Available online at www.sciencedirect.com

ScienceDirect

Journal of Organometallic Chemistry 691 (2006) 5278–5288

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

New selectivities from old catalysts. Occlusion of Grubbs' catalysts in PDMS to change their reactions

M. Brett Runge, Martin T. Mwangi, Ned B. Bowden *

University of Iowa, Department of Chemistry, 423K Chemistry Building, Iowa City, IA 52242, United States

Received 28 June 2006; received in revised form 10 September 2006; accepted 12 September 2006
Available online 20 September 2006

Abstract

This article describes new selectivities for Grubbs' first and second generation catalysts when occluded in a hydrophobic matrix of polydimethylsiloxane (PDMS). Occlusion of catalysts in mm-sized slabs of PDMS is accomplished by swelling with methylene chloride then removing the solvent under vacuum. The catalysts are homogenously dissolved in PDMS yet remain catalytically active. Many substrates that react by olefin metathesis with Grubbs' catalysts freely dissolved in methylene chloride also react by olefin isomerization with occluded catalysts. Eleven examples of substrates that exhibit dual reactivity by undergoing olefin isomerization with occluded catalysts and olefin metathesis with catalysts dissolved in methylene chloride are reported. Most of these substrates have olefins with allylic phosphine oxides, carbonyls, or ethers. Control experiments demonstrate that isomerization is occurring in the solvent by decomposition of the catalyst from a ruthenium carbene to a proposed ruthenium hydride. This work was extended by heating occluded Grubbs' first generation catalyst to 100 °C in 90% MeOH in H_2O in the presence of various alkenes to transform the Grubbs' catalyst into an isomerization catalyst for unfunctionalized olefins. This work demonstrates that occlusion of organometallic catalysts in PDMS has important implications for their reactions and can be used as a method to control which reactions they catalyze.

Keywords: Grubbs' catalysts; Polydimethylsiloxane; Metathesis; Olefin isomerization; Ruthenium

1. Introduction

The Grubbs' olefin metathesis catalysts have proven to be invaluable in small molecule synthesis for their ability to catalyze ring closing metathesis reactions and to bond two molecules together through cross metathesis [1]. These catalysts are notable as they are stable to many different functional groups and solvents while the second generation catalyst is as active as the Schrock metathesis catalyst [2]. Recently, new reactions beyond metathesis have been discovered that are catalyzed by the Grubbs' catalysts that open up new synthetic transformations. Examples of these new reactions include olefin isomerization, deprotection of tertiary amines, isomerization of allylic alcohols to ketones, Kharasch reaction, and hydrosilylation of carbonyls [3–16]. One prominent example of a new reaction catalyzed by the Grubbs' catalysts is its transformation into an olefin isomerization catalyst. Many examples of these isomerization reactions are for only a select range of substrates with an olefin allylic to an amide, ether, or alcohol [6,8,12,14,15,17]. In other work, transformation of the Grubbs' catalyst into an olefin isomerization catalyst is more general but requires heat or the addition of H_2 or alkoxides [3,12,18]. In many of these prior examples, olefin isomerization was in competition with olefin metathesis and a complex mixture of products was observed. In one report, isomerization was favored when a silyl enol ether was added to the reaction mixture, and in other reports the ratio of isomerization to metathesis product was affected by the choice of solvent or other additives [6,8,12,14,15,17]. The exact mechanism for isomerization is unknown, but it is believed to proceed through a ruthenium hydride that forms during the course of the reaction.

---

* Corresponding author. Tel.: +1 319 335 1198; fax: +1 319 335 1270.
E-mail address: ned-bowden@uiowa.edu (N.B. Bowden).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.09.022

In this article, we report two important advances with Grubbs' metathesis catalysts. First, we describe a method that allows one to decide whether to react substrates by olefin metathesis or isomerization with the Grubbs' catalysts. Second, we report a method to make the Grubbs' first generation catalyst an isomerization catalyst for a wide range of substrates. These methods increase the number and types of products that can be synthesized with the Grubbs' catalysts and add another level of control to how they react.

This work is built on our prior efforts to occlude the Grubbs' catalysts in a cross-linked, hydrophobic membrane of polydimethylsiloxane (PDMS) [19]. Catalysts are swelled into mm-sized PDMS slabs with methylene chloride that is removed under vacuum to yield occluded catalysts. PDMS is a new "solvent" for the catalysts that is both apolar and very viscous [20]. To react, reagents diffuse from an aqueous solvent into PDMS, react with the catalyst, and then the product diffuses from PDMS back to the solvent. Occluding catalysts in PDMS membranes has an important impact on how they react and introduced new selectivities and reactivities to mature catalysts. During our work, we discovered that although many substrates react by metathesis with occluded Grubbs' catalysts, some substrates reacted by olefin isomerization with occluded catalysts (Fig. 1). Interestingly, substrates that reacted by isomerization with occluded catalysts also reacted by metathesis with freely dissolved Grubbs' catalyst in methylene chloride. This difference in products was very interesting as it made it possible to *choose* whether to react a substrate by metathesis or isomerization.

We extended this work to develop a general olefin isomerization catalyst from the Grubbs' first generation catalyst that reacts with a wide range of substrates. In this article, we will report which reagents react by olefin isomerization with occluded catalysts but still react by metathesis with freely dissolved catalysts in methylene chloride. In addition, we will describe how heating the Grubbs' first generation catalyst caused it to become a general isomerization catalyst.

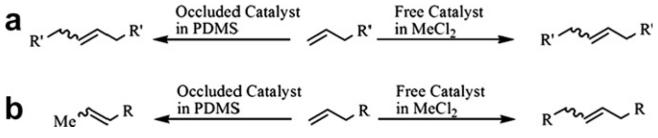


Fig. 1. (a) Many terminal olefins react with Grubbs' catalysts dissolved in methylene chloride and with occluded catalysts in methanol/water by cross metathesis. (b) We discovered that some olefins react by metathesis with Grubbs' catalysts in methylene chloride will also react by isomerization with occluded catalysts in methanol/water. This discovery allows one to choose whether to use these catalysts to promote metathesis or isomerization.

2. Methods and characterization

2.1. Materials

Allyldiphenylphosphine oxide, dimethyl allylphosphonate, diethyl allylphosphonate, allyl phenyl ether, eugenol, diethyl allylmalonate, 10-undecene-1-ol, allyl bromide, 1-hepten-4-ol, pyridinium chlorochromate, 1-hexanol, vinyl acetic acid, benzylidene-bis(tricyclohexylphosphine)dichlororuthenium, and benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)-ruthenium were purchased from Acros or Aldrich at their highest purity and used as received. 2-Propenylhexanoate, hept-1-en-4-one, and phenyl-2-propenylether were synthesized using literature procedures [21,22]. All solvents were reagent grade, purchased from Acros, freeze-pump-thawed three times, and stored under N_2. Geduran silica gel 60 was purchased from Fisher and used for all purifications. Sylgard 184 elastomer (PDMS) was purchased from Essex Brownell.

2.2. Characterization

^1H and ^{13}C NMR spectra were recorded with a Bruker DPX 300 using $CDCl_3$ with 1% TMS as the solvent and internal standard. ^1H NMR and ^{13}C NMR were recorded at 300 and 75 MHz, respectively. A few complex mixtures of isomers were formed that were unable to be separated. As a result, partial hydrogen assignments are given where appropriate. Isomers present include *E* and *Z* olefins and single or multiple isomerization products. NMR spectra were compared with the same molecules published in the literature or very similar molecules and literature references are provided for these molecules.

