

EXPERIMENT 6

Methyl Migration to Coordinated CO

REFERENCES

Meisler, G.L., Tarr, D.A. Inorganic Chemistry, 3rd Ed., Prentice Hall, Upper Saddle River, NH, 2004, Chapters 13 and 14.

SAFETY RECOMMENDATIONS

Cyclopentadienyl iron dicarbonyl dimer: Volatile solid. Harmful if swallowed, inhaled or absorbed through the skin.

Tetrahydrofuran: Harmful if swallowed, inhaled or absorbed through the skin.

Sodium naphthalide solution: air sensitive, potentially pyrophoric liquid. Handle under nitrogen

Iodomethane: Toxic if swallowed or in contact with skin Causes skin irritation. May cause an allergic skin reaction. Causes serious eye damage. Fatal if inhaled. Suspected of causing cancer.

Triphenylphosphine: Harmful if swallowed. Causes mild skin irritation.

INTRODUCTION

When alkyl groups and carbon monoxide are bound to a transition metal, a reaction can occur where the alkyl group migrates to the CO to create a formyl ($-\text{C}=\text{O}(\text{R})$) ligand. This carbon-carbon

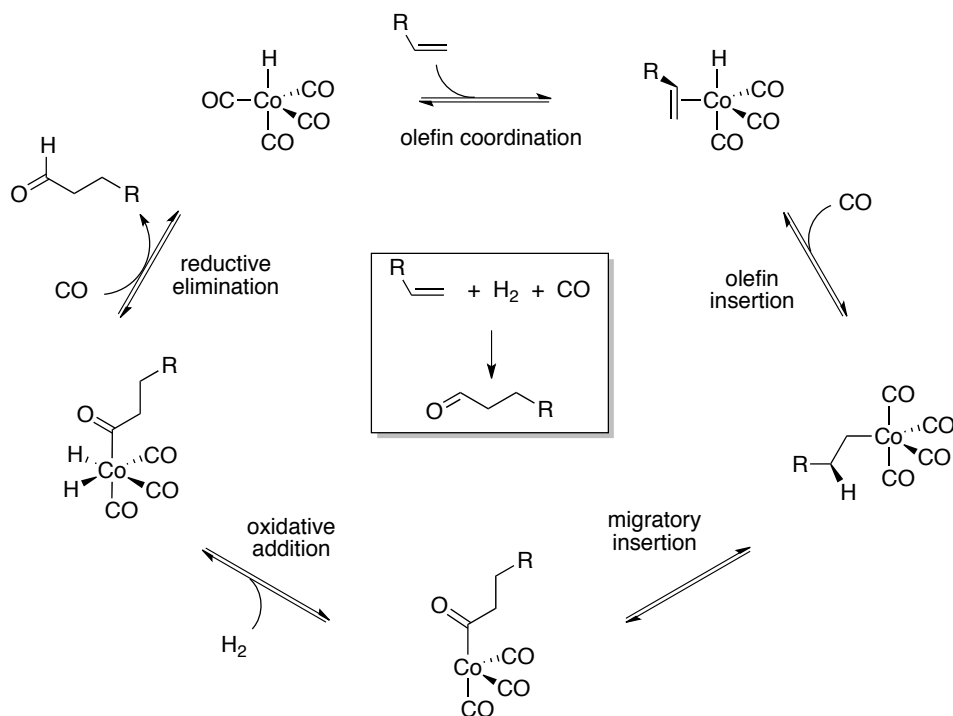
bond forming process is one of the most fundamental reactions in organometallic chemistry. This reaction has Michigan roots as Closson, Kozikowski, and Coffield who worked in the research laboratories of the Ethyl Corporation in Detroit Michigan described the first example of an alkyl carbonyl complex (**1**) in 1957. Their reason for studying this chemistry was to find antiknock additives that could replace tetraethyl lead.

In the same journal issue, they showed that in the presence of CO, a new compound, **2**, was produced and it possessed an acyl ligand that resulted from migration of the methyl ligand to a coordinated CO ligand. They found that this process was reversible. This reaction has come to be known as **migratory insertion**.



