# Solvent-Free Isomerization of Allylic Alcohols Catalyzed by a Rhodium Catalyst-Organic Framework

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## I. General Procedures

$^1$H-NMR and $^{31}$P-NMR were recorded using Varian Inova (300, 400, 500 MHz) spectrometers. $^1$H-NMR chemical shifts are reported in parts per million (δ) relative to TMS with the solvent as the internal reference. $^{31}$P-NMR chemical shifts are reported in parts per million (δ) relative to an external reference of 85% $H_3PO_{4(aq)}$.

Unless otherwise stated, all experiments were performed under an inert atmosphere using standard Schlenk and glove-box techniques. Argon and nitrogen gas (Praxair, 99.998%) were passed through a drying train containing 3Å molecular sieves and indicating Drierite$^{TM}$ before use. All allylic alcohols and Mosher's acid chloride were obtained from Sigma-Aldrich Co. and were distilled under a nitrogen atmosphere. The ROMP catalyst bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride and (*R*)-BINAP were obtained from Strem Chemicals, Inc. and used without further purification. $[RhCl(C_2H_4)_2]_2$ was synthesized according to literature procedures.[1] $BaSO_4$ (white reflectance) was obtained from Eastman Chemical Co., Inc. and washed thoroughly with $CH_2Cl_2$ and MeOH and dried under vacuum prior to use.

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[1] R. Cramer, *Inorg. Synth.* 1990, **28** (Reagents Transition Met. Complex Organomet. Synth.), 86-88.

## II. Synthesis of $BaSO_4$ Supported Rhodium Catalyst-Organic Framework

We recently reported this synthesis and a detailed analysis of the rhodium catalyst-organic framework. For more detailed information see reference 2.

### *Synthesis of [RhCl((R)-5,5'-dinorimido-BINAP)]$_2$*

Under a nitrogen atmosphere, a solution of 17.1 mg (1.81 x $10^{-5}$ mol) of rotamerically pure (*R*)-5,5'-dinorimido-BINAP in 0.5 mL of $CD_2Cl_2$ was added to a slurry of 3.6 mg (9.05 x $10^{-6}$ mol) $[RhCl(C_2H_4)_2]_2$ in 0.1 mL of $CD_2Cl_2$ in an NMR tube. The NMR tube was shaken, and occasionally purged with nitrogen gas for 30 minutes, before $^1$H-NMR and $^{31}$P-NMR spectra were obtained. Upon addition of the ligand solution to the $[RhCl(C_2H_4)_2]_2$ slurry, there was a rapid color change from yellow-orange to brick red, with accompanying evolution of ethylene gas. After identification by NMR, the compound was used immediately and without isolation as attempts at isolation resulted in decomposition of the product. The spectroscopic data was identical to the literature.[2] $^1$H-NMR (400 MHz, $CD_2Cl_2$) $\delta$ ppm 1.67 (d, J=8.4Hz, 2H), 1.81 (d, J=8.4Hz, 2H), 3.48-3.53 (m, 4H), 3.56-3.60 (m, 4H), 6.28 (dd, J=2.0Hz, 2H), 6.38 (dd, J=2.0Hz, 2H), 6.47 (d, J=4.8Hz, 2H), 6.57 (d, J=4.8Hz, 2H), 6.60-6.76 (m, 4H), 6.81-6.90 (m, 2H), 6.92 (d, J=7.2Hz, 2H), 7.05 (m, 2H), 7.22 (t, J=8.6Hz, 2H), 7.41 (m, 6H), 7.73 (br s, 4H), 7.98 (br s, 4H); $^{31}$P-NMR (161 MHz, $CD_2Cl_2$) $\delta$ ppm 50.77 (d, J=194.1Hz, 2P).

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[2] E. G. Corkum, M. J. Hass, A. D. Sullivan and S. H. Bergens, *Org. Lett.* 2011, **13**, 3522-3525.

### *Preparation of Rhodium Catalyst-Organic Framework*

In a typical experiment, 19.6 mg ($9.05 \times 10^{-6}$ mol) of [RhCl((*R*)-5,5'-dinorimido-BINAP)]$_2$ was prepared in 0.6 mL of $CD_2Cl_2$ in an NMR tube as described above. Under a nitrogen atmosphere, 14.1 µL of COE ($1.09 \times 10^{-4}$ mol) was added to the solution and the tube was shaken. The color of the solution remains brick red. This solution is then cannulated, under a nitrogen atmosphere, into a Schlenk tube equipped with a stir bar, and rinsed in with 0.5 mL of $CD_2Cl_2$. Next, 0.8 mg ($9.05 \times 10^{-7}$ mol) of *trans*-$RuCl_2(PCy_3)_2(=CHPh)$ (Grubbs' 1st Generation) is dissolved in 0.5 mL of $CD_2Cl_2$, yielding a purple solution. This solution is then cannulated, under a nitrogen atmosphere, into the Schlenk tube. The vessel is then sealed and placed with moderate stirring, into an oil bath at 40°C for 24 hours. After 24 hours, an aliquot of the mixture was taken and NMR spectra recorded confirmed that polymerization was complete. The spectroscopic data was identical to the literature.[2] This mixture was then diluted with 10 mL more of $CH_2Cl_2$.