2.3. Preparation of occluded Grubbs' catalyst in polydimethylsiloxane (PDMS)

Sylgard 184 elastomer base and curing agent were mixed in a 10:1 ratio respectively, degassed for 30 min, poured into petri dishes to approximately a 1 mm thickness, and degassed for 1 h before placing in a 65 °C oven overnight. The PDMS slabs were swelled with CH_2Cl_2 and pentane three times to remove residual platinum catalyst and oligomers. The PDMS slabs were cut into mm-sized slabs, dried, and degassed before taking into a glove box. Grubbs first generation catalyst (1.045 g, 1.27 mmol) was dissolved in 14.7 mL of CH_2Cl_2 and added to a Schlenk flask with 21.98 g of PDMS. The PDMS was allowed to swell with the catalyst solution for 3 h with frequent shaking upon which the solution was completely absorbed into the PDMS. The CH_2Cl_2 was then removed under vacuum overnight. The PDMS slabs were washed with CH_2Cl_2 three times to remove residual catalyst from the outer surface, dried under vacuum, weighed (22.64 g) and then stored in a glove box. The concentration of catalyst in PDMS was determined from the difference in weight of the PDMS before and after the occlusion of the catalyst to give 29.93 mg of catalyst per g of PDMS.

2.4. General olefin isomerization procedure for Undec-9-en-1-ol (**8b**)

In a glove box, 1.69 g of PDMS occluded with Grubbs first generation catalyst (50.6 mg, 61.5 μmol) was placed in a Schlenk flask, removed from the glove box, and attached to a Schlenk line. Seven milliliter of 10% H_2O/90% MeOH were added under N_2 and freeze-pump-thawed twice. 10-Undecene-1-ol (1.036 g, 6.1 mmol) was added under N_2 and the flask was placed in a 100 °C oil bath for 15 h. The solvent was decanted off and diluted with 50 mL H_2O and the product was extracted with CH_2Cl_2. The product was purified by vacuum distillation to yield a colorless oil: (0.788 g, 76%). The NMR spectra matched literature precedents [23]. Multiple isomers were present. ^1H NMR ($CDCl_3$): δ 0.86–0.99 (m, 1H), 1.29 (m, 10H), 1.53–1.64 (m, 5.4H) 1.94–2.02 (m, 2.6H), 3.62 (t, $J = 6.9$ Hz, 2H), 5.38–5.42 (m, 2H). ^{13}C NMR 12.70, 13.96, 17.88, 22.71, 25.57, 25.68, 25.71, 26.78, 27.02, 28.87, 29.08, 29.19, 29.27, 29.29, 29.37, 29.42, 29.45, 29.47, 29.51, 29.53, 29.56, 29.66, 32.48, 32.50, 32.56, 32.75, 62.99, 123.60, 124.54, 129.18, 129.23, 130.23, 130.79, 131.58, 131.91.

2.4.1. Diethyl-1-propenylphosphonate (**1b**)

The procedure above was followed with 5 mol% of Grubbs' second generation catalyst in 3 mL solvent at 50 °C for 20 h. The product was purified by distillation and its NMR spectra matched those from the literature [24]. ^1H NMR ($CDCl_3$): δ 1.32 (t, 6H), 1.92 (m, 3H), 4.10 (m, 4H), 5.68 (m, 1 H), 6.69–6.89 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 16.31 (d, $J = 5.9$ Hz), 20.08 (d, $J = 24.0$ Hz), 61.65 (d, $J = 5.4$ Hz), 118.37 (d, $J = 187.5$ Hz), 149.09 (d, $J = 5$ Hz).

2.4.2. Dimethyl-1-propenylphosphonate (**2b**)

The general procedure was followed with 5 mol% of Grubbs' second generation catalyst in 5 mL solvent at 65 °C for 20 h. NMR spectra matched those from the literature [24]. ^1H NMR ($CDCl_3$): δ 1.87 (m, 3H), 3.64 (d, $J = 11.1$ Hz, 6H), 5.58 (m, 1H) 6.75 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 19.98 (d, $J = 23.3$ Hz), 52.05 (d, $J = 5.9$ Hz), 116.87 (d, $J = 187.4$ Hz), 149.92 (d, $J = 4.7$ Hz).

2.4.3. 1-Propenyldiphenylphosphine oxide (**3b**)

The general procedure was followed with 1 mol% of Grubbs' second generation catalyst in 7 mL solvent at 50 °C for 13 h. NMR spectra matched those found in the literature [25]. ^1H NMR ($CDCl_3$): 1.99 (m, 3H), 6.26 (m, 1H), 6.69 (m, 1H), 7.42–7.55 (m, 6H), 7.65–7.72 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 19.41 (d, $J = 18.4$ Hz), 122.62 (d, $J = 103.2$ Hz), 127.48 (d, $J = 11$ Hz), 130.15 (d, $J = 9.4$), 130.66 (d, $J = 2.9$ Hz), 132.26 (d, $J = 104.3$ Hz), 146.70 (d, $J = 2.9$ Hz) [25].

2.4.4. Hexyl-2-butenoate (**4b**)

The general procedure above was followed with 5 mol% of Grubbs' second generation catalyst in 3 mL solvent at 50 °C for 20 h. ^1H NMR ($CDCl_3$): δ 0.89 (t, 3H), 1.29–1.37 (m, 6H), 1.64 (m, 2H), 1.87 (m, 3H), 4.11 (t, $J = 6.6$ Hz, 2H), 5.84 (m, 1.8 Hz, 1H), 6.96 (dq, $J = 15.6$, 6.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 13.98, 17.92, 22.53, 25.60, 28.63, 31.44, 64.32, 122.79, 144.34, 166.66.

2.4.5. Isoeugenol (**5b**)

The general procedure was followed with 1 mol% of Grubbs' second generation catalyst in 7 mL solvent at 100 °C for 20 h. ^1H NMR ($CDCl_3$): δ 1.85 (dd, $J = 6.6$, 1.8 Hz, 3H, $\mathrm{C}H_3\mathrm{CH{=}CH}$), 3.87 (s, 3H), 5.61 (s, 1H, OH), 6.07 (dq, $J = 15.6$, 6.6 Hz, 1H, $\mathrm{CH_3C}H\mathrm{{=}CH}$), 6.31 (dq, $J = 15.6$, 1.8 Hz, 1H, $\mathrm{CH_3CH{=}C}H$), 6.82–6.87 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 18.30, 55.77, 107.83, 114.30, 119.24, 123.36, 130.67, 130.59, 144.69, 146.50.

2.4.6. Phenyl-1-propenylether (**7b**)

The general procedure above was followed with 4 mol% of Grubbs' second generation catalyst in 3 mL solvent at 50 °C for 18 h. NMR spectra matched those in the literature [21]. ^1H NMR ($CDCl_3$): δ 1.67 (dd, E isomer, $J = 6.9$, 1.8 Hz, 0.75H), 1.72 (dd, Z isomer, $J = 6.9$, 1.8 Hz, 2.25H), 4.88, (dq, Z isomer $J = 6$, 6.9 Hz, 0.75H), 5.36 (dq, E isomer, $J = 12.2$, 6.9 Hz, 0.25H), 6.36–6.45 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 9.36, 12.24, 107.45, 108.27, 116.14, 116.27, 122.31, 129.52, 140.84, 141.94, 157.52.

