

Introducing Catalysis to Undergraduate Chemistry Students: Testing a Ru–NHC Complex in the Selective Dehydrogenative Coupling of Hydrosilanes and Alcohols

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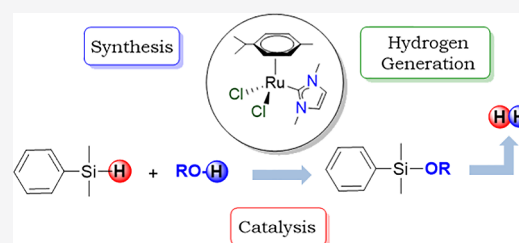
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Supporting Information

ABSTRACT: This work describes a complete laboratory experiment that involves the synthesis of a ruthenium complex $[\text{Ru}(p\text{-cym})(\text{NHC})\text{Cl}_2]$ (NHC = N-heterocyclic carbene) and its use as a catalyst for the coupling of hydrosilanes and alcohols. The hydrogen gas produced in the reaction is measured using an inverted buret to trap the gas which allows student to monitor the evolution of the reaction. The complete experience constitutes an opportunity to focus on experimental skills and fundamental concepts in organometallic chemistry and catalysis.

KEYWORDS: Upper-Division Undergraduate, Inorganic Chemistry, Hands-On Learning/Manipulatives, Synthesis, Catalysis, Organometallics, NMR Spectroscopy



INTRODUCTION

Catalysis is a fundamental concept that must be taught in every undergraduate chemistry program. By definition, a catalyst is a substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction. In addition, it is both a reactant and product of the reaction. The use of catalysts is recommended in the 12 principles of green chemistry proposed by Prof. Paul Anastas.¹ Consequently, catalysis has been a subject of intense research in both academic and industrial settings.

One of the most important types of catalysts are the organometallic complexes. To develop this type of catalyst, a fundamental knowledge of organometallic chemistry and a specialized training in Schlenk techniques are required. In this report, we describe a complete experiment that deals with the synthesis of a ruthenium complex bearing an N-heterocyclic carbene ligand (compound **3**, see Figure 1) and its application

- The coupling of hydrosilanes and alcohols is a practical catalytic reaction for teaching purposes in a laboratory session.
- The reaction shows quick kinetics, so multiple experiments can be carried out the same day.
- The reaction is very selective and the only products are a silyl ether and molecular hydrogen.
- The reaction generates hydrogen gas, which is regarded as an energy vector for the near future.⁵
- As hydrogen gas is produced, the reaction is monitored using an inverted buret. Gas chromatography or ¹H NMR may also be used for monitoring the reaction evolution, but the inverted buret is suitable due to the low cost of the system and the immediacy of the results.

The catalytic reaction between hydrosilanes and alcohols represents a straightforward methodology for the production of pure molecular hydrogen. Different catalysts based on iridium,⁴ manganese,⁶ iron,⁷ or zinc⁸ have been reported to carry out the dehydrogenative coupling between hydrosilanes and alcohols. Manganese and zinc catalysts are interesting as they are based on earth abundant metals. The major drawback when using these species is that high temperatures, high catalyst loadings, or long reaction times are needed to effectively catalyze the silane–alcohol coupling, which is not convenient for a teaching

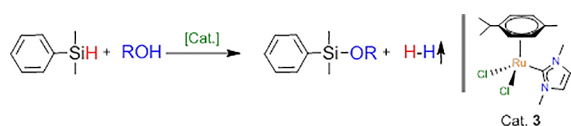


Figure 1. Dehydrogenative coupling of hydrosilanes and alcohols.

in catalysis. This laboratory experiment derives from our own research in the field of developing efficient catalysts for hydrogen storage in the form of liquid organic hydrogen carriers (LOHCs).^{2–4} Complex **3** is active in the selective dehydrogenative coupling between hydrosilanes and alcohols to produce silyl ethers and hydrogen (Figure 1). This transformation is an interesting reaction in different regards:

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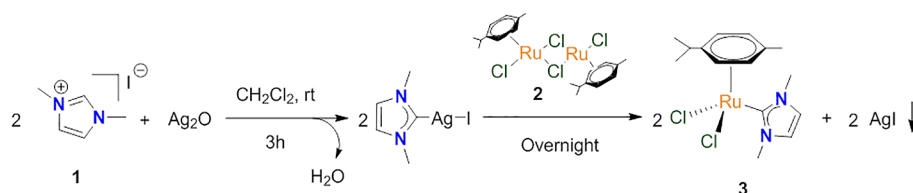


Figure 2. Synthesis of complex 3.

