

# UCD Chem 124L: Lab Manual

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## Licensing

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*A detailed breakdown of this resource's licensing can be found in [Back Matter/Detailed Licensing](#).*

## CHAPTER OVERVIEW

### 1: Preface and Acknowledgements

#### Preface

This course is designed to give you an opportunity to experiment with inorganic compounds derived from the main group elements, the transition metals and nanomaterials. We hope that this experience is going to motivate you to get engaged in chemical research.

#### Acknowledgements

We thank the developers of this course: Prof. Philip Jessop, Dr. Dara Gilbert, Mr. Richard Brown, Prof. Frank Osterloh, Prof. Susan Kauzlarich, Prof. Philip Power and Prof. Marilyn Olmstead.

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## 1.1: Original Sources of Experiments

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Experiment 8: *Preparation of  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  (dppe) and  $\text{NiCl}_2(\text{dppe})$*

Experiment 11: *Metal-Metal Quadruple Bonds in Chromium (II) Acetate*

Experiment 12: *The Paramagnetic Complex  $\text{Mn}(\text{acac})_3$*

Experiment B: *Synthesis and Properties of Silver Nanowires*

Experiment H: *Synthesis and Hydrogenation with Wilkinson's Catalyst*

Experiments 8, 11, and 12 are from the assigned textbook, *Synthesis and Technique in Inorganic Chemistry, A Laboratory Manual*, Third Edition, Girolami, G. S., Rauchfuss, T. B., Angelici, R. J. **1999**, University Science Books. Experiment 11 is modified to prepare  $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$  instead of the Mo analog.

Experiment B is adapted from Hu, L., Kim, H. S., Lee, J.-Y., Peumans, P., Cui, Y. Scalable Coating and Properties of Transparent, Flexible, Silver Nanowire Electrodes. *ACS Nano* **2010**, 4, 2955-2963 for background and synthetic procedure (first or second paragraph).

Experiment H is adapted from Experiment 34 in Szafran, Z.; Pike, R. M.; Singh, M. M. *Microscale Inorganic Laboratory*, **1991**, John Wiley.

The following TAs will be in charge of grading and supervising the following experiments. However, any TA on duty can be consulted while the lab work is being carried out.

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## 1.2: Safety Information

### Safety Information

Work in the chemistry laboratory may involve the use of highly flammable solvents, some corrosive and toxic chemicals, and apparatus which, if handled improperly, can cause minor to severe injuries. Before you start an experiment you need to know about all possible dangers of the chemicals and of the procedures involved. Read the specific safety advisories listed for each experiment and review the Standard Operating Procedures and MSDS's.

Relevant information on hazards of various compounds can also be obtained from the library resources for chemistry at the website <https://safetyservices.ucdavis.edu/units/ehs/research/safety-data-sheets>. For off-campus access, click on VPN first.

Material Safety Data Sheets (SDS or MSDS) provide information on how chemical substances can be safely handled, stored, and used. They indicate health, material, and physical hazards, exposure limits, and precautions. MSDS are produced by every supplier of a substance (if there are many suppliers for a substance there will be many MSDS as well. Select one with a recent issue date). Two good sites are:

**MSDS via Chemical Safety.com** (<https://chemicalsafety.com/sds-search/>)

**Sigma-Aldrich, MSDS** (<http://www.sigmaaldrich.com/safety-center.html>)

Record all hazard information in your lab notebook before you show up for the laboratory session. The TA's will check that you have done this before you are given the OK to begin the experiment.