2.4.7. Hexan-1-ol (**9b**)

The above procedure was followed with 5 mol% of Grubbs' second generation catalyst in 3 mL solvent at 50 °C for 24 h. NMR spectra matched that of hexanol. ^1H NMR ($CDCl_3$): δ 0.86 (t, $J = 6.6$ Hz, 3H), 1.24–1.32 (m, 6H), 1.50–1.55 (m, 2H), 3.58 (t, $J = 6.6$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 13.91, 22.55, 25.37, 31.58, 32.65, 62.83.

2.4.8. Hept-2-en-4-one (**10b**)

The above procedure was followed with 1 mol% of Grubbs second generation catalyst at 100 °C for 2 h. The product was purified by distillation. ^1H NMR ($CDCl_3$): δ 0.92 (t, $J = 7.5$ Hz, 3H), 1.60–1.70 (m, 2H) 1.90 (dd, $J = 6.9$, 1.5 Hz, 3H), 2.51 (t, $J = 7.5$ Hz, 2H), 6.12 (dq, $J = 15.6$, 1.8 Hz, 1H), 6.85 (dq, $J = 15.6$, 6.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 13.74, 17.64, 18.13, 41.83, 131.94, 142.22, 200.52.

2.4.9. N,N-Dibutyl-2-buteneamide (**11b**)

The general procedure above was followed with 2 mol% of Grubbs second generation catalyst at 100 °C for 4 h. The NMR spectra agreed with the literature [26]. ^1H NMR ($CDCl_3$): δ 0.88–0.95 (m, 6H), 1.24–1.37 (m, 4H), 1.48–1.58 (m, 4H), 1.88 (dd, $J = 6.6$, 1.8 Hz, 3H), 3.27 (t, $J = 7.5$ Hz, 2H), 3.35 (t, $J = 7.5$ Hz, 1H), 6.21 (dq, $J = 14.1$, 1.8 Hz, 1H), 6.91 (dq, $J = 14.1$, 6.9 Hz, 1H).

^{13}C NMR ($CDCl_3$): δ 13.81, 13.90, 18.17, 20.06, 20.29, 30.04, 31.76, 46.34, 47.77, 121.97, 141.01, 166.11.

2.5. Cross metathesis with freely dissolved Grubbs' first generation catalyst in methylene chloride for 1,4-dihexoxy-1-butene (**9c**)

Using Schlenk techniques, Grubbs' second generation catalyst (53 mg, 63 μmol) was dissolved in 3 mL of degassed CH_2Cl_2. Hexyl-2-propenylether (0.179 g, 1.3 mmol) was added and the reaction was heated to reflux for 12 h. The solvent was evaporated and the product was purified by chromatography on silica gel eluting with 5% ethyl acetate/95% hexane to give product as colorless liquid. NMR spectra matched those in the literature [21]. ^{1}H NMR ($CDCl_3$): 0.86–0.91 (m, 6H), 1.26–1.38 (m, 12H), 1.53–1.64 (m, 4H), 2.14–2.22 (m, 1H), 2.32–2.39 (m, 1H), 3.35–3.43 (m, 4H), 3.63 (t, *E* isomer, $J = 6.6$ Hz, 1H), 3.71 (t, *Z* isomer, $J = 6.6$ Hz, 1H), 4.36 (q, *Z* isomer, $J = 7.2$ Hz, 0.5H), 4.74 (dt, *E* isomer, $J = 12.6$, 7.2 Hz, 0.5H), 5.98 (dt, *Z* isomer, $J = 6.3$, 1.2 Hz, 0.5H), 6.29 (d, *E* isomer $J = 12.6$ Hz, 0.5 Hz). ^{13}C NMR ($CDCl_3$): δ 13.95, 13.98, 22.55, 22.60, 24.71, 25.46, 25.65, 25.84, 28.43, 29.23, 29.69, 29.72, 31.54, 31.56, 31.68, 31.71, 69.10, 70.47, 70.77, 70.96, 71.57, 72.17, 99.79, 102.40, 146.12, 147.54.

2.5.1. Tetraethyl-2-butene-1,4-diphosphonate (**1c**)

The general procedure was followed and the product was purified by distillation. *E* and *Z* isomers were isolated and the NMR spectra matched those in the literature [27]. ^{1}H NMR ($CDCl_3$): 1.32 (t, $J = 6.9$ Hz, 12H), 2.59–2.65 (m, 4H), 4.11 (m, 8H), 5.61–5.69 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 16.38 (d, $J = 3.2$ Hz), 16.42 (d, $J = 2.8$ Hz), 30.52 (d, $J = 146$ Hz), 30.52 (d, $J = 137$ Hz), 61.87 (d, $J = 3.8$ Hz), 61.91 (d, $J = 3.1$ Hz), 122.76 (t, $J = 1.8$ Hz), 124. 28 (t, $J = 1.8$ Hz).

2.5.2. Tetramethyl-2-butene-1,4-diphosphonate (**2c**)

The general procedure above was followed with the exception 2 mol% of catalyst was used. NMR spectra agreed with those in the literature [27]. ^{1}H NMR ($CDCl_3$): *E* and *Z* isomers δ 2.64–2.77 (m, 4H), 3.80 (d, $J = 10.8$ Hz, 12H), 5.64–2.77 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 29.48, (d, $J = 141.8$ Hz), 29.54 (d, $J = 142.1$ Hz) 52.63 (d, $J = 6.7$ Hz), 52.68 (d, $J = 7.4$ Hz), 122.61 (t, $J = 1.7$ Hz), 124.16 (t, $J = 2.1$ Hz).

2.5.3. 1,6-Dihexyl-3-hexenedioate (**4c**)

The general procedure above was followed with the exception 2 mol% of catalyst was used. The product was purified by chromatography on silica gel eluting with 5% ethyl acetate/95% hexane. Mixture of *E* and *Z* isomers. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, $J = 6.9$ Hz, 6H), 1.27–1.37 (m, 12H), 1.57–1.67 (m, 4H), 3.07–3.11 (m, 4H), 4.05–4.10 (m, 4H), 5.68–5.80 (m, 2H), ^{13}C NMR ($CDCl_3$): δ 13.99, 22.51, 25.54, 28.53, 31.40, 33.19, 37.93, 64.91, 124.52, 125.95, 171.66.

2.5.4. 1,4-Bis(3-methoxy-4-hydroxyphenyl)-but-2-ene (**5c**)

The general procedure above was followed with 1 mol% of Grubbs second generation catalyst at 25 °C for 5 h. The product was purified by chromatography on silica gel eluting with 20% ethyl acetate/80% hexane and increasing to 50% ethyl acetate/50% hexane. Mixture of *E* and *Z* isomers. NMR spectra matched those in the literature [28]. ^{1}H NMR ($CDCl_3$): δ 3.29 (*E* isomer, d, $J = 4.8$ Hz, 2.4H), 3.44 (*Z* isomer, d, $J = 6.9$ Hz, 1.6H), 3.83–3.85 (overlapping singlets, 6H), 5.55–5.67 (m, 2H), 6.67–6.72 (m, 3H), 6.82–6.88 (m, 3H).