laboratory experiment. The formation of silyl ethers mediated by iron catalysts is highly desirable as iron is an abundant and cheap metal. However, the reaction needs the use of additives that have to be separated from the reaction media. Recently, complexes of type $[\text{IrCp}^*(\text{NHC})\text{Cl}_2]$ have been reported to effectively catalyze the dehydrogenative coupling between hydrosilanes and alcohols.⁴ The required catalyst loadings are low (≈ 0.1 mol %), and the reaction proceeds at room temperature, without additives and using the alcohol as reactant and solvent. The problem with iridium is its high price that prevents its use in large scale systems. As an alternative, complexes of type $[\text{Ru}(p\text{-cym})(\text{NHC})\text{Cl}_2]$, based on a cheaper metal such as ruthenium, catalyze the silane–alcohol coupling reaction at even lower loadings and temperatures.³ Furthermore, these complexes can be obtained in high yields and are stable in the solid state and in solution, which make them adequate for using in an undergraduate chemistry laboratory.

■ PEDAGOGICAL GOALS

This integrated catalytic laboratory experiment will help students to improve or acquire the skills expected in the organometallic and catalysis field for graduate students.

During this experiment students should:

- Become familiar with synthesis of organometallic complexes over air-sensitive techniques.
- Learn about dangers and cautions in the use of the solvents and reagents involved in each session.
- Gain knowledge about the use of liquid organic hydrogen carriers (LOHCs) as a source of green hydrogen storage.
- Learn how to measure the progress of reactions when a gas is evolved.
- Practice their knowledge of ^1H NMR from an experimental point of view.
- Acquire basic concepts of catalysis such as turnover number (TON) and turnover frequency (TOF) in homogeneous catalysis.
- Evaluate the experimental results, make conclusions, and acquire a critical point of view with respect to the results obtained.

■ EXPERIMENT DESCRIPTION

The exercise described here is designed for students with experience in general laboratory practices. The use of Schlenk techniques is not required, but improved yields are obtained in the syntheses of metal complexes. All reagents and metal precursors are commercially available and could be used for comparative purposes.

The complete procedure is designed for two consecutive laboratory sessions. The first day is dedicated to the preparation of the ruthenium complex that acts as a catalyst (see Figure 2). The procedure involves the reaction in

dichloromethane between the imidazolium salt **1** (120 mg, 0.53 mmol) and silver oxide (61.4 mg, 0.26 mmol) to obtain the silver–carbene intermediate. This intermediate is not isolated and reacts in situ with the ruthenium dimer **2** (162 mg, 0.26 mmol), to produce the catalyst **3**. This first session should be completed in 4 h. Better yields of catalyst **3** are obtained after overnight stirring. Session one also includes the theoretical introductions to basic concepts of catalysis that will be used in session two. The second day (3 h) deals with the isolation of the organometallic complex **3**, its characterization by ^1H NMR, and the catalytic studies. After overnight stirring, complex **3** is isolated after filtration over Celite and recrystallization from a CH_2Cl_2 /hexane mixture. Having the catalyst **3** in hand, its activity was tested in the dehydrogenative coupling of hydrosilanes and alcohols to produce silyl ethers and hydrogen gas. To that end, 1 mmol of silane is reacted with 1 mL of alcohol in the presence of complex **3**. Dimethylphenyl silane and methanol are used as model substrates, and an inverted buret is used to measure the gas evolution and follow the reaction kinetics. Experiments with different catalyst loadings are performed to check the influence of this parameter on the reaction. The yields of the catalytic reactions are calculated on the basis of the amount of gas collected, and the purity of the generated silyl ether is checked by ^1H NMR.

Before the first laboratory session, it is advisable to do a prelab seminar to give a general view of the experience and to let the students become familiar with the material used in air-sensitive techniques such as Schlenk flasks, vacuum lines, or Dewar containers (a set of pictures of these materials is included in the Supporting Information). After the experience, a complete final laboratory report must be written. It should include an introduction, goals of the different experiments, experimental details (calculations, yields), reaction profiles obtained in the catalytic reactions, ^1H NMR spectra, conclusions, and related literature. Some indications to prepare the final report are included in the Supporting Information (Section F).

