

*Supplementary Materials For:*

**Photolithographic Olefin Metathesis Polymerization**

Raymond A. Weitekamp, Harry A. Atwater, Robert H. Grubbs

*JACS 2013*

---

**Materials and Methods  
Supplementary Experiments  
Figures S1 – S3**

## Materials and Methods:

(H<sub>2</sub>IMes)(PPh<sub>3</sub>)(Cl)<sub>2</sub>RuCHPh was received as a research gift from Materia Inc. and converted to **1** via literature procedure.<sup>1</sup> All other chemicals were purchased from Sigma Aldrich. Printed photomasks were purchased from CAD/Art Services, Inc. (<http://outputcity.com>). Silicon coupons were ordered as a pre-diced 4" wafer from Ted Pella (Part # 16006). Dichloromethane, ethyl vinyl ether and 5-ethylidene-2-norbornene were first degassed by bubbling argon through for 15 minutes.

The lamp used was an 8-watt "MRL-58 Multiple Ray Lamp" from Ultra Violet Products (#UVP 95-0313-01). The 254 nm bulb used was a General Electric germicidal bulb (#GEG8T5, from <http://bulbtronics.com>), with a FWHM of only a few nm. The 352 nm bulb was an Eiko blacklight bulb (#WKF8T5BL, from <http://bulbtronics.com>), with a FWHM of approximately 50 nm. Samples were placed approximately 1.5" away from the bulb during exposure.

### *A standard PLOMP resist recipe:*

Compound **1** (1.3 mg) was placed under argon and dissolved in 2 mL dichloromethane. To this catalyst solution was quickly added 1.5 mL 1,5-cyclooctadiene, the solution became a semi-solid in 10 seconds and was allowed to react for 1 minute before quenching with 3 mL ethyl vinyl ether. The viscous solution was slowly stirred for 5 minutes, sealed under argon, and sonicated for 1 hour. The volatiles were removed on a rotary evaporator, to yield semisolid poly(COD), colored light yellow by the quenched catalyst (the photoactive vinyl ether complex). Ethylidene norbornene (10 mL) was added to this mixture, which was cooled to 0 °C and sonicated for 1 hour. The partially dissolved mixture was placed on an ice bath and stirred until fully dissolved, while allowing the bath to warm to room temperature. The result is a light yellow, viscous solution weighing approximately 10 grams.

### *General Film Casting Procedures*

1x1 cm silicon coupons were cleaned in a piranha solution (3:1 concentrated H<sub>2</sub>SO<sub>4</sub> : 30 % H<sub>2</sub>O<sub>2</sub>), rinsed with deionized water ("Nanopure"), isopropanol and acetone. (*Caution! Piranha solution reacts violently with organic matter.*) Before spin casting, the coupons were heated to 140-150 °C for 1-2 minutes to drive off adventitious moisture, cooled to room temperature under a stream of argon gas, and quickly loaded onto the spinner. While this pre-heating step was not always necessary, it led to the most reproducible results. Samples were spun between 1500 – 7000 RPM for 60 seconds to achieve films of varying thickness. These cast films should be exposed and developed quickly, prolonged delay after spinning lead to inconsistent results.

### *Specific conditions for the samples in Figures 2 & 3:*

The samples in Figures 2 & 3 were prepared by using various dilutions of the standard resist preparation outlined above. For Figure 2, 0.75 mL of the standard resist described above was diluted with 1.25 mL ENBE. The 2" diameter wafer was cleaned using the procedure outlined for the coupons, heated to 150 °C for 2 minutes and cooled

---

<sup>1</sup> Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2002**, *41*, 4035–4037.

under a stream of argon. Approximately 0.9 mL of the solution was used to cover the entire wafer, which was spun at 3500 RPM for 60 seconds. The film was irradiated through the mask for 15 minutes, and developed in hexanes for 90 seconds. For Figure 3, 1.00 mL of the standard resist described above was diluted with 0.1 mL ENBE. Approximately 0.1 mL of this solution was used to cover the 1 cm<sup>2</sup> coupons, which were spun at 7000 RPM for 60 seconds. The films were irradiated through the grid test mask for 10 minutes, and developed in 10% dichloromethane/hexanes for 2 minutes.