2.5.5. 2,7-Bis-ethoxycabonyl-oct-4-enedioic acid diethylester (**6c**)

The general procedure was followed with the exception 2 mol% of Grubbs second generation catalyst was used and the reaction was performed at 25 °C for 5 h. The product was purified by column chromatography on silica gel eluting with 10% ethyl acetate/90% hexane. NMR spectra matched those in the literature [19,29]. ^{1}H NMR ($CDCl_3$): δ 1.24–1.29 (m, 12H), 2.55–2.59 (m, 3.2 H), 2.65–2.70 (m, 0.8H), 3.38 (t, $J = 7.5$ Hz, 2H), 4.15–4.24 (m, 8H), 5.42–5.45 (m, 0.4H), 5.49–5.52 (m, 1.6H) ^{13}C NMR ($CDCl_3$): δ 14.05, 26.57, 31.61, 51.75, 51.95, 61.36, 127.86, 128.85, 168.80.

2.5.6. 1,4-Diphenoxy-2-butene (**7c**)

The general procedure was followed except the reaction was performed at 25 °C. The product was purified by chromatography on silica gel eluting with 5% ethyl acetate/95% hexane. NMR spectra matched those in the literature [30]. ^{1}H NMR ($CDCl_3$): δ 4.57–4.59 (m, 4H), 6.09–6.11 (m, 2H), 6.90–6.98 (m, 6H), 7.24–7.31 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 67.61, 114.70, 120.92, 128.41, 129.47, 158.47.

2.5.7. Icos-10-ene-1,20-diol (**8c**)

The general procedure above was followed with the exception 2 mol% catalyst was used. The product was purified by chromatography on silica gel eluting with 30% ethyl acetate/70% hexane. NMR spectra matched those in the literature [19,29]. ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 26H), 1.52–1.58 (m, 4H), 1.95–2.02 (m, 4H), 3.64 (t, $J = 6.6$ Hz, 4H), 5.35–5.40 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 25.74, 27.18, 28.71, 29.10, 29.26, 29.41, 29.43, 29.46, 29.57, 29.61, 29.73, 32.57, 32.80, 63.09, 129.88, 130.35.

2.6. Control experiment

In a glove box, 1.06 g of PDMS occluded with Grubbs' second generation catalyst (30.5 mg, 36 μmol) was placed in a Schlenk flask. Using standard Schlenk techniques, 4 mL solvent (degassed 10% H_2O/90% MeOH) was added, followed by the addition of dimethyl allylphosphonate (108 mg, 0.72 mmol). The reaction was heated to 65 °C for 2 h. The reaction was cooled to 25 °C and dimethyl allylphosphonate (50.4 mg, 0.36 mmol) was added. The reaction was stirred vigorously for 1 min to ensure the mixture was homogenous. Solvent (2 mL) was separated under N_2 from the PDMS via syringe and placed in a separate Schlenk flask already under N_2 and a small aliquot was removed. ^1H NMR of the aliquot revealed the reaction mixture to consist of 60% of the starting olefin and 40% of the isomerized product. Both reaction mixtures where then heated to 65 °C for 9 h. Aliquots were removed from both reaction mixtures and ^1H NMR showed the reaction mixtures to be identical with starting olefin quantitatively transformed to the isomerized product.

2.7. Reaction of free Grubbs' catalyst in methanol/water with terminal olefins

In a glove box, Grubbs' second generation catalyst (66.6 mg, 78 μmol) was put into a Schlenk flask. Using standard Schlenk techniques, 4.3 mL of degassed 90% MeOH/10% H_2O was added followed by allyl phenylether (25.3 mg, 1.9 mmol). The reaction was then heated to 50 °C for 18 h, monitored by ^1H NMR, and compared with known compounds. Reactions of other substrates were performed under similar conditions as those reported for reactions with occluded catalysts.

3. Results and discussion

3.1. Difference in catalysis by occluded catalysts

We first occluded catalysts in hydrophobic PDMS membranes as described in the experimental section. These PDMS slabs were stored under N_2 until used. Next, we investigated the ability of occluded catalysts to catalyze ring closing and cross metathesis reactions [19]. These reactions were run in methanol/water solvent mixtures as the catalysts do not dissolve in these solvents and remain occluded throughout the reaction. Substrates diffused into PDMS to react and products diffused out of PDMS to the solvent. Most substrates we studied reacted by metathesis, but we discovered numerous examples that reacted by isomerization. This result was surprising because substrates that yielded isomerization products with occluded Grubbs' catalysts yielded cross metathesis products with freely dissolved Grubbs' catalysts in methylene chloride. In Table 1 we list substrates that reacted by olefin isomerization with occluded catalysts and metathesis with freely dissolved catalysts.

We began each reaction with catalyst occluded in PDMS and ran these reactions in MeOH/H_2O mixtures. Although the Grubbs' catalysts are insoluble in the solvents used in these reactions, it is likely that the Grubbs' catalysts are decomposing to new catalysts with different solubilities. Thus, we ran control experiments to learn whether isomerization was occurring exclusively in PDMS or solvent. We reacted 20 equiv of **2a** with occluded Grubbs' second generation catalyst in 90% MeOH in H_2O (Fig. 2). After 2 h, an additional 10 equiv of **2a** were added and the solvent was thoroughly mixed. Immediately after mixing, a small aliquot was removed for ^1H NMR spectroscopy and half of the solvent was transferred to a new Schlenk flask under N_2. The ratio of isomerized product to starting material was approximately 2/3 by the crude ^1H NMR spectrograph. The reactions were run for a further 9 h and both were studied by ^1H NMR spectroscopy. Reactions with and without PDMS went to 100% conversion to the isomerization product. This experiment demonstrated that the isomerization reaction was occurring in the solvent and, possibly, in the PDMS.

This result is in contrast to what we observed in our previous paper where the Grubbs' catalysts remained occluded throughout the reaction and catalyzed ring closing and cross metathesis reactions [19]. These reactions were run with similar solvents, temperatures, and concentrations as those reported in Table 1. We carried out similar control experiments to demonstrate that the Grubbs' catalysts remained occluded throughout reactions where it reacted by metathesis. The difference in these reactions was that some substrates reacted by metathesis in the PDMS and others reacted by isomerization outside of the PDMS when these reactions were run under identical conditions.

