

Synthesis and Characterization of Versatile Ruthenium Catalyst via Benchtop NMR



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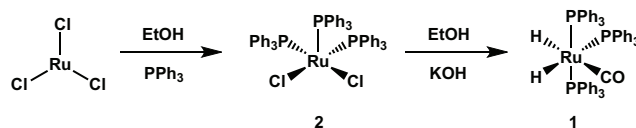
INTRODUCTION

Organometallic chemistry is a branch of chemistry that focuses on studying chemical compounds containing at least one metal – carbon bond. Additionally, these compounds typically involve a metal atom or ion bonded to one or more organic ligands.¹ Organometallic compounds are used in various fields, including pharmaceuticals, material science and catalysis. In the pharmaceutical industry, organometallic compounds can be used in catalytic reactions which increase the efficiency of synthetic routes used to produce medicinal compounds that contribute to aiding human health.²

Dihydridocarbonyltris(triphenylphosphine)ruthenium(II), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$, **1**, is an example of an important organometallic catalyst that can be used in a multitude of reactions. For example, this catalyst can be used in a specific step that involves the cleaving of the C–H bond in chemical reactions.³ This mechanistic step can aid in streamlining the arylation of aromatic compounds.³ Nuclear Magnetic Resonance (NMR) spectroscopy is a viable way for students and instructors to comprehend the spectroscopic properties of this catalyst. Notably, with 1D ^1H and ^{31}P experiments, students are provided with the tools to observe the unique multinuclear coupling between hydride and phosphorous in the proton spectrum of this catalyst.

The procedure was adapted from an article in *Organometallics* published by Samouei and Grushin.⁴ This procedure is an air-sensitive, two-step synthesis that can be further adjusted to suit the time and resources of the instructor. The purpose of this experiment is to expose students to the synthesis and characterization of an important organometallic catalyst, **1**. Furthermore, by using benchtop NMR instrumentation students can set experiments themselves with the aid of instructors. This builds on relevant NMR experience that is advantageous in more advanced courses and industrial settings, creating more hands-on experience making the transition to these fields smoother.⁵

The first step of this two-step reaction involves the reduction of ruthenium(III) chloride hydrate from Ru(III) to Ru(II) by the addition of ethanol (EtOH), and triphenylphosphine (PPh_3). The second step of the reaction proceeds by the synthesized intermediate, **2**, and the addition of 4 equivalents of potassium hydroxide (KOH) in ethanol to form the desired product, **1**, as seen in Scheme 1.



Scheme 1. Reaction scheme for the two step organometallic reaction of ruthenium chloride in ethanol to yield catalyst, **1**.

To note, for this sample experiment, the synthesis of the product was conducted from the second step for simplicity. All NMR experiments, ^1H and ^{31}P , were acquired using a Nanalysis 100PRO benchtop NMR instrument.

Procedure

Materials

Tris(triphenylphosphine)ruthenium(II) dichloride, 97%, was purchased from BLD Pharmatech. Ethanol, 90%, was purchased from Acros Organics. Potassium hydroxide, 90%, was purchased from Sigma Aldrich. Distilled water was purchased from a local grocery store. Furthermore, chloroform- d , 99.8%, was purchased from Deutero GmbH. All reagents were used without further purification.

Instrumentation

All the NMR data was obtained using a Nanalysis 100 MHz instrument. The ^1H experiments were performed using the following acquisition parameters: spectral width, 40 ppm; spectral center, 0 ppm; number of number of points, 16384; scans, 32; dummy scans, 0; interscan delay, 1 second; pulse angle, 90° ; receiver gain, auto. The ^{31}P experiments were performed using the following acquisition parameters: spectral width, 100 ppm; spectral center, 50 ppm; number of number of points, 16384; scans, 32; dummy scans, 0; interscan delay, 1 second; pulse angle, 90° ; receiver gain, auto. All spectra were manually corrected for phase and baseline distortions using the MestReNova software (v14.2.3).

Synthesis

Ruthenium Catalyst

A 50 mL three-neck round-bottom flask was equipped with a stir bar and reflux condenser. 475 mg of the intermediate compound, **2**, was added to the flask, followed by the addition of potassium hydroxide (110 mg, flakes, 4 equiv.) and 37.5 mL of ethanol. Under a nitrogen atmosphere, the mixture was stirred at room temperature for half an hour in which a green precipitate formed in solution. After this, the temperature of the reaction was set to 60°C for another half-hour in which a yellow precipitate formed in solution. Then, the reaction was refluxed for 2 hours.