### Solvents

1. Many accidents that happen in chemical laboratories are caused by burning organic solvents. To avoid similar accidents in the class, you need to keep organic solvents away from any potential ignition sources, such as hot plates, stirrers, electrical equipment and connections, motors, heaters, etc. Before turning on a hot plate or other spark source, always confirm that no flammable materials are nearby. Never heat even small amounts of a flammable solvent with or near a hot plate or other spark source unless a condenser is attached to the vessel in which the solvent is contained. Never pour a solvent in the vicinity of a hot plate or other spark source.
2. If a solvent is spilled, have all workers at the bench turn off their stir plates, hot plates, or other hot or electrical devices. If the spill is very small (for example, a few drops), while wearing protective gloves and avoiding the vapors, soak up the solvent with a paper towel. If possible, wring the solvent from the towel into a beaker in the hood, and transfer it to the appropriate "Waste Solvent" bottle in the hood. **In case of larger spills, or spills of mercury, inform the TA at once.**
3. Flammable solvents with which you may have contact are ether, cyclohexane, benzene, toluene, xylene, alcohols, ethyl acetate, ammonia, acetone, dioxane, etc. If in doubt about a particular solvent, always assume that the solvent is hazardous.
4. Ethyl ether and petroleum ether (b.p. 30-60°) are especially dangerous. Always heat or distill them by heating with a water or steam bath, and collect the distillate in an ice-cooled flask. Carbon disulfide is extremely hazardous. It has been known to ignite even on hot steam pipes.
5. Avoid inhaling organic solvent vapors. Benzene and chlorinated solvents are especially toxic and some of these are carcinogenic. These solvents should only be handled in a fume hood.
6. Whenever acetone is used for cleaning or drying glassware, use it sparingly and away from flames or spark sources such as stir plates, hot plates, or other electrical equipment. Collect used acetone into the organic liquid waste container. Do not put it down the drain!
7. Waste solvents (and other waste chemicals) are to be collected in appropriate containers for environmentally safe disposal. Separate containers are provided for **(1) solid wastes, (2) waste flammable solvents, and (3) waste chlorinated organic solvents. (e.g. CHCl<sub>3</sub>).**
8. **Advice on gloves from Sigma Aldrich:** Chemically resistant laboratory gloves come in a variety of materials such as natural rubber or latex, butyl rubber, polychloroprene, nitrile, polyethylene, PVC etc. in differing glove thickness and glove style. Each material protects well against certain chemicals but poorly against others. The choice of material and its thickness depends on its resistance to permeation taking into account the factors listed above. Commonly, manufacturers' literature and performance tables have to be consulted to find this information.

### Some Rules for Glove Use:

Select gloves which are resistant to the chemicals you may be exposed to. Consult the relevant Material Safety Data Sheet (MSDS) that may recommend a particular glove material.

Select gloves of the correct size and fitting; gloves that are too small are uncomfortable and may tear whereas overlarge gloves may interfere with dexterity. In some cases, such as use of HF, it may be advisable to select gloves that can be removed very rapidly in an emergency.

Before use, check gloves for physical damage such as tears or pin-holes and for previous chemical damage: this is especially important when dealing with dangerous materials such as HF.

When working, it may be advisable to wash the external surface of the gloves frequently with water.

Some gloves, especially lightweight disposables, may be flammable: keep hands well away from naked flames or other high temperature heat sources. When removing gloves, do so in a way that avoids the contaminated exterior contacting the skin.

- Wash hands after removing gloves.
- Dispose of contaminated gloves properly.
- Do not attempt to re-use disposable gloves.
- Never wear possibly contaminated gloves outside of the laboratory or to handle telephones, computer keyboards, etc.

### Safe Handling of Some Other Chemicals

1. Most compounds are toxic, at least to some extent. Avoid breathing their fumes. If they are spilled on the skin or clothing, wash them off with soap and water as soon as possible. Solvents can carry toxic solutes through the skin, so be especially careful when handling solutions of toxic compounds in organic solvents.
2. Certain especially corrosive reagents which give off noxious fumes (e.g. bromine, acetyl chloride, acetic anhydride, phosphorous trichloride, fuming nitric and sulfuric acids, aluminum chloride, chlorosulfonic acid, benzene-sulfonyl chloride, etc.) should be handled in the hoods. Avoid spilling these substances on yourself or on the desk top. They cause painful burns. Bromine is especially bad; if it is accidentally spilled on the skin, wash off the area immediately with water and alcohol and cover it with glycerol.
3. Sodium cyanide and potassium cyanide are very poisonous; a few milligrams are sufficient to cause death. They may even be absorbed through cuts in the skin. Do not allow cyanides to come into contact with acids since the very deadly gas, hydrogen cyanide, is formed. Therefore, use these compounds in a fume hood. Rubber gloves should be worn when handling these compounds, and extreme care should be taken to avoid spilling them on the desk top. Solutions of cyanide in DMSO or other organic solvents are easily absorbed through the skin.
4. Sodium and potassium metals react explosively with water. They are rapidly corroded by the atmosphere and should be stored under kerosene or oil. These metals must not be allowed to come into contact with the skin. They should be handled with dry filter paper or tweezers. Unused pieces of sodium may be returned to the bottle. Avoid all contact between chlorinated solvents and sodium or potassium. Organic solvents containing bits of sodium or potassium metal should never be added to waste bottles. Contact a TA for help.
5. Concentrated acids and alkalis are corrosive to the desk tops, clothing and skin. If any is spilled, dilute it with a large volume of water. If the spill is larger than a few drops, contact a TA. Neutralize acids with solid sodium bicarbonate. Neutralize bases with 3% acetic acid. Sulfuric acid is especially troublesome since drops adhering to the tops of bottles tend to absorb moisture and run down the outsides of the bottles.
6. Mercury and its salts are very toxic. If any is spilled, inform the teaching assistant at once.
7. Never use nitric acid for cleaning laboratory glassware. It may form explosive compounds with organic materials.
8. Explicit directions will be given for the collection or disposal of waste chemicals from all experiments.

