Supporting Information

The Synthesis of Ruthenocene- A Methodology Appropriate for the Inorganic Undergraduate Curriculum

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Student Instructions:

ORGANOMETALLIC COMPLEXES
Synthesis of Ruthenocene ($Ru(C_5H_5)_2$), Bis(cyclopentadienyl)Ruthenium(II)

Introduction

The discovery of ferrocene, $Fe(C_5H_5)_2$ and subsequent determination of its sandwich structure in the early 1950's, led to the development of modern organometallic chemistry. This was quickly followed by the discovery of the analogous Ru and Os complexes.[1] These sandwich complexes and their derivatives are examples of metallocene complexes, with ferrocene being the first example. The general definition of metallocenes are complexes with a metal sandwiched between two planar carbon ring ligands.[2] A stricter definition is also employed, where metallocene complexes only consist of two cyclopentadienyl ($C_5H_5^-$, C_p) ligands sandwiching the metal.[3] Metallocenes have found importance in the fields of biological chemistry, medicine, catalysis and non-linear optics.[1]

All metallocene complexes adopt a structure based on the "sandwich" form found in $M(C_5H_5)_2$ (M = Fe, Ru, Os) (see Figure S1). Bent metallocene structures occur when the valence state of the metal allows for additional ligands, such as Cl.[4]

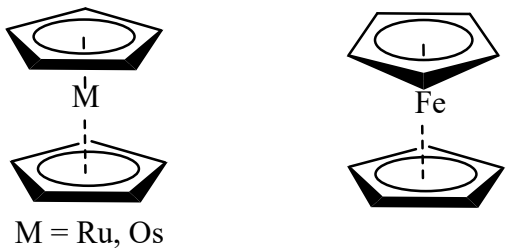

Figure S1.

In this experiment, you will make the ruthenocene complex and examine the nature of the metal-ligand bond through NMR. Cp is an aromatic ligand with 1-5 π electrons available to bond to the metal center, in either a η^1, η^3 or η^5 fashion. These three bonding modes will render different H's in the Cp as equivalent, resulting in predictable ^1H and ^{13}C NMR patterns.

To address the environmental impact of our chemistry laboratories, experiments have been revisited to introduce elements of the Principles of Green Chemistry.[5] In this experiment we have modified published methods,[6] to develop a new procedure that minimizes the number of synthetic steps and material required to make ruthenocene.

Experimental Procedure

Safety Reminder: This reaction must be carried out in a fume hood.

To a 50 mL round bottom flask, add 10 mL of 95% ethanol. Purge the ethanol with nitrogen for at least 5 min (Attached a Pasteur pipette to the nitrogen line and place it in the solution). After the ethanol is flushed with nitrogen, cap the flask with an inlet tube connected to the nitrogen line. This is to maintain a nitrogen environment in the round bottom flask. Quickly, remove the inlet tube to add 200 mg of $RuCl_3 \bullet xH_2O$ and 225 mg of zinc dust (A blue solution may be seen. What is it?) followed by 1.0 mL of freshly prepared cyclopentadiene, using a graduated pipette. Replace the inlet tube and allow the mixture to stir at room temperature for 1.5 hours under a nitrogen environment.

After the stirring period, the inlet tube is removed as the reaction is no longer air sensitive (ruthenocene is air stable). Remove the solvent on the rotary evaporator to obtain the crude product containing the ruthenocene. Your instructor/TA will provide further instruction on the correct use of the rotary evaporator.

Sublimation:

Ruthenocene readily sublimes at atmospheric pressure. After the removal of the solvent, using a spatula transfer the crude product to a Petri dish bottom. As ruthenocene is the only portion of the crude solid soluble in acetone, rinse the round bottom flask with ~0.5 mL of acetone. Add the acetone solution to the Petri dish bottom containing the crude product. Allow the acetone to evaporate in the fume hood. During this time, prepare a 400 mL beaker filled with ice.

When most of the acetone has evaporated, place the Petri dish bottom on the hotplate and turn on the hotplate to the lowest setting for 5 min to aid in the complete removal of the acetone. This will give a pale brown solid. Cap the Petri dish bottom with the Petri dish cover (record the weight of the Petri dish cover), and place the ice filled beaker on top (see Figure S2).

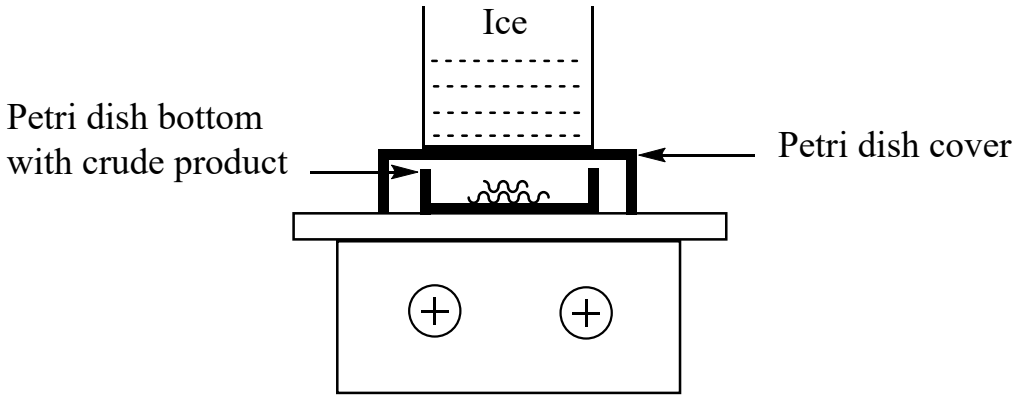

Figure S2: Ruthenocene sublimation set-up.

With the addition of heat, ruthenocene will sublime from the crude product and collect on the Petri dish cover. If condensation initially forms on the Petri dish cover, remove it, wipe it dry with a paper towel, and replace the cover before any ruthenocene sublimes. Slowly raise the temperature of the hotplate (5-10 min. to get to ~70°C). Around 70°C sublimation will start. Keep increasing the temperature until 100-105°C. At 105°C sublimation quickly occurs.

After 5 min. at 105^{o}C you can assume sublimation is complete. A white film/crystals will have formed on the Petri dish cover.

Carefully remove the Petri dish cover to check if ruthenocene has collected on the sides of the bottom dish. (Note: Some of the ruthenocene solid will be "feathery" and easily lost.) If the ruthenocene has crystalized on the sides of the bottom Petri dish, scrap the crystals into the middle of the dish, replace the cover and ice filled beaker, and continue the sublimation at 100-105 ^{o}C for another 5 min. Repeat this step if necessary.

When the side of the bottom dish is free of ruthenocene, the cover can be removed. Replace it with another Petri dish cover (and ice filled beaker) and allow the sublimation to continue while you weigh the collected product. A further small amount of product may be collected on the second cover.

Weigh the first Petri dish cover containing the collected ruthenocene. Collect the ruthenocene in into a pre-weighed vial. Remove the second Petri dish cover and recover any ruthenocene collect into the same pre-weighted vial. Determine the amount of product collected and hand in your sample.

Characterization:

Obtain an infrared spectrum (ATR) and melting point of your product. You will be provided with ^{1}H and ^{13}C NMR spectra and a mass spectrum of your product.

References

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