After reflux, the reaction mixture was removed from stirring and heat to allow the mixture to cool to room temperature. The resulting yellow precipitate was separated by vacuum filtration and then washed with ethanol (2×5 mL), distilled water (2×5 mL), and ethanol (2×5 mL). The pale-yellow precipitate was then air-dried and isolated. No further purification was necessary.

Results and Discussion

50 mg of the product was dissolved in 0.6 mL of chloroform- d . The sample was vortexed and transferred to an NMR tube which can be used for all NMR experiments.

The zoomed-in ^1H NMR spectrum of the product, **1**, pertaining to the hydrides is shown in **Figure 1**. The hydride at $\delta(^1\text{H}) = -6.8$ ppm, is a triplet of doublets of doublets ($J = 30, 15, 6$ Hz) and the hydride at $\delta(^1\text{H}) = -8.8$ ppm, is a doublet of triplets of doublets ($J = 74, 28, 6$ Hz). This coupling information aids in identifying the location of the hydrides in relation to the other ligands in the compound.

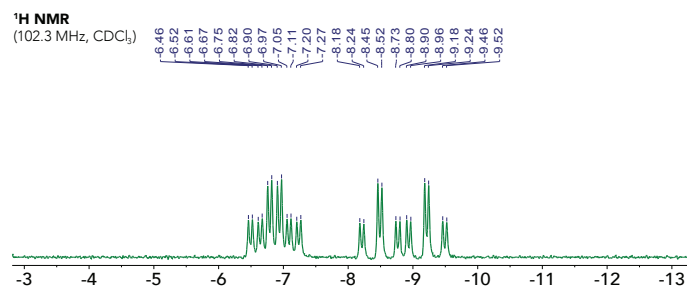


Figure 1. ^1H (102.3 MHz) NMR spectrum of the hydride region of ruthenium catalyst (**1**) in chloroform- d .

In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product (**Figure 2**), **1**, the signals to note are the doublet at $\delta(^{31}\text{P}) = -56.7$ ppm ($J = 18$ Hz) and triplet at $\delta(^{31}\text{P}) = -44.5$ ppm ($J = 18$ Hz). This confirms the presence of two equivalent and another inequivalent triphenylphosphine in the octahedral structure of the product.

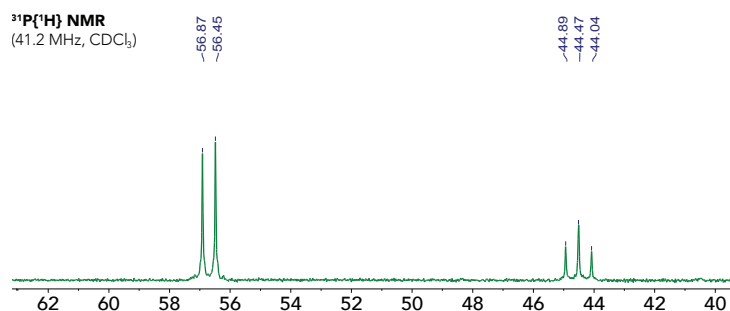


Figure 2. $^{31}\text{P}\{^1\text{H}\}$ (41.2 MHz) NMR spectrum of catalyst (**1**) in chloroform- d .

Recommendations

As noted by Samouei and Grushin in *Organometallics*, to ensure a high yield of the product, absolute ethanol and fresh potassium hydroxide are recommended as reagents. It is also recommended to double the quantity of reagents and time as outlined in the synthesis to increase the yield of the product. 70-100 mg of the product, **1**, in 0.6 mL of chloroform- d is recommended for NMR analysis.

Conclusion

The adapted procedure utilizes greener reagents, in contrast to older methods, which reduces the potential hazards and carbon footprint of the reaction. The procedure offers a method for students and instructors to characterize a significant catalyst used in different industries. Notably, **1** is a catalyst used in a multitude of reactions, allowing for this catalyst to be used in other experimental syntheses. Overall, this undergraduate experiment exploits the use of benchtop NMR and elevates the entire laboratory experience.

References

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Bay 1, 4600 – 5 Street NE
Calgary, Alberta, Canada
T2E 7C3

Tel: +1.403.769.9499

nanalysis.com

sales@nanalysis.com

