Synthetic, Structural, Kinetic and Thermodynamic Study of $Mo(CO)_4(PR_3)_2$

ABSTRACT

The synthesis of the title organometallic compound is accomplished by the student. A cis-trans isomerization can be investigated by isolating one isomer, then heating to give the second; the two isomers are idetified and characterized by IR spectroscopy.

Equipment

Characterization is done by IR spectroscopy. Piperidine reactions should be done in a fumehood.

Safety Hazards

Piperidine and $Mo(CO)_6$ are toxic. Halogenated solvents are carcinogenic. Heptane and methanol are flammable.

Year Level: 3rd-year organometallic
Student time required: two to three 3-hour lab periods
Instructor time required: ??

Technician notes? Available upon request
Study question solutions? Available upon request
Contact: Greg Spivak (greg.spivak@lakeheadu.ca)

Lakehead
UNIVERSITY

Chemistry 3371: Inorganic Chemistry II Laboratory Manual

Instructor: G. Spivak
Department of Chemistry
Faculty of Science and Environmental Studies

Experiment 2:

# Synthetic, Structural, Kinetic and Thermodynamic Study of $Mo(CO)_4(PR_3)_2$

Purpose of the Experiment

In this experiment, students will use IR spectroscopy to study the kinetics and thermodynamics of the *cis-trans* isomerization of $Mo(CO)_4(PR_3)_2$ (R = alkyl or aryl). Students will learn to use IR data to assist in determining the geometry of a metal complex.

Introduction

Infrared spectroscopy is a useful tool for providing insight into the electronic environment around the metal in a complex, as well as determining the structural geometry of metal complexes (*e.g.*, metal carbonyls). In the latter case, the *number* of IR signals observed in a spectrum can provide information on the relative positions of the ligands in a metal complex. More specifically, using IR data to determine molecular geometry depends on the *symmetry* of the complex.

Carbonyl complexes can be studied readily by IR spectroscopy since the C-O vibration (*i.e.,* $\nu(CO)$) generally falls in a convenient region in the IR spectrum (~2200-1600 cm^{-1}). Recall that in order for a vibrational mode to be infrared active, there must be a change in dipole moment of the molecule. Not all vibrations result in a change in dipole moment and, thus, do not appear in the IR spectrum. For example, a metal complex containing two CO ligands might have them arranged in the following manner:
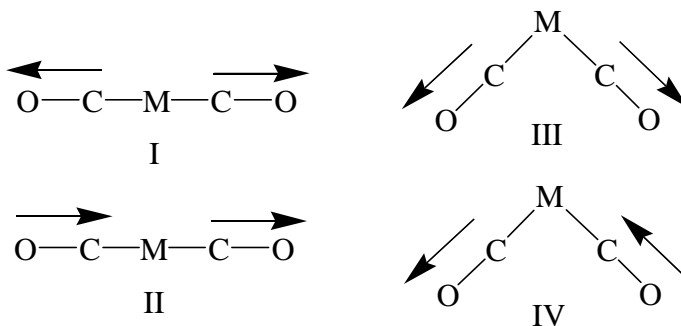
In cases I and II, the CO ligands are arranged linearly, however only the asymmetric vibration of II would yield a change in dipole moment of the overall complex. Hence, example I is IR-inactive (*no* signal observed) while II is IR-active (a signal *is* observed). In cases III and IV, the CO ligand are arranged in a non-linear fashion. Notice now that both the symmetric vibration of III and the asymmetric vibration in IV would result in a change in dipole moment of the complex. Hence, both III and IV are IR active.

As said earlier, the number of C-O IR bands provides structural information for a particular metal carbonyl complex. The exact number of IR signals can be predicted using the method of group theory, however this subject is beyond the scope of this course. Summarized below are the structures and corresponding numbers of C-O signals observed for complexes containing *four* CO ligands (*e.g.,* $Mo(CO)_4(PR_3)_2$). This information will help you determine the geometries of the kinetic and thermodynamic products in the reactions studied as part of this experiment:

IR signals = 1   IR signals = 4   IR signals = 1

IR signals = 3   IR signals = 4
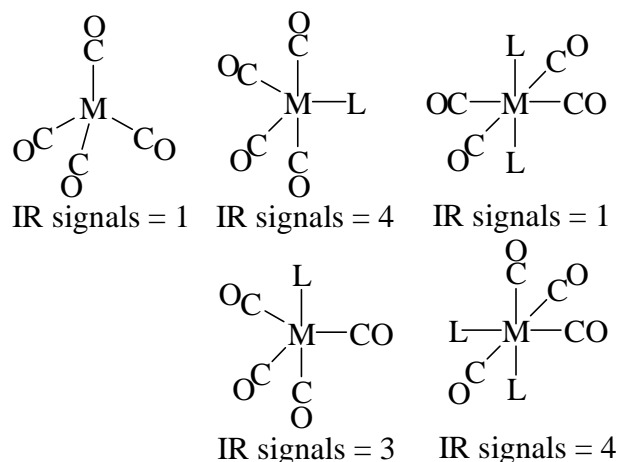
Experimental Procedure

Special Notes and Safety Precautions

Gloves must be worn during all manipulations in this experiment. The metal complex $Mo(CO)_6$ is highly toxic. If contact is made with the skin, be sure to wash the area immediately and thoroughly. Piperidine is also toxic and similar precautions must be taken. Heptane, methanol and toluene are flammable solvents. Care must be taken when using these solvents. Be sure all ignition sources are extinguished prior to using these solvents. Chloroform and dichloromethane are toxic solvents and must be handled with care. Be sure to wash any areas on your skin that may come in contact with these solvents.