### *Deposition of Rhodium Catalyst-Organic Framework onto $BaSO_4$*

10 g of $BaSO_4$ was washed consecutively with 4 x 50 mL of $CH_2Cl_2$ followed by 3 x 50 mL of MeOH, and then dried under vacuum at room temperature overnight.

1.633 g ($6.99 \times 10^{-3}$ mol) of the washed and dried $BaSO_4$ in a 250 mL round-bottom flask equipped with a stir bar was back-filled with nitrogen gas. To this flask was added 20 mL of $CH_2Cl_2$, which was stirred slowly to create a slurry. The reaction mixture that contained the catalyst-organic framework prepared above was cannulated onto the $BaSO_4/CH_2Cl_2$ slurry, creating a tan-coloured mixture. The polymer reaction vessel was rinsed with 3 x 5 mL of $CH_2Cl_2$ that were added to the slurry and the slurry was stirred for 20 minutes to achieve an even distribution of the catalyst-organic framework on the $BaSO_4$. The solvent was then removed slowly under reduced pressure (1 hour) with rapid stirring at room temperature. After the removal of the solvent to dryness, the flask was dried further under vacuum for 1 hour. After the initial drying, the supported catalyst was rinsed with 3 x 50 mL of MeOH to remove any polymerized COE and low molecular weight polymer. The MeOH portions were decanted off the support with a cannula under a nitrogen atmosphere. Filtration was avoided to prevent plugging of the filter. After the final rinse, the catalyst was dried for 1 hour under vacuum, then immediately transferred to the glove-box, where it was stored in the freezer. NMR spectra recorded in $CD_2Cl_2$ of the pumped down MeOH residue showed only poly(COE) present. There was also no observable signal in the $^{31}P$-NMR spectrum. The final loading of rhodium was 12 mg per gram of $BaSO_4$ support.

## III. Representative Procedure for Rhodium Catalyzed Isomerization of Allylic Alcohols

For these experiments, the allylic alcohols were bubbled with either nitrogen or argon gas for 30 minutes prior to use.

In a typical experiment, under nitrogen or argon atmosphere, a Schlenk flask equipped with a Teflon$^{TM}$ valve was charged with 0.0987 g of supported catalyst (1.16 mg of "[RhCl((*R*)-5,5'-dinorimido-BINAP)]$_2$", 5.27 x 10$^{-4}$ mmol) and 5.27 x 10$^{-3}$ mmol of the desired Ag salt. Next, the desired amount of allylic alcohol was added to the catalyst/Ag mixture and the Schlenk flask was sealed with the Teflon$^{TM}$ valve. The Schlenk flask was then placed in an oil bath set to the desired temperature. Conversion was monitored by $^1$H-NMR of aliquots.

## IV. Homogeneous Catalyzed Isomerization of 5

For this experiment, **5** was bubbled with nitrogen gas for 30 minutes prior to use.

1.2 mg of $[RhCl((R)\text{-}BINAP)]_2$ ($7.88 \times 10^{-4}$ mmol) was weighed out in a glove box into an NMR tube equipped with a rubber septa. 1.5 mg ($7.88 \times 10^{-3}$ mmol) of $AgBF_4$ was weighed out in a glove box into a Schlenk flask equipped with a Teflon$^{TM}$ valve. The catalyst was then dissolved in 1 mL of **5** and transferred to the Schlenk tube, followed by another 1 mL rinse of **5**. The remainder of **5** (4.55 g, 63.1 mmol, 5.45 mL total) was then added directly to the Schlenk flask. The flask was then sealed and stirred in an oil bath set to 70ºC. Conversion was monitored by $^1$H-NMR of aliquots.

## IV. Determination of Kinetic Resolution

For these experiments, the $CDCl_3$ and pyridine were distilled over $CaH_2$ prior to use.

### *Racemic Substrate 5*

1 equiv of substrate **5** was weighed out into an NMR tube and sealed with a rubber septa. 0.7 mL of $CDCl_3$ was then added to the NMR tube. Next, 6 equiv of pyridine were added to the NMR tube and this was shaken for 5 minutes. Finally, 3 equiv of Mosher's acid chloride ((*S*)-(+)-α-methoxy-α-trifluoromethyl-phenylacetyl chloride) was added to the NMR tube and this was periodically shaken for 30 minutes before being analyzed by $^1$H-NMR.

### *Aliquots from Allylic Alcohol Isomerization Reactions*

The above outlined procedure was repeated for aliquots taken from the isomerization of substrate **5**. The $^1$H-NMR spectra obtained were then compared to the racemic $^1$H-NMR spectrum of **5** to determine the % *ee* of the remaining unreacted allylic alcohol.