### Safety Considerations when Handling Apparatus

1. Do not use your hand as a backstop when boring corks. Use another cork or a rubber stopper. Cork borers are very sharp.
2. When inserting tubing or thermometers into bored stoppers, it is wise to take some simple precautions. Very serious cuts have resulted from carelessness. The tubing and stopper should be held by a towel so that if the tubing breaks, the towel and not the hand will receive the impact of the jagged edge. If the tubing does not enter the hole in the stopper easily, the hole may be made larger with a file (if a cork), or lubrication with water, alcohol, or glycerol may help. Hold the tubing close to the stopper. When removing the tubing from the stopper, follow the same technique.
3. After bending a piece of hot glass, be sure to let it cool sufficiently before touching it.



4. Do not support apparatus on books, boxes, pencils, etc. Use large strong wooden blocks or rings. Assemblies with a high center of gravity (as when a reagent is added through the top of a condenser) should be set up and handled with much care.
5. Never begin heating a solution for refluxing or distillation without first adding several boiling stones or chips or ensuring that the solution is being rapidly stirred; otherwise severe bumping may occur and the solution may shoot out the top of the condenser. If you have forgotten the boiling stones and already begun the heating, cool the solution to well below its boiling point before adding the boiling stones.
6. **Completely closed systems must never be warmed, thawed or heated. Pressure buildup may cause explosions.**
7. Distillations must never be carried out to dryness. Small amounts of peroxide or side product residues may explode at the high temperatures which would occur in the distilling flask.
8. Do not use glass stirring rods for breaking up solids. They are liable to break. Use a metal spatula instead.
9. When carrying out extractions using a separatory funnel, always make sure it will hold the stopper and stopcock securely. Otherwise they may pop out and release the possibly corrosive or flammable contents of the funnel over yourself and others. Also, when releasing pressure from a separatory funnel, never point the outlet toward yourself or others in the laboratory.
10. Oil baths and melting point baths can cause severe burns if spilled. Make sure they are well supported.
11. Never evacuate ordinary Erlenmeyer flasks which are larger than 50 ml. They may implode.
12. Dewar flasks, because they are evacuated, implode easily when tipped over or dropped. Make sure the ones you use are wrapped on the outside with friction tape so they will not shower glass around the laboratory if broken

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## 1.3: Laboratory Rules and Notebooks

### Laboratory Rules

1. Students are expected to have read the procedures and to understand the reactions and apparatus before starting an experiment. If you finish an assignment ahead of time, or in cases where an experimental procedure calls for allowing a reaction to reflux or stand until the next laboratory period, ask for permission to use the time to catch up with unfinished earlier experiments (e.g. spectroscopy).
2. Before you begin an experiment, obtain the teaching assistant's approval. Normally, this approval will be signified by the TA initialing the page in your laboratory notebook that contains the title of the experiment and a report of hazards as well as an experimental plan.
3. If no yield is obtained in an experiment, obtain the teaching assistant's written approval before repeating the experiment.
4. This class offers the student a unique opportunity to work with equipment which is commonly used in graduate school as well as many inorganic laboratories. They are very sensitive and are not really meant for the multiple user mode necessary for the class. The instruments are prone to breakdown. We ask, therefore, that everyone takes good care of the instruments. You will be graded on technique which involves making sure that the instrument is in the proper condition before, during and after its use. **If complaints occur from subsequent groups, points will be subtracted from report grades.**
5. Students who miss a laboratory session must bring a doctor's note explaining the medical reason for their absence. The missed session must be made up in "catch-up day", or (with the TA's *written* permission) the student may do the missed work during breaks in other experiments.
6. Laboratory reports which show evidence of plagiarism or copying from another student's laboratory report will be given a grade of zero for all affected sections. If the plagiarism is substantial (as determined by the instructor) then the entire report will be given a grade of zero. **Don't even copy from your own partner's report!**

### Laboratory Notebooks

Carefully prepared write-ups of each experiment are to be kept in a bound, ruled notebook. The notebook must have a Table of Contents, and all entries are to be made in ink. Handwriting must be neat and legible. Data are to be entered in the notebook at the time they are obtained. No page should ever be torn out of the notebook.