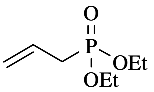
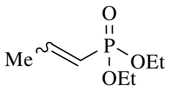
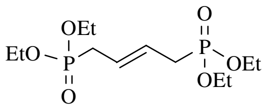
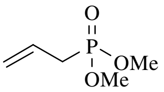
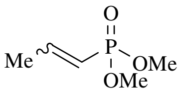
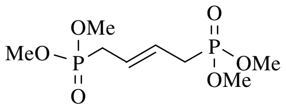
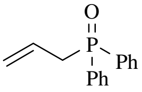
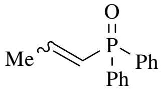
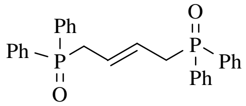
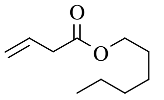
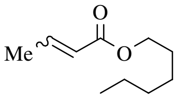
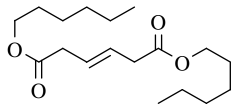
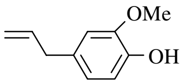
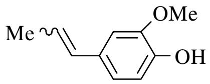
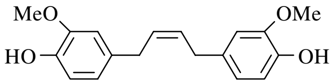
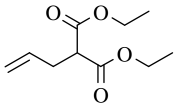
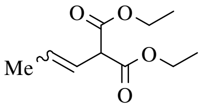
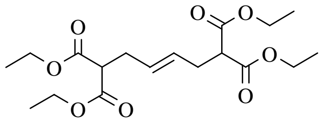
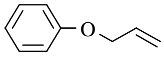
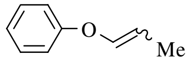
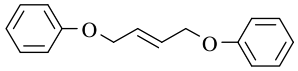
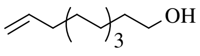
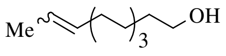
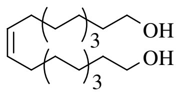
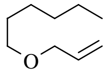
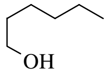
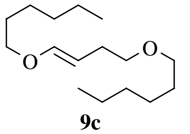
The main difference between reactions that yielded metathesis or isomerization products were functional groups on the substrates being reacted. We observed that most of the substrates that yielded isomerization products also had a functional group bonded to the allylic carbon. These results suggest that occlusion of catalysts in PDMS affects their reactions and leads to isomerization based largely on the presence of a functional group in the substrate. To probe this hypothesis, we investigated three different sets of olefins for how they reacted with occluded catalysts in methanol/water and freely dissolved catalysts in methylene chloride.

3.2. C=O and P=O functional groups bonded to the allylic carbon and their affect on metathesis or isomerization

Reactions with allylic phosphine oxides (entries 1–3 in Table 1) and occluded Grubbs' second generation catalyst yielded only the isomerization products by crude ^1H NMR. These same reagents cleanly yielded the metathesis products with freely dissolved Grubbs' catalyst with no isomerization products visible by ^1H NMR spectroscopy as shown by others and us [19,31]. Both phosphine oxides and phosphate esters showed the same selectivities.

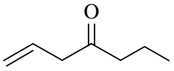
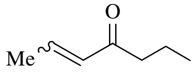
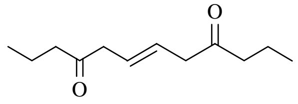
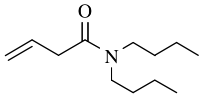
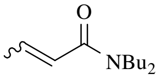
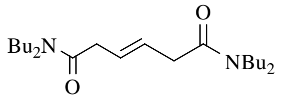
These results led us to hypothesize that allylic carbonyl bonds may exhibit similar reactivity. The P=O and C=O bonds are both highly polar and increase the acidity of protons bonded to adjacent carbons. To test this hypothesis, we reacted occluded Grubbs' second generation catalyst with allylic esters, amides, carboxylic acids, and ketones (Fig. 3).

Table 1
Substrates that reacted by isomerization with occluded catalysts and by metathesis with catalysts dissolved in methylene chloride

Substrate	Occluded catalyst			Free catalyst		
	Product[a]	Catalyst[b]	Yield[c] (%)	Product[a]	Catalyst[a]	Yield[c] (%)
 **1a**	 **1b**	G2	58	 **1c**	G2	78
 **2a**	 **2b**	G2	24	 **2c**	G2	99
 **3a**	 **3b**	G2	90	 **3c**	G2	96[d]
 **4a**	 **4b**	G2	54	 **4c**	G2	62
 **5a**	 **5b**	G2	82	 **5c**	G2	63
 **6a**	 **6b**	G2	75	 **6c**	G2	75
 **7a**	 **7b**	G2	57	 **7c**	G2	53
 **8a**	 **8b**	G1	82	 **8c**	G1	68
 **9a**	 **9b**	G2	77[e]	 **9c**	G2	59[f]

(*continued on next page*)

Table 1 (*continued*)

Substrate	Occluded catalyst			Free catalyst		
	Product[a]	Catalyst[b]	Yield[c] (%)	Product[a]	Catalyst[a]	Yield[c] (%)
 **10a**	 **10b**	G2	61	 **10c**	G2	30[g]
 **11a**	 **11b**	G2	72	 **11c**	G2	60[g]

[a] Products were obtained as *E*/*Z* mixtures.

[b] G1 refers to the Grubbs' first generation catalyst and G2 refers to the Grubbs' second generation catalyst.

[c] Isolated yields.

[d] From literature Ref. [31].

[e] We isolated the deprotected alcohol.

[f] The substrate underwent metathesis and isomerization.

[g] Crude yield based on ^{1}H NMR.

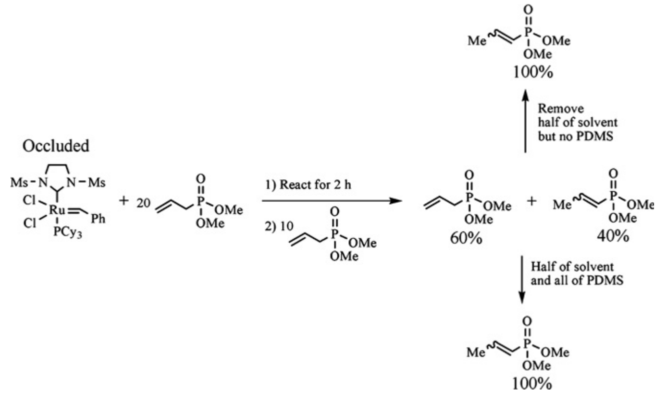


Fig. 2. Control experiments to learn whether isomerization was occurring in the solvent. We reacted occluded Grubbs' catalyst with **2a** for 2 h then added another 10 equiv of **2a**. A crude ^{1}H NMR showed that 60% of **2a** was unreacted. We removed half of the solvent and no PDMS with a syringe under N_2 and placed it into a new Schlenk flask. Both reactions were heated and went to 100% of the isomerized product.

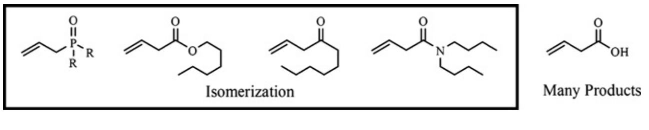


Fig. 3. These substrates have allylic phosphine oxides or carbonyl groups. Substrates in the box reacted to yield cross metathesis products with Grubbs' catalysts in methylene chloride and isomerization products with occluded catalysts. The allylic carboxylic acid yielded a complex mixture of products with occluded Grubbs' catalyst.

The esters, amides, and ketones in Fig. 3 reacted as expected with occluded Grubbs' second generation catalysts and yielded isomerized products in 54–72% yields. No evidence of cross metathesis products were observed in the crude ^{1}H NMR spectra for these reactions. When these reactions were catalyzed by Grubbs' second generation catalysts in methylene chloride, all three reacted by cross metathesis, although forcing conditions were needed for two of them. Although the ester reacted by cross metathesis with an isolated a yield of 62%, the ketone and amide were mostly unreactive. After 24 h in refluxing methylene chloride at 5 mole% loading of the catalyst, only 30% of **10a** had undergone cross metathesis by ^{1}H NMR spectroscopy. Similarly, the amide, **11a**, only cross metathesized to a conversion of 60%. Both were challenging reagents toward the Grubbs' second generation catalyst in methylene chloride, but they reacted well by isomerization with occluded catalysts.