*Analytical equipment:*

Profilometry was performed on a Bruker DektakXT stylus profiler. Optical micrographs were obtained on a Zeiss Axio Observer inverted microscope equipped with a 10× objective. NMR spectra were recorded at room temperature on a Varian Inova 500 (at 500 MHz). The NMR spectra were analyzed on MestReNova software and are reported relative to CD<sub>2</sub>Cl<sub>2</sub> ( $\delta = 5.320$ ).

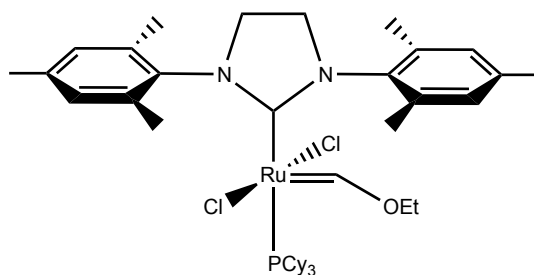
**Supplementary Experiments:**

To show that the catalyst is necessary for the resist to function, the standard resist prep was used except the polymer was precipitated into methanol to extract the quenched catalyst. Compound **1** (1.3 mg) was placed under argon and dissolved in 2 mL dichloromethane. To this catalyst solution was quickly added 1.5 mL 1,5-cyclooctadiene, the solution became a semi-solid in 10 seconds and was allowed to react for 1 minute before quenching with 3 mL ethyl vinyl ether. The viscous solution was very slowly stirred for 5 minutes, after which 5 mL methanol was added. The suspension was sonicated for 20 minutes, the brown solution was decanted and the off-white solid polymer was washed three times with 10 mL of methanol. The polymer was dried *in vacuo*, and dissolved in 10 mL 5-ethylidene-2-norbornene to afford a very pale yellow, viscous solution. This solution was cast as before and exposed for 6 minutes at 254 nm (4 times the standard exposure for the analogous resist) with no evidence of pattern formation. After developing with hexanes, a clean Si surface was recovered. As well, prolonged irradiation of pure ENBE at both 254 nm and 352 nm did not render any change in viscosity or other evidence of crosslinking. The addition of BHT (2,6-Di-*tert*-butyl-4-methylphenol) to the PLOMP resist did not appear to change its behavior, which suggests that the mechanism does not involve radicals.