Parts A and B of the write-up should be neatly written in your laboratory notebook.

#### Title of Experiment

Reference to the procedure being used.

A. Pre-Lab Write-Up List all chemical s to be used, physical state, fw, and chemical safety (see **Sources for Chemical Hazard Data**). To be done before class and initialed by TA.

- I. Main Reactions: Write balanced equations.
- II. Side Reactions: (If any. Write balanced equations if possible.)
- III. List of spectra required.
- IV. Quantities of Materials.

#### B. Experimental Write-up

- I. Procedure: (Only give variations in procedure from that in the reference)
- II. Observations: (To be recorded as they are obtained.)
  - a. Comments: (On unusual color changes, difficulties, etc.)
  - b. Products: (Physical characteristics, weight, m.p. or b.p. ranges, spectra, etc.)
  - c. Experimental yields : (Show all calculations)
  - d. Spectroscopic and other data : (Use correct units)

Synthetic products should be placed in tared bottles or vials of an appropriate size and labeled.

Student Name

Chemistry 124L

Product Name

Tare Weight

Notebook Reference

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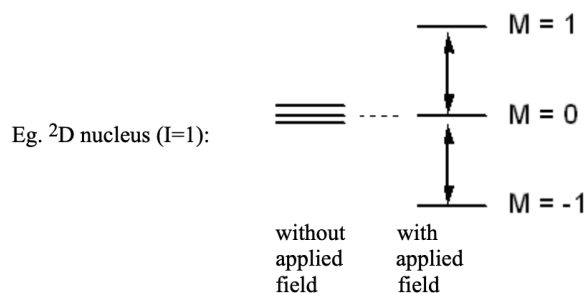
## 1.4: Introduction to NMR Spectroscopy

### Chemical Shift

A nucleus of spin quantum number  $I$  can have an angular momentum  $M$  of

$$M = I, I - 1, I - 2, \dots -I + 1, -I \text{ (in units of } h/2\pi) \quad (1.4.1)$$

Therefore, every nucleus has a spin degeneracy of  $2I+1$  (i.e. the energy level of the nucleus is independent of the value of  $M$ ). In an NMR experiment, one places a sample inside a strong magnetic field. Inside such a magnetic field the degeneracy is lifted (i.e. the energy level of the nucleus does depend on the value of  $M$ ).



**Scheme 1.** The effect of applied magnetic field on the energy levels of a nucleus

Transitions between these levels ( $\Delta M=1$  only) can be detected by spectroscopy at frequency  $\nu$ , where

$$\nu = \frac{\gamma H_{eff}}{2\pi} \quad (1.4.2)$$

$$\gamma = \text{magnetogyric ratio for that isotope} \quad (1.4.3)$$

$$H_{eff} = \text{applied magnetic field as experienced by the nucleus} \quad (1.4.4)$$

However, the applied magnetic field as experienced by the nucleus may be slightly lower than the magnetic field put out by the magnet of the spectrometer because the nucleus may be shielded from the main field by electron density. Therefore, we must modify the equation to take such shielding into account.

$$H_{eff} = H_0(1 - \sigma) \quad (1.4.5)$$

$$\nu = \frac{\gamma H_0(1 - \sigma)}{2\pi} = \frac{\gamma H_{eff}}{2\pi} \quad (1.4.6)$$

or

$$\frac{\nu}{H_0} = \frac{\gamma(1 - \sigma)}{2\pi} \quad (1.4.7)$$

$$H_0 = \text{applied magnetic field} \quad (1.4.8)$$

$$\sigma = \text{screening constant, which decreases the effective magnetic field} \quad (1.4.9)$$

If one keeps the frequency constant and scans  $H$ , one can plot intensity versus  $H$ . One will then observe an intensity peak when absorption occurs, at the  $H$  value which allows equation 3 (and 4) to be true (see figure below). On the other hand, one may choose to keep the magnetic field constant and scan frequency instead. This is experimentally easier to do. The positions of the peaks are described in terms of their distance from a chosen standard.