The carboxylic acid in Fig. 3 gave a different result with occluded Grubbs' second generation catalyst. This reaction yielded many products with the isomerized product a minor component. This reaction was too complex to isolate the isomerization product.

These reactions suggest that olefins with allylic P=O or carbonyl bonds will react by isomerization with occluded Grubbs' second generation catalyst. Of course, many more reagents must be studied to find the limits of this selectivity; our results suggest isomerization will be the main reaction with these substrates.

3.3. Allylic ethers and their affect on metathesis or isomerization

Others have shown that allylic ethers can react by either olefin metathesis or isomerization with Grubbs' catalysts freely dissolved in methylene chloride [6,10,13,14,32]. Allylic ether appears to be a special functional group, these molecules either cleanly isomerize or undergo metathesis with Grubbs' catalysts. Because these substrates undergo two reactions, we decided to investigate how allylic ethers reacted with occluded catalysts. We showed two examples,

7a and **9a**, that reacted by olefin metathesis with Grubbs' second generation catalyst in methylene chloride. When these reagents were reacted with occluded Grubbs' second generation catalyst they isomerized and, in the case of **9a**, deprotected to yield the alcohol. Our results are exciting as they demonstrate that allylic ethers that react by metathesis with freely dissolved catalysts can also react by olefin isomerization with occluded Grubbs' catalysts. This result provides a method to exert control over the distribution of products from allylic ethers.

3.4. Long straight-chain alkenes and their affect on metathesis or isomerization

Our work demonstrated that allylic groups were important for deciding whether a substrate reacted by isomerization with occluded Grubbs' catalysts. We wished to extend this work by finding a method to turn isomerization into a general reaction for any alkene. This effort was challenging because we showed in a previous study that many alkenes undergo metathesis with occluded Grubbs' catalysts [19]. For instance, long *n*-alkenes underwent cross metathesis and the products were isolated in high yield.

Our work was inspired by the impressive results of Snapper, Grubbs, Dinger, and Schmidt who described methods to generate isomerization catalysts through the suspected formation of a ruthenium hydride from a ruthenium carbene. In recent work, Grubbs showed that a ruthenium carbene could be transformed into a ruthenium hydride by heating, and Dinger showed that he could access a ruthenium hydride by the addition of alcohols and bases [3,5]. Schmidt formed an isomerization catalyst from the Grubbs' catalyst by the addition of a dilute hydrogen atmosphere [7,8]. Most closely related to our work is that by Snapper who used inorganic hydrides in one article to generate an isomerization catalyst and in another article he used the method of Dinger to generate an effective isomerization catalyst [16,18].

We knew from previous work that salts did not diffuse into PDMS, but alcohols would diffuse into it at low concentrations. We hypothesized that the method of Dinger may apply here although he used alkoxides to generate a ruthenium hydride. Initially, we explored the reactivity of 10-undecenol with occluded Grubbs' first generation catalyst at various temperatures (Fig. 4 and Table 2). These results demonstrate that as we raised the temperature of the reaction, the ratio of isomerized to cross metathesis product increased.

We wished to study whether the change in reactivity from metathesis to isomerization was a general reaction or unique for 10-undecenol at high temperatures. We reacted the substrates shown in Fig. 5 with occluded Grubbs' first generation catalyst at 100 °C in 90% MeOH in H_2O (Table 3). Each of these substrates reacted by cross metathesis with Grubbs' first generation catalyst dissolved in methylene chloride and, importantly, occluded PDMS at room temperature. At 100 °C these substrates reacted mostly by olefin isomerization (Table 3). A mixture of isomerized products was obtained where one or more isomerizations occurred. For instance, approximately 10% of the isomerized product of **13** was the aldehyde.

This work demonstrated that occluded Grubbs' first generation catalyst could be readily turned into general isomerization catalyst by heating to 100 °C. This result was not unprecedented as it followed work by others, but it did demonstrate that catalysts occluded in a hydrophobic matrix of PDMS could rapidly be turned into active isomerization catalysts without the addition of a base or additives. These experiments extended the types of reactions that occluded catalysts can undergo.

3.5. Reactions with free Grubbs' catalysts in methanol/water

We wished to learn if occlusion was necessary for isomerization in methanol/water or if we would get the same result by using freely dissolved Grubbs' catalyst in methanol/water. To probe this question, we investigated the reactions of free Grubbs' second generation catalyst in the presence of 90% methanol/water with olefins from Table 1 that we know isomerized in high yields in the presence of occluded catalysts (Table 4). We ran experiments under identical conditions for identical times to those experiments

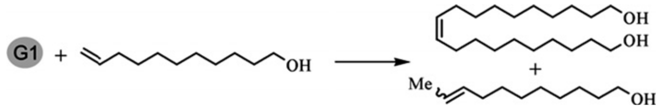


Fig. 4. We reacted the occluded Grubbs' first generation catalyst, shown as G1, with 10-undecenol to learn the ratio of cross metathesis to isomerization product.

Table 2
The effect of temperature on the ratio of isomerization to cross metathesis product for 10-undecenol reacted with occluded Grubbs' first generation catalyst

Entry	Mole % catalyst	Temperature[b] (°C)	Product[a]	
			Isomerization[c]	Cross metathesis
1	1	100	95	4
2	2	50	35	55
3	2	25	18	82

[a] The ratio of isomerization to cross metathesis products by ^1H NMR.
[b] 10-Undecenol was added to a degassed solution of 90% MeOH in H_2O with the occluded catalysts under N_2 and heated if necessary.
[c] The isomerization products were a mixture of one or multiple isomerizations.

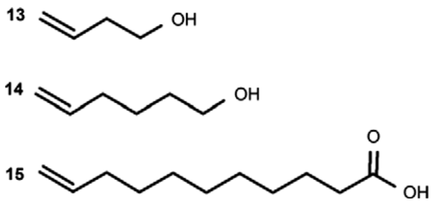


Fig. 5. Olefins that reacted by cross metathesis with occluded Grubbs' first generation catalyst at room temperature were further studied for their distribution of products when reacted at 100 °C. The results are shown in Table 3.

reported in Table 1 with one important difference: the Grubbs' catalyst was added as a powder rather than occluded in PDMS. We observed complex mixtures with varying amounts and combinations of cross metathesis and isomerization products. Some reactions yielded mixtures that were too complex to distinguish the presence of any product.

The reactions with occluded Grubbs' catalysts cleanly yielded isomerization products, reactions with Grubbs' catalyst as a powder were more complex. The desired isomerization product was formed in moderate conversion for the phosphine oxides, ketones, and long chain alkyl alcohols. Other olefins with more distinct functional groups such as amides, ethers, esters, and phenol derivatives resulted in lower conversions to the desired isomerization product with large amounts of side products formed.

Table 3
The reaction of substrates shown in Fig. 5 with occluded Grubbs' first generation catalyst at 100 °C

Entry[b]	Substrate	Mole % catalyst	Product[a]	
			Isomerization[c]	Cross metathesis
1	**13**	2	88	10
2	**14**	1	85	13
3	**15**	1	95	0

[a] The ratio of products by crude ^{1}H NMR.