■ HAZARDS

Dichloromethane is harmful in cases of eye contact, ingestion, or inhalation, and it is a carcinogen. 1,3-Dimethylimidazolium iodide is harmful by inhalation, in contact with skin, and if swallowed. It is also irritating to the eyes, respiratory system, and skin. Silver(I) oxide is irritating to the eyes, respiratory system, and skin. $[\text{Ru}(p\text{-cym})\text{Cl}_2]_2$ is harmful if swallowed, causes serious eye irritation, and is harmful to aquatic life with long-lasting effects. Celite constitutes an inhalation hazard owing to the small particle size. Hydrogen gas is highly flammable. Adequate ventilation and removal of ignition sources are mandatory when doing the catalytic reactions. Furthermore, as hydrogen gas is evolved, catalytic reactions must not be performed in closed systems under any circumstance. Carefully check the measuring system shown

in the [Supporting Information](#) before starting any catalytic experiment. Alcohols are flammable and toxic. Hydrosilanes are flammable, toxic, and corrosive. It is truly important to check all of the glass material. It must not show chips or cracks in order to avoid implosions when Schlenk techniques are carried out. In addition, liquid nitrogen can cause severe burns. Adequate PPEs and containers must always be used. In general, a laboratory coat, gloves, and safety glasses must be worn at all times.

RESULTS AND DISCUSSION

Day 1: Transmetalation Reaction and Introduction of Catalysis Concepts

The traditional method for the preparation of M–NHC complexes requires the use of strong bases to produce the free NHC that then is coordinated to an appropriate metal precursor. Alternatively, the transmetalation procedure using silver oxide allows the coordination of the NHC ligand to different metals under mild reaction conditions.⁹ This strategy is straightforward, and its easy implementation in a teaching laboratory has already been demonstrated.¹⁰ During the following section, the students have the possibility to acquire knowledge in the use of air-sensitive techniques.

The synthesis of the ruthenium complex **3** involves, in a first step, the reaction between the imidazolium salt **1** and silver oxide to form the silver–carbene intermediate product (see [Figure 2](#)).¹¹ This intermediate can be reacted “in situ” with $[\text{Ru}(p\text{-cym})\text{Cl}_2]_2$ in the second step to afford the desired ruthenium complex **3**.¹² The formation of the silver–carbene product has to be done under the exclusion of light, as silver(I) compounds have been reported to be reduced to silver(0) in the presence of light. By using this approach, students become familiar with transmetalation reactions and avoid the use of strong and sensitive bases such as KO^tBu or KHMDS frequently used for the isolation of free carbenes and its coordination to metals.^{13,14}

The experimental procedure for the synthesis of the Ru–NHC complex requires the addition of 2 equiv of the commercially available imidazolium salt **1** and 1 equiv of silver(I) oxide in a Schlenk flask fitted with a Teflon cap and covered with aluminum foil. Then, the Schlenk flask is connected to a double-manifold Schlenk line and is evacuated and refilled with nitrogen three times. Then, dry dichloromethane is added, and the mixture is stirred at room temperature for 3 h. After this time, without removing the aluminum foil and under a light stream of nitrogen, the ruthenium precursor $[\text{Ru}(p\text{-cym})\text{Cl}_2]_2$ (**2**) is added, and the mixture is stirred overnight at room temperature. Catalyst **3** is stable in the solid state and in dichloromethane solution for several hours. Although complex **3** is stable, the reaction is performed under an inert atmosphere to avoid the degradation of unstable intermediates. Thus, the use of an expensive apparatus that is not commonly found in teaching laboratories (Schlenk line) can be replaced by a primitive air-free apparatus.¹⁵ Additionally, commercially dry dichloromethane can be expensive for a teaching laboratory, and distillation of dichloromethane over phosphorus pentoxide is not always possible. Instead of that, dichloromethane could be dried over activated molecular sieves. Day one is also devoted to the introduction of the catalytic reaction under study (see [Figure 1](#)).

The catalytic coupling between hydrosilanes and alcohols generates silyl ethers and molecular hydrogen at high rates when using Ru–NHC complexes as a catalyst. The evolution of H₂ gas allows the monitoring of the reaction by using an inverted buret system (vide infra). Prior to starting the experiment, students calculate the volume of hydrogen produced according to the reaction depicted in [Figure 1](#) and considering that they will use 1 mmol of substrate. For simplicity, the volume of hydrogen produced is obtained using the ideal gas equation ($V = nRT/P$). Other equations that incorporate deviation from the ideal gas may be used,¹⁶ but the experimental differences are not appreciable under these reaction conditions, however, they could be used for introducing the concepts and evaluating the differences.

Other important parameters that are shown to the students and calculated are the catalyst loading and the turnover number (TON) and turnover frequency (TOF) of the catalyst. For the sake of brevity, the explanation of these two concepts is included in the [Supporting Information \(Section B.1\)](#).