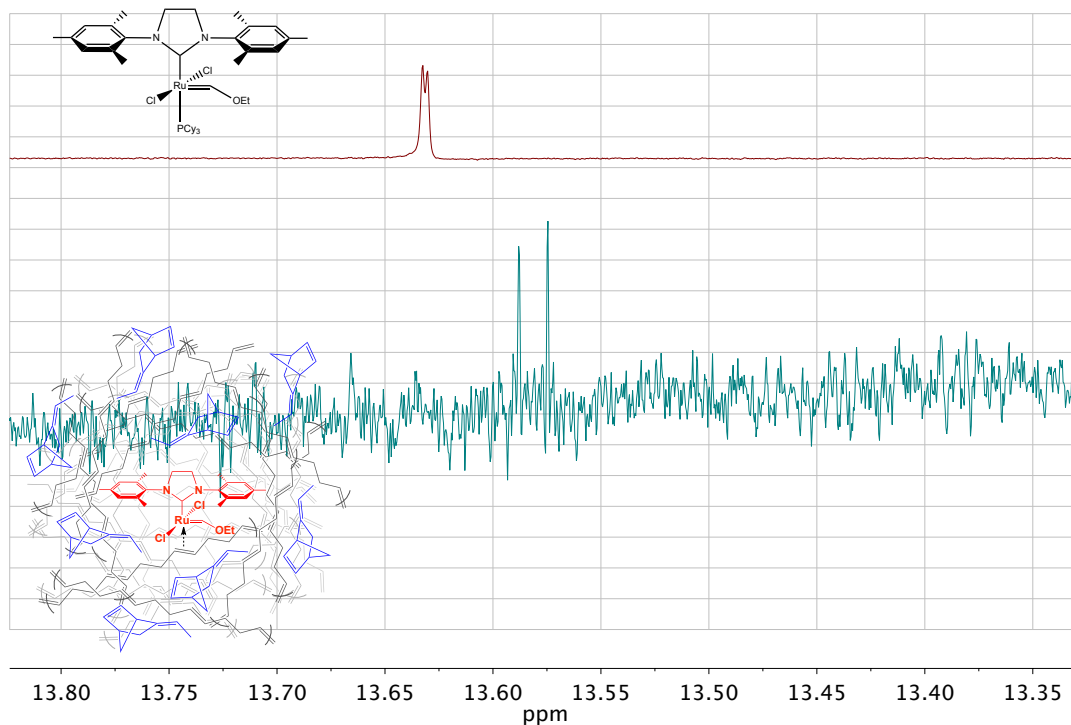
To support the hypothesis that the ruthenium vinyl ether complex is intact inside the PLOMP resist, the <sup>1</sup>H NMR spectra of a PLOMP resist and complex **2** were compared. The resist was prepared by the standard recipe above. Complex **2** was prepared as reported by Louie.<sup>2</sup> The spectra strongly support the proposed composition of the PLOMP photoresist; the alkylidene protons in each spectrum are less than 1 ppm apart (Figure S2).

---

<sup>2</sup>Louie, J.; Grubbs, R. H. *Organometallics* **2002**, *21*, 2153–2164.