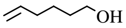
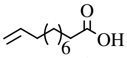
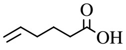
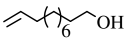
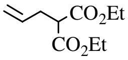
[b] The substrates were added to a degassed solution of 90% MeOH in H_2O with occluded Grubbs' first generation catalyst under N_2 and heated to 100 °C.

[c] The isomerization products were a mixture where the olefin isomerized between one and several times.

Occlusion in PDMS affected the product distributions for many substrates, but we wished to learn what effect occlusion had for substrates that reacted by metathesis with occluded Grubbs' catalyst. In our previous work, we demonstrated that some substrates selectively undergo cross metathesis with occluded Grubbs' catalysts using methanol/water solvents in yields from 63% to 87% [19]. These substrates were reacted with free Grubbs' catalyst in 90% methanol/water to study if they react by isomerization or metathesis when the catalysts is not occluded (Table 5).

The results in Table 5 demonstrate that olefins that react by metathesis with occluded Grubbs' catalysts yield a sig-

Table 5
Reaction of free Grubbs' catalysts in methanol/water with substrates that reacted by metathesis with occluded catalysts

Substrate[a]	Product distribution		
	Isomerization[b] (%)	Metathesis[b] (%)	Starting olefin[b] (%)
	0	100	0
	50	50	0
	[c]	[c]	[c]
	40	60	0
	50	20	30

[a] These reactions were carried out with Grubbs' second generation catalyst in 90% methanol/water under conditions similar to that in Table 4. These reagents all reacted by cross metathesis with occluded Grubbs' catalyst.

[b] Reactions were monitored by ^{1}H NMR and reported as % conversion.

[c] This reaction yielded a complex mixture of products.

Table 4
Reactions with free Grubbs' catalysts in methanol/water with substrates that isomerized with occluded Grubbs' catalysts

Substrate	Occluded Grubbs' catalyst	Free Grubbs' catalyst in methanol/water[b]		
	Isomerization[a] (%)	Isomerization[b] (%)	Metathesis[b] (%)	Starting olefin[b] (%)
1a	70	70	0	30
3a	99	80	0	0
4a	97	60	0	5
5a	99	30	50	10
6a	90	75	0	20
7a	90	75	0	0
8a	97	90	10	0
9a	99	[c]	[c]	[c]
10a	80	75	0	0
11a	70	[c]	[c]	[c]

[a] These are the crude yields for each product by NMR prior to chromatography. The isolated yields are shown in Table 1.

[b] These reactions were run at the same temperature, concentration, and times as those with occluded reactions. In these reactions, we added Grubbs' catalyst to the solvent as a powder rather than occluded in PDMS, which was the only difference in these reactions. The product conversions were determined by ^{1}H NMR.

[c] This reaction yielded a complex mixture of products.

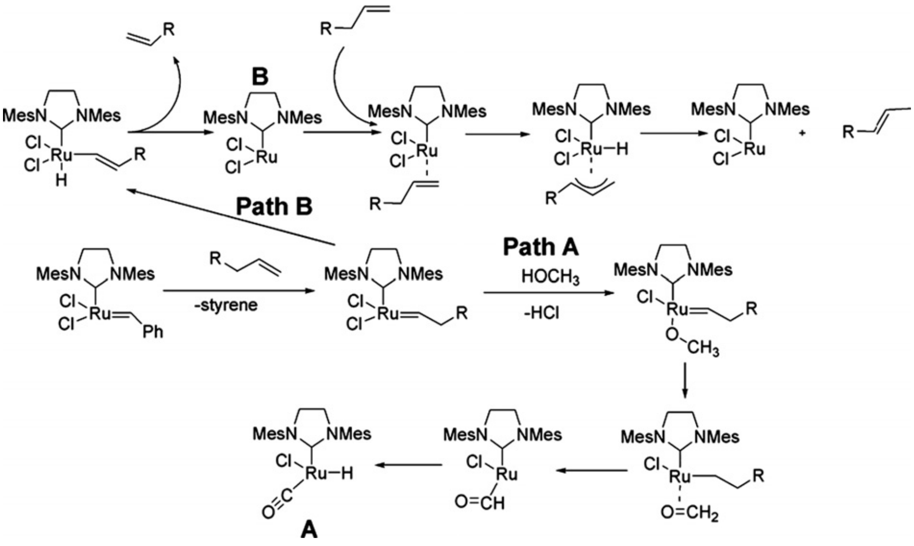


Fig. 6. Two pathways for the transformation of the Grubbs' second generation catalyst into a hydrogenation catalyst.

nificant amount of isomerization product when reacted with Grubbs' catalyst that was not occluded. This result demonstrates that the solvent is not the only factor influencing the outcome of this reaction, it is necessary to consider whether the catalysts are occluded in PDMS.

Reactions with occluded or freely dissolved Grubbs' catalysts in the presence of methanol/water appear to be a complex system where multiple variables effect the product distribution. Product distributions were influenced by temperature, solvent, substrate, and occlusion of catalyst. Our results are important because we described how some reagents could selectively react by isomerization or metathesis with occluded catalysts. Although more work will be necessary to fully elucidate a mechanism, we will propose a mechanism for how these transformations may occur.

Isomerization catalysts from Grubb's catalysts is not new and has been reported to proceed by multiple pathways [3,4,6–10,13,32,33]. Of the pathways proposed, the ones that are most relevant for our work are the pathways that proceed by degradation of the catalyst in the presence of protic solvents and a pathway that proceeds by reaction of a vinylic ether with Grubbs' catalysts at elevated temperatures. Although the catalysts are initially occluded in PDMS, methanol and water have a finite solubility in PDMS and may catalyze the degradation of the Grubbs' catalysts which then leaches from PDMS.

Mol has shown that the first and second generation Grubbs' catalysts decompose in the presence of protic solvents and oxygen into ruthenium hydrides [3,33]. These new molecules are catalytically active toward isomerization. In our mechanism shown in Fig. 6, path A corresponds to the mechanism proposed by Mol for the formation of a ruthenium hydride, molecule **A**, by protic solvents. Path B corresponds to another valid mechanism similar to that proposed by others where an isomerization catalyst, molecule **B**, is formed by β-hydride extraction from the ruthenium carbene [4,13,16,18]. Based on our current work, we cannot distinguish between these mechanisms and, in fact, believe that the mechanism is substrate dependent.

4. Conclusions

We described a method where we made the Grubbs' first and second generation catalysts react by isomerization or metathesis by either occluding them in PDMS or allowing them to be dissolved in methylene chloride. Certain functional groups such as allylic phosphine oxides, carbonyls, and ethers transformed occluded Grubbs' second generation catalyst into an isomerization catalyst that leached from PDMS to react in the solvent. We extended this work to demonstrate a method to turn occluded Grubbs' first generation catalyst into an isomerization catalyst by heating it to 100 °C.

This work is exciting as it demonstrates that PDMS is a new solvent for these catalysts that can affect their reactivity. This work allows one to choose to react substrates by metathesis or isomerization by whether the catalysts are occluded or not. In addition, this work is a part of an ongoing research program in our lab and others to occlude catalysts in PDMS to study their reactivity [19,34]. PDMS is an interesting matrix for catalysts as it allows small molecules to diffuse into it, is apolar, and can be readily molded into many different shapes. PDMS is a new "solvent" that strongly affects the types of reactions that are catalyzed by catalysts within their membranes. In future work we will describe how to extend this method to other catalysts and study how to control their reactivities.