The required laboratory time for this experiment is **2-3 periods**.

Synthesis of Mo(CO)₄(piperidine)₂.

Before the phosphine complexes $Mo(CO)_4(PR_3)_2$ can be prepared, the precursor complex $Mo(CO)_4(piperidine)_2$ must be prepared first.
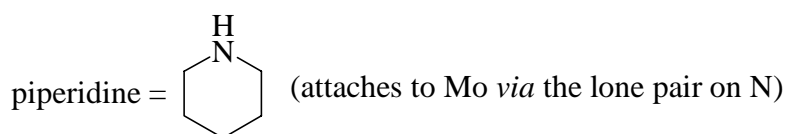
piperidine =   (attaches to Mo *via* the lone pair on N)

This procedure must be performed in the fumehood. In a 50 mL round-bottomed flask containing a stir-bar, add $Mo(CO)_6$ (about 2 g, **weighed accurately**) followed by heptane (20 mL) and excess piperidine (5 mL). Fit the flask with a reflux condenser (be sure to use a little grease on the joint) and reflux the mixture for 2.5 hours using a hot oil bath. After this time, filter (Büchner) the yellow solid **while the mixture is hot** and wash the solid with heptane (2×10 mL). Allow the product to dry over the week in a lab locker. Record the yield and calculate the yield based on the amount of $Mo(CO)_6$ used.

Synthesis of $Mo(CO)_4(PPh_3)_2$ (Isomer A).

This procedure must be performed in the fumehood. In a 100 mL round-bottomed flask containing a stir-bar, add $Mo(CO)_4(piperidine)_2$ (about 1 g, **weighed accurately**) and triphenylphosphine (1.5 g). Next, add dichloromethane (20 mL), fit the flask with a condenser (grease the joint) and reflux the mixture for 30 minutes using a hot oil bath. Allow the mixture to cool to room temperature and then filter (Büchner) (**use a <u>small</u> filter flask that is clean!**). Next, add methanol (50 mL) to the filtrate and cool the mixture in ice. Finally, collect the crystals that form by filtering using a small glass filter frit, wash with methanol (2×10 mL) and allow the crystals to air-dry. The product can be recrystallized from $CHCl_3$/methanol in ice **if necessary**; consult with the lab demonstrator. Record the yield and calculate the yield based on the amount of $Mo(CO)_4(piperidine)_2$ used. Record the IR spectrum of the product (Nujol).

Thermal Isomerization of $Mo(CO)_4(PPh_3)_2$ (Isomer B).

This procedure must be performed in the fumehood. In a 50 mL round-bottomed flask containing a stir-bar, add $Mo(CO)_4(PPh_3)_2$ (Isomer A, about 0.5 g, **weighed accurately**) followed by toluene (15 mL). Fit the flask with a condenser (grease the joint) and reflux the mixture for 30 minutes using a hot oil bath. Allow the mixture to cool to room temperature, and then add chloroform (30 mL). Filter (Büchner) the mixture (**be sure to use a <u>small</u> filter flask that is clean!**) and add excess methanol (60 mL) to the filtrate. Cool the mixture in ice and collect the crystals that form using a small glass filter frit. Wash the product with methanol (2×10 mL) and allow the crystals to air-dry. The product can be recrystallized from $CHCl_3$/methanol in ice **if necessary**; consult with the lab demonstrator. Record the yield and calculate the yield based on the amount of $Mo(CO)_4(PPh_3)_2$ used. Record the IR spectrum of the product (Nujol).

Final Report

The report should include all measurements (*e.g.,* weighings, etc.) and calculated yields, colours of the products, and the two IR spectra. **You need only concentrate on the IR absorptions pertaining to the CO ligands (*i.e.*, between *ca.* 2200-1600 cm^{-1}) when examining the peaks in your IR spectra.** The following literature reference is useful in interpreting the IR spectra: *Inorganic Chemistry* **1978**, volume 17, p. 2680. Include discussions on the following:

(1)   What are the structures of Isomer A and Isomer B? How do you know?

(2)   Isomer A is the kinetic product (the first product formed in these reactions), however it can be converted to the more thermodynamically stable Isomer B. Why might Isomer B be the more stable isomer?

(3)   How might you account for the lability (*i.e.,* they are easily removed) of the piperidine ligands in $Mo(CO)_4(piperidine)_2$?

References

1.   Darensbourg and Kump, *Inorg. Chem.* **1978**, *17*, 2680.