**Figure S1** - The chemical structure of complex 2.

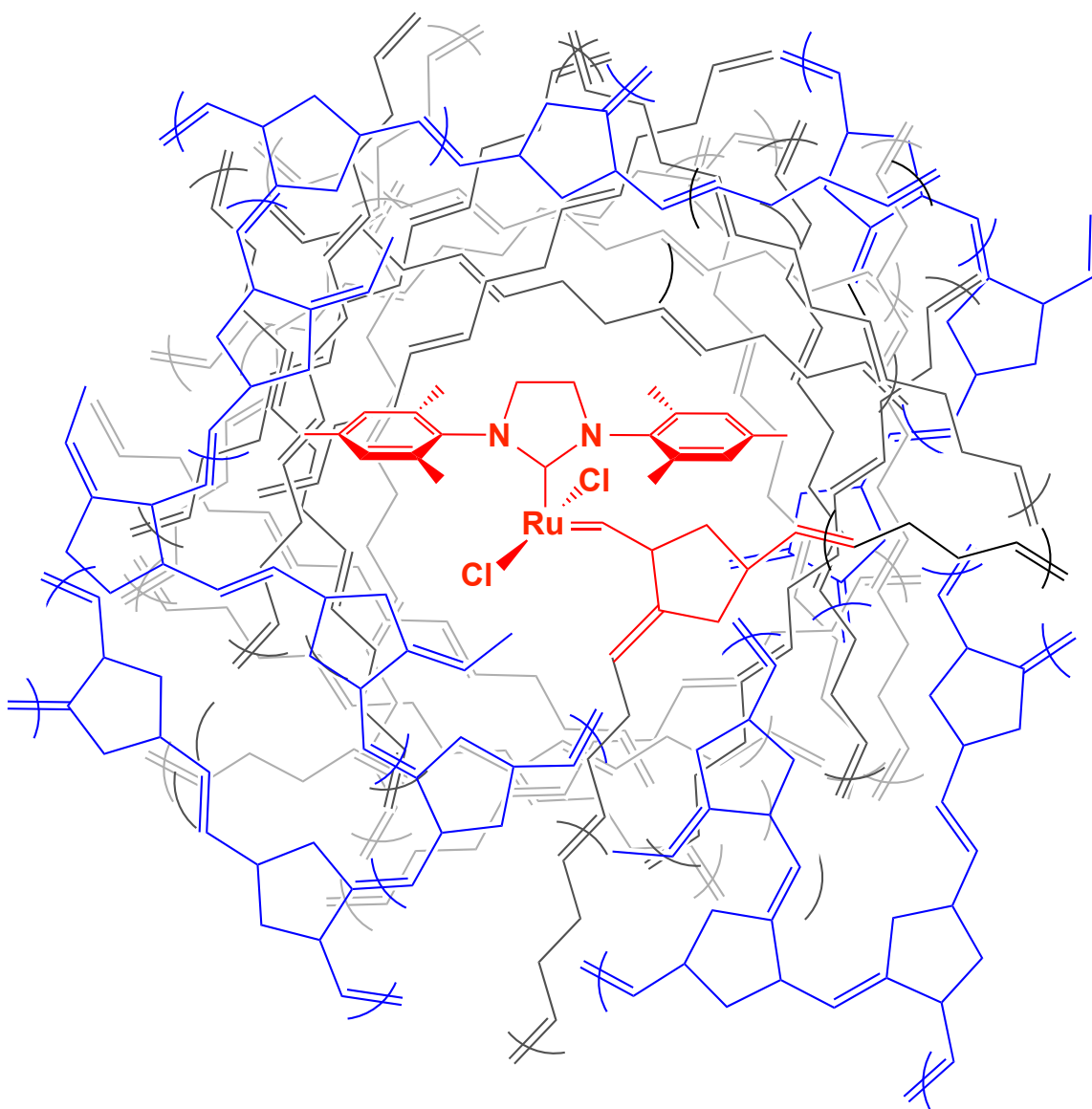


**Figure S2** –  $^1\text{H}$  spectra in  $\text{CD}_2\text{Cl}_2$  of complex 2 and a PLOMP photoresist. The region of the alkylidene proton is shown to highlight the similarity between the two. No other peaks were observed in the downfield region ( $\delta = 11 - 22$  ppm), suggesting that no other ruthenium alkylidene species are present in any significant quantity.

To support the hypothesis that dative bonding from the highly olefinic resist stabilizes the photoactive complex, two experiments were performed. First, the formally 14-electron ruthenium vinyl ether species can be prepared by quenching the 2<sup>nd</sup> generation Grubbs-Hoveyda catalyst with ethyl vinyl ether.<sup>3</sup> This complex immediately crosslinks ENBE, suggesting that there is a ligand present in the resist that stabilizes the photoactive catalyst. Obvious candidates for this ligand include the original pyridine ligands from complex 1 or the olefins in the viscous resist material. Wenzel and coworkers have demonstrated the ability to remove pyridine ligands using acids such as

<sup>3</sup> Li, J. *Caltech Ph.D. Thesis* 2012

trifluoroacetic acid (TFA).<sup>4</sup> If only the removal of a pyridine ligand was required to reactivate the complex, we would expect that crosslinking could also be triggered by acid. However, the addition of TFA lead to no change in viscosity after 24 hours. In fact, the PLOMP resist was still able to function in the presence of TFA; no change in behavior was observed for 254 nm photopatterning 30 minutes after adding TFA. While these experiments do not explicitly rule out the presence of a pyridine-coordinated complex, they strongly suggest that dative bonding from the surrounding olefins is the more likely mechanism of catalyst stabilization. This olefin could belong to the poly(COD), ENBE or excess ethyl vinyl ether.



**Figure S3** – A cartoon depicting the proposed crosslinking process of a PLOMP resist.

<sup>4</sup> Wenzel, A. G.; Blake, G.; VanderVelde, D. G.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 6429–6439.