Day 2: Isolation of Complex **3**, NMR Characterization and Catalytic Studies

The transmetalation of the “in situ” formed silver carbene to ruthenium should be completed overnight. The formation of an insoluble precipitate of silver iodide (AgI) constitutes visual evidence that the reaction has been successful. At this stage of the workup, the absence of light is not necessary. The crude reaction was filtered over Celite to remove the AgI, and the Celite was washed with clean dichloromethane (2 × 10 mL). Before the filtration, it is necessary to wet the Celite with dichloromethane. After the removal of the insoluble salt, the resulting mother liquors were concentrated to ca. 5 mL using a rotary evaporator. Addition of 10 mL of *n*-hexane afforded the precipitation of complex **3** as an orange solid which was filtered, washed with *n*-hexane, and dried under vacuum for 15 min. The vast majority of the students that performed the experiment were able to obtain complex **3** in good yield (30–80%). Typical mistakes that could be done by students and led to a decrease in final yield are the following:

- (1) They dropped the round-bottom flask into the bath while using the rotatory evaporator.
- (2) After the filtration over Celite, they discarded the mother liquors instead of the solid (AgI).

The characterization and purity of compound **3** are checked by ¹H NMR spectroscopy. The NMR sample was prepared by dissolving ca. 5 mg of **3** in 0.6 mL of deuterated chloroform in an NMR tube. This experiment provides students with a good opportunity to practice the theoretical concepts of NMR learned at the classrooms. In a first step, the students were asked to predict which would be the protons of interest to check if the reaction had happened. After that, they are required to assign every signal of the spectrum they acquired. In general, all of the students obtained **3** in high purity, and in just a few cases, minor impurities related to the presence of dichloromethane or unreacted **2** appeared, most probably due to mistakes in weighing the amount of **2** added in the transmetalation step. Then, in order to double-check that the assignment of signals was correct, spectra of pure compounds **1** and **3** were delivered to students (see [Supporting Information](#)). A comparison of the ¹H NMR spectra of the commercially available compound **1** and the isolated compound **3** constitutes an efficient tool for evaluating the changes in the reaction. The ¹H NMR spectrum of compound

1 (see Section E.1 of the Supporting Information) shows three singlets that correspond with the three different inequivalent protons of the molecule. It is in agreement with the 2-fold symmetry of the compound, with the signal for the acidic NCHN proton ($\delta = 8.91$ ppm) being the most characteristic. The absence of the acidic signal in the ^1H NMR spectrum of complex 3 (see Section E.2 of the Supporting Information) and the presence of two singlets ($\delta = 6.97$ and 3.98 ppm) that correspond with the protons of the imidazole ring and the methyl groups, respectively, constitute the first evidence that the metalation has occurred.

Complex 3 was tested as a catalyst in the coupling between silanes and alcohols. The catalytic silane/alcohol coupling is versatile and allows the use of different hydrosilanes and alcohols. In this session, dimethylphenylsilane and methanol are the selected substrates.

The experimental setup for measuring the gas produced during the reaction is shown in Figure 3. The system consists



Figure 3. Experimental setup for the measurement of the molecular hydrogen evolved.

of one buret connected through the bottom to a graduated cylinder with two connections. This cylinder is linked to the reaction through the upper connection. The system is filled with water until the water level remains at approximately the mark of 50 mL of the buret.

To carry out the catalytic reaction, a 50 mL two-necked round-bottom flask was charged with the appropriate amount of 3 (see Section B.1 of the Supporting Information) and with 1 mL of methanol. One neck of the flask was connected to the measurement system, and the other one was closed using a rubber septum. Then, dimethylphenylsilane (1 mmol) was added, whereupon the reaction immediately produced a stream of hydrogen gas. With the aid of a chronometer, students recorded the generated volume at intervals of 3 s, so then a reaction profile can be built (see Section F.2.2 of the Supporting Information). Once the evolution of gas had stopped, the solvent was removed under vacuum, and the remaining oily product was analyzed by ^1H NMR. The spectra for the formed silyl ether and the hydrosilane that serve as substrate can be found in the SI (see Section E.3 of the Supporting Information).

Three different experiments (without catalyst and using catalyst loadings of 0.125 and 0.25 mol %) should be

performed to analyze the effect of the loading on the kinetics of the reaction. As an alternative, the alcohol used can be modified to ethanol, propanol, or butanol in order to check the effect of modifying the length of the alcohol chain. After the experiments, students were asked to write and deliver a final laboratory report (see Section F of the Supporting Information).

CONCLUSIONS

This complete experiment constituted a good approach to the procedure usually followed for researchers working in catalysis. The process starts with the synthesis and characterization of a metal complex using air-sensitive techniques to then evaluate the catalytic activity of the prepared compound and analyze the influence of modifying different parameters in the catalytic reaction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at <https://pubs.acs.org/doi/10.1021/acs.jchemed.1c00032>.

Student information section including safety notes, general comments, and experimental section; notes for the instructors including calculations, NMR data, catalysis; timeline of experiments; pictures of the experimental procedure; ^1H NMR spectra; and details on the final laboratory report including contents of the laboratory report and reaction progress profile (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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