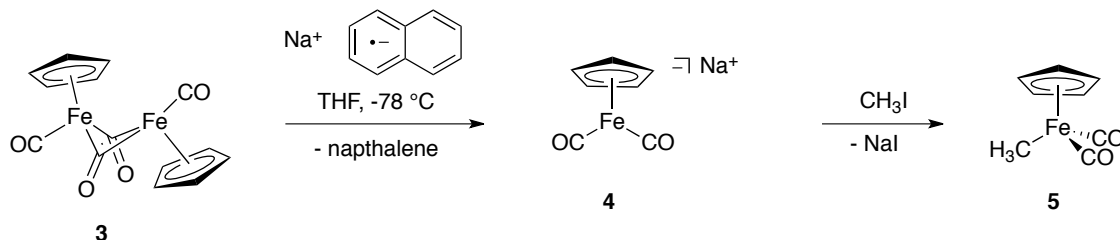
The formation of a carbon-carbon bond from CO under neutral conditions is remarkable. As is often the case in science, new discoveries often have applications beyond the original objective of the research. In the case of migratory insertion, a catalytic process for the synthesis of aldehydes from olefins, hydrogen gas, and CO was eventually developed (Scheme 1).

Scheme 1

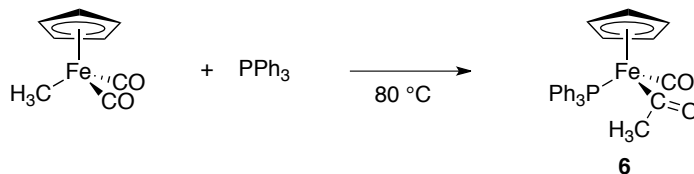


Aldehydes are high valuable chemicals. They are used in the flavor and fragrance industry and are intermediates in numerous chemical processes.

In this experiment, you will generate an anionic iron carbonyl (**4**) from which you will synthesize an iron methyl complex (**5**). You will characterize **5** by ^1H NMR and IR spectroscopies.



The migratory insertion of methyl to CO will be accomplished by heating a mixture of **5** and triphenylphosphine (PPh_3) in the solid state. You will characterize the resulting acyl complex, **6**, by ^1H and ^{31}P NMR and IR spectroscopies.



PROCEDURE

1st Lab Period

Part A: Preparation of Cyclopentadienylmethyliron dicarbonyl (**5**)

NOTE: All experiments should be carried out in the hood.

A solution of 2.5 mmol of the dimeric complex **3** is prepared in 10 mL of THF. The solution is transferred to a round bottom flask fitted with a septum and is purged with nitrogen gas. The solution is cooled to -78°C and 5 mmol of sodium naphthalide solution in THF is slowly added over 20 min to the stirred solution. The reaction flask is removed from the bath and warmed to room temperature.

The resulting metalate solution is then cooled to $-78\text{ }^{\circ}\text{C}$, and 2 equivalents of methyl iodide is added dropwise via syringe. The solution is removed from the bath and warmed to room temperature. The reaction mixture is then heated to $40\text{ }^{\circ}\text{C}$ for 2 h after which the THF is removed on the rotovap to afford the crude product.

2nd Lab Period

Part A: Preparation of Cyclopentadienylmethyliron dicarbonyl (5) continued.

Extract the crude product with pentane and filter. Rotovap the resulting orange solution to afford solid compound 5.

Product Characterization: Record the ^1H NMR spectrum of 5 in CDCl_3 and record an IR spectrum of the solid.

Part B: Preparation of compound 6.

Weigh equimolar amounts of compound 5 ($\sim 0.10\text{ g}$) and triphenylphosphine in a round bottom flask. Prepare an intimate solid mixture by dissolving the compounds in methylene chloride and removing the solvent on the rotovap. It is important to make sure all of the solvent is removed.

Place the flask under N_2 and heat the solid to $80\text{ }^{\circ}\text{C}$ for 4 hours. You will not have time to complete the reaction during this lab period. 30 minutes before the end of the lab period, remove to flask from the bath and allow it to cool to room temperature. Record the time that the flask was heated.

3rd Lab Period

Part A: Preparation of compound 6, continued.

Resume heating the solid until the 4 h total is reached.

Product Characterization: Measure the ^1H and ^{31}P NMR spectra of 6 in CDCl_3 and record an IR spectrum of the solid.

In your report, address the following points:

1. Assign the formal oxidation states of Fe in compounds **4**, **5**, and **6**. Show your reasoning.
2. Assign the ^1H NMR spectrum of **5**. Explain why the cyclopentadienyl methyl resonance chemical shifts deviate from those of cyclopentadiene and propane.
3. Assign the IR spectrum for compound **5**. Provide an explanation for the number of bands you observe.
4. Give a detailed mechanism for the formation of **6** from **5**. The correct mechanism has intermediate(s) and requires more than one step.
5. Assign the ^1H and ^{31}P NMR spectra of **6**. How does the methyl chemical shift compare to that for acetone? Explain the difference in chemical shift between free and coordinated triphenylphosphine.
6. Assign the IR spectrum for compound **6**. Provide an explanation for the number of bands you observe and rationalize difference in energies relative to the absorptions you saw in compound **5**.