbs' second-generation catalyst (56 mg, 0.066 mmole, 1.9 g PDMS) was added to a Schlenk flask in a glove box followed by **7** (90 mg, 0.49 mmole). The Schlenk flask was removed from the glove box and 4 mL of 10% water in methanol, *p*-toluenesulfonic acid (0.13 g, 0.66 mmole), and **5** (0.1 g, 0.49 mmole) was added. The reaction was heated to 50 °C for 19 h. The solvent was decanted and the reagents were extracted from PDMS by immersing in a large excess of methylene chloride for several hours. The products were purified by column chromatography eluting with 10% to 50% ethyl acetate in hexanes. We isolated **6** (0.07 g, 85 % yield) and **8** (0.08 g, 90 % yield).

Reaction with sodium hydroxide. NaOH (0.03 g, 0.7 mmole) was added to a Schlenk followed by 4 mL of 10% water in methanol. **7** (90 mg, 0.49 mmole) was added to the flask under N₂ and allowed to stir for *ca.* 6 min. The flask was then charged with **5** (0.1 g, 0.49 mmole) followed by occluded Grubbs' second-generation catalyst (56 mg, 0.066 mmole, 1.9 g PDMS). The reaction was heated to 50 °C for 23 h. The products were purified as before. Both **6** (0.06 g, 65 % yield) and **7** (0.09 g, 94 % yield) were isolated and characterized as before.

Recycling Experiments with Occluded Grubbs' Catalyst. Occlusion of Grubbs' catalysts in PDMS strongly suggests that they can be recycled. We carried out experiments to address this issue.

Grubbs' second generation catalyst (38 mg, 0.044 mmoles, 1.9 g PDMS) was added to a Schlenk flask in a glove box. The Schlenk flask was removed from the glove box, attached to a Schlenk manifold, and placed under N₂ for the duration of the experiment. We added 5 mL of 10% water in methanol that had been thoroughly degassed followed by diethyldiallylmalonate (107 uL, 0.44 mmoles). The reaction was heated to 50 °C. Every two hours the solvent was removed via syringe and evaporated to yield the ring closed product. Fresh solvent and diethyldiallylmalonate (107 uL, 0.44 mmoles) was added to the occluded catalyst and reacted for 2 h as before. The conversions were found by ¹H NMR spectroscopy and the yields were found from the weight of products isolated (Table 1).

Table 1. Recycling of Occluded Grubbs' Catalyst in MeOH/Water.

Cycle	1	2	3	4	5	6
Conversion (%)	>98	>98	>98	>98	>98	90
Yield (%)	74	85	86	88	93	88

Although we have not optimized these experiments, it is clear that we can recycle the catalyst.

Stability of Occluded Grubbs' Catalyst to Ambient Conditions. Occluded Grubbs' first generation (33 mg, 0.040 mmol, 3.2 g PDMS) and second generation (30 mg, 0.035 mmol, 1.5 g PDMS) catalysts were placed in two different vials in the glove box. The vials were removed and exposed to ambient temperature and atmosphere for 27 days. Grubbs' first generation (33 mg, 0.040 mmol) and second generation (30 mg, 0.035 mmol) catalysts were added to separate vials in a glove box and dissolved in 5 mL of dichloromethane. They were removed from the glove box and exposed to air for *ca* 3 h, then the vials were tightly sealed and left standing for 27 d. In a third experiment, Grubbs' first generation (33 mg, 0.040 mmol) and second generation (30 mg, 0.035 mmol) catalysts were removed from the glove box and as solids and exposed to ambient conditions for 27 d.

After 27 d, each batch of catalyst was tested for their reactivity. The catalysts that were dissolved in dichloromethane were transferred to Schlenk flasks and placed under N₂. Diethyldiallylmalonate (500 μ L, 497 mg, 2.07 mmol) was added and the reactions were run for 11 h. The solvent was removed in *vacuo* and samples analyzed by ¹H NMR spectroscopy. The granular catalysts were transferred to Schlenk flasks under N₂ and 5 mL of degassed dichloromethane was added to each flask followed by diethyldiallylmalonate (500 μ L, 497 mg, 2.07 mmol). After 11 h, the solvent was removed and the products were analyzed by ¹H NMR spectroscopy. In the final experiment, occluded Grubbs' catalysts were added to 5 mL of degassed 10% H₂O in MeOH followed by diethyldiallylmalonate (500 μ L, 497 mg, 2.07 mmol). The reactions were heated to 50 °C for 11 h. The solvent was removed from the PDMS slabs, and they were swelled in 30 mL of dichloromethane and added to the MeOH/H₂O.

Finally, the solvent was removed in *vacuo*. The products were analyzed by ^1H NMR spectroscopy.

The distribution of products shows that the occluded catalysts were still active after exposure to ambient conditions for 27 d (Table 2). Future work is needed to investigate the stability of these occluded catalysts.

Table 2. Activities of catalysts that were exposed to ambient conditions for 27 d.

Catalysts	First generation catalyst (% conversion)	Second generation catalyst (% conversion)
Occluded catalysts	61	54
Granular catalysts	100	100
Catalysts dissolved in DCM	0	0

Infrared Spectroscopy of 2,2-Diallylmalonic Acid Occluded in PDMS.

In the functional group selective reactions shown in Figure 2 in our communication, we stated that 2,2-diallylmalonic acid did not diffuse into PDMS under basic conditions because it was a salt but it did diffuse into PDMS under acidic conditions because it was neutral. It is well known that small, polar salts either do not diffuse into PDMS or diffuse very slowly.⁹⁻¹¹ For instance, ionic liquids do not diffuse into PDMS but water will.⁹ To provide more evidence for our claim in this paper, we studied the infrared spectroscopy of PDMS slabs that had been exposed to 2,2-diallylmalonic acid under acidic and basic conditions.

To a flask was added 2,2-diallylmalonic acid (95 mg, 0.625 mmoles) and 5 mL of 90/10 (v/v) of MeOH/10% HCl in H₂O. After stirring for 5 min, thin strips of PDMS (~ 100 mg, thicknesses of approximately 70 microns) were added to the flask and it was placed in an oil bath at 50 °C for 12 h. In a second flask, 2,2-diallylmalonic acid (101 mg, 0.664 mmoles), 90/10 (v/v) of MeOH/H₂O, and NaOH (40 mg, 1 mmole) were added and stirred for 5 min. Thin films of PDMS (~ 100 mg, thicknesses of approximately 70 microns) were added to the flask and heated

at 50 °C for 12. In a third flask, thin films of PDMS were added to the same solvent and heated to 50 °C for 12 without HCl, NaOH, or 2,2-diallylmalonic acid. The PDMS strips were removed from the solvent, dried under a stream of N₂, and studied by transmission infrared spectroscopy using a Bruker Tensor spectrometer. All of the IR spectrums were obtained under the same conditions (same number of scans, detector, and resolution) using air as a background.

In Figure 1 we overlay the C-H and C=O regions of the IR spectrums for all three samples. Both regions show that under acidic conditions the diacid diffused into the PDMS, and under basic conditions no diacid was observed in the PDMS. These results demonstrate that the salt of the diacid was unable to diffuse into PDMS under the reaction conditions.

Figure 1. Infrared spectrums of the C-H and C=O regions for the three PDMS samples prepared as described above.

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