Acknowledgements

We thank the Research Corporation, the American Chemical Society-Petroleum Research Funds, the American Cancer Society, and the University of Iowa for financial support.

References

[1] R.H. Grubbs, Handbook of Metathesis Catalysts, Wiley-VCH, Weinheim, Germany, 2003;
T.M. Trnka, R.H. Grubbs, Accts. Chem. Res. 34 (2001) 18;
K. Harries-Rees, Y. Chauvin, R. Grubbs, R. Schrock, Chem. World 2 (2005) 42;
R.H. Grubbs, Angew. Chem., Int. Ed. 45 (2006) 3760;
R. Schrock, Angew. Chem., Int. Ed. 45 (2006) 3748;
Y. Chauvin, Angew. Chem., Int. Ed. 45 (2006) 3740.

[2] C.W. Bielawski, R.H. Grubbs, Angew. Chem., Int. Ed. 39 (2000) 2903;
P. Schwab, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 100.

[3] M.B. Dinger, J.C. Mol, Organometallics (2003) 1089.

[4] M.K. Gurjar, P. Yakambram, Tetrahedron Lett. 42 (2001) 3633;
J. Louie, C.W. Bielawski, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 11312.

[5] J. Louie, R.H. Grubbs, Organometallics 21 (2002) 2153.

[6] C. Cadot, P.I. Dalko, J. Cossy, Tetrahedron Lett. 43 (2002) 1839;
B. Alcaide, P. Almendros, Chem. Eur. J. 9 (2003) 1259;
B. Alcaide, P. Almendros, J.M. Alonso, M.F. Aly, Org. Lett. 3 (2001) 3781.

[7] B. Schmidt, Angew. Chem., Int. Ed. 42 (2003) 4996;
B. Schmidt, Eur. J. Chem. (2003) 816.

[8] B. Schmidt, Chem. Commun. (2004) 742.

[9] K.A. Burdett, L.D. Harris, P. Margl, B.R. Maughon, T. Mokhtar-Zadeh, P.C. Saucier, E.P. Wasserman, Organometallics 23 (2004) 2027;
K. Nakashima, S. Okamoto, M. Sono, M. Tori, Molecules 9 (2004) 541;
S. Fustero, M. Sanchez-Rosello, D. Jimenez, J.F. Sanz-Cervera, C. del Pozo, J.L. Acena, J. Org. Chem. 71 (2006) 2706;
M. Arisawa, Y. Terada, M. Nakagawa, A. Nishida, Angew. Chem., Int. Ed. 41 (2002) 4732.

[10] S.H. Hong, D.P. Sanders, C.W. Lee, R.H. Grubbs, J. Am. Chem. Soc. 127 (2005) 17160;
M. Arisawa, Y. Terada, K. Takahashi, M. Nakagawa, A. Nishida, J. Org. Chem. 71 (2006) 4255;
B.R. McNaughton, K.M. Bucholtz, A. Camaano-Moure, B.L. Miller, Org. Lett. 7 (2005) 733.

[11] F.-D. Boyer, I. Hanna, Eur. J. Org. Chem. (2006) 471;
A. He, B. Yan, A. Thanavaro, C.D. Spilling, N.P. Rath, J. Org. Chem. 69 (2004) 8643.

[12] A. Furstner, O.R. Thiel, L. Ackermann, H.-J. Schanz, S.P. Nolan, J. Org. Chem. 65 (2000) 2204.

[13] B. Alcaide, P. Almendros, J.M. Alonso, Chem. Eur. J. 12 (2006) 2874.

[14] J.C. Sworen, J.H. Pawlow, W. Case, J. Lever, K.B. Wagener, J. Mol. Catal. A: Chem. 194 (2003) 69.

[15] H. Werner, C. Grunwald, W. Stuer, J. Wolf, Organometallics 22 (2003) 1558.

[16] A.E. Sutton, B.A. Seigal, D. Finnegan, M.L. Snapper, J. Am. Chem. Soc. 124 (2002) 13390.

[17] M. Arisawa, Y. Terada, M. Nakagawa, A. Nishida, Angew. Chem., Int. Ed. 41 (2002) 4732;
P. Formentin, N. Gimeno, J.H.G. Steinke, R. Vilar, J. Org. Chem. 70 (2005) 8235.

[18] D. Finnegan, B. Siegel, M. Snapper, Org. Lett. 8 (2006) 2603.

[19] M.T. Mwangi, M.B. Runge, N.B. Bowden, J. Am. Chem. Soc., in press.

[20] J.N. Lee, C. Park, G.M. Whitesides, Anal. Chem. 75 (2003) 6544;
G.M. Whitesides, MRS Bull. 27 (2002) 56.

[21] J.V. Crivello, S. Kong, J. Org. Chem. 63 (1998) 6745.

[22] M.G. Organ, H. Gheasemi, J. Org. Chem. 69 (2004) 695.

[23] J.S. Cowie, P.D. Landor, S.R. Landor, N. Punja, J. Chem. Soc., Perkins Trans. (1972) 2197.

[24] Y. Kobayashi, A.D. Williams, Y. Tokoro, J. Org. Chem. 66 (2001) 7903.

[25] P. Cuadrado, A.M. Gonzalez-Nogal, M.A. Sarmentero, Chem. Eur. J. 10 (2004) 4491.

[26] S.G. Alcock, J.E. Baldwin, R. Bohlmann, L.M. Harwood, J.I. Seeman, J. Org. Chem. 50 (1985) 3526.

[27] J.M. Kauffman, G. Moyna, J. Org. Chem. 68 (2003) 839.

[28] H.E. Blackwell, D.J. O'Leary, A.K. Chatterjee, R.A. Washenfelder, D.A. Bussman, R.H. Grubbs, J. Am. Chem. Soc. 122 (2000) 58.

[29] S. Dutta, M. Perring, S. Barrett, M. Mitchell, P.J.A. Kenis, N.B. Bowden, Langmuir 22 (2006) 2146.

[30] E. Roversi, F. Monnat, P. Vogel, Helv. Chim. Acta 85 (2002) 733.

[31] F. Bisaro, V. Gouverneur, Tetrahedron Lett. 44 (2003) 7133.

[32] P. Formentin, N. Gimeno, J.H. Steinke, R. Vilar, J. Org. Chem. 70 (2005) 8235.

[33] M.B. Dinger, J.C. Mol, Eur. J. Inorg. Chem. (2003) 2827.

[34] I. Vankelecom, K. Vercruysse, N. Moens, R. Parton, J.S. Reddy, P. Jacobs, Chem. Commun. (1997) 137;
I.F.J. Vankelecom, D. Tas, R.F. Parton, V. Van de Vyver, P.A. Jacobs, Angew. Chem., Int. Ed. 35 (1996) 1346;
A. Wolfson, S. Janssens, I. Vankelecom, S. Geresh, M. Gottlieb, M. Herskowitz, Chem. Commun. (2002) 388;
D.F.C. Guedes, T.C.O. Mac Leod, M.C.A.F. Gotardo, M.A. Schiavon, I.V.P. Yoshida, K.J. Cuiffi, M.D. Assis, Appl. Catal. A: Gen. 296 (2005) 120.