$$\delta = \frac{\nu - \nu_{ref}}{\nu_0} * 10^6 \text{ ppm} = \frac{(H - H_{ref})}{H_0} * 10^6 \text{ ppm} \quad (1.4.10)$$

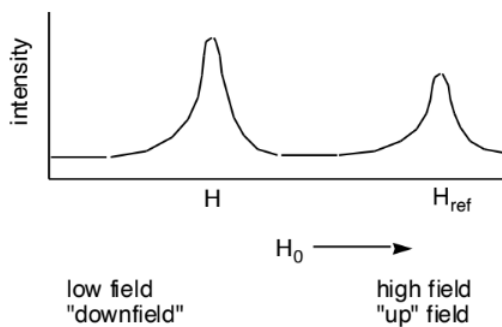


Figure 1

Usually, downfield is referred to as being positive; a nucleus that appears downfield of the reference will have a positive  $\delta$ . The reference is usually assigned a chemical shift of zero. The reference for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra is  $\text{SiMe}_4$  (TMS). The reference for  $^{31}\text{P}$  NMR is 85%  $\text{H}_3\text{PO}_4$  in water.

Looking at equation 4 you will understand why the direction of increasing field and the direction of increasing frequency are opposite. A nucleus with negligible shielding ( $\sigma \approx 0$ ) will need a large  $\nu$  or a small  $H_0$  and therefore will have a downfield shift. Acidic protons such as  $\text{RCO}_2\text{H}$  fit this description. In contrast, a nucleus with a lot of shielding ( $0 < \sigma$ ) will need a small  $\nu$  or a large  $H_0$  and therefore will have an upfield shift. Hydrogen atoms attached to electropositive atoms or groups will fit this description. For example,  $\text{Si}(\text{CH}_3)_4$ .

All nuclei can be observed on the same scale of field vs intensity, but the distance on the scale between the signals for H and P, for example, is so large that they are usually shown separately. A table of some of the magnetically active nuclei is shown below. A larger table is in Appendix 7 of the textbook.

The strength of a magnet is usually measured in Tesla, but NMR magnets are more often described in terms of the resonance frequency for  $^1\text{H}$  NMR. This can be misleading if you are planning to use a nucleus other than  $^1\text{H}$ . For example, a 7.0 Tesla magnet has a resonance frequency of 300 MHz for  $^1\text{H}$  (and will be referred to as a 300 MHz NMR magnet) but the resonance frequency for  $^{31}\text{P}$  NMR on the same instrument will be 121 MHz. You can calculate the resonance frequency for any isotope from the magnetic field strength using equation 1.

Use a modification of equation 5 to convert between Hz and ppm units. For example, if two peaks are 106 Hz apart in a  $^1\text{H}$  NMR spectrum on an NMR with a proton resonance frequency of 60 MHz, how many ppm apart are they?

$$\delta = \frac{\Delta\nu}{\nu_0} * 10^6 \text{ ppm} = \frac{106 \text{ Hz}}{60 * 10^6 \text{ Hz}} * 10^6 \text{ ppm} = 1.77 \text{ ppm} \quad (1.4.11)$$

Nucleus	Spin	$\gamma^a$ (1.4.12)	nat. abund. %	relative sensitivity <sup>b</sup>	Reference
$^1\text{H}$	1/2	26.75	99.99	1.00	$\text{SiMe}_4$
$^2\text{H}$	1	4.11	$1.5 \times 10^{-2}$	$9.7 \times 10^{-3}$	$\text{Si}(\text{CD}_3)_4$
$^{13}\text{C}$	1/2	6.73	1.1	$1.6 \times 10^{-2}$	$\text{SiMe}_4$
$^{15}\text{N}$	1/2	-2.71	0.37	$1.0 \times 10^{-3}$	$\text{MeNO}_2$ or $\text{NO}_3^-$
$^{19}\text{F}$	1/2	25.17	100	0.833	$\text{CFCl}_3$
$^{31}\text{P}$	1/2	10.83	100	$6.6 \times 10^{-2}$	$\text{H}_3\text{PO}_4(\text{aq})$
$^{35}\text{Cl}$	3/2	2.62	76	$4.7 \times 10^{-3}$	$\text{NaCl}(\text{aq})$
$^{51}\text{V}$	7/2	7.04	99	0.382	$\text{VOCl}_3$
$^{55}\text{Mn}$	5/2	6.62	100	0.175	$\text{KMnO}_4(\text{aq})$
$^{59}\text{Co}$	7/2	6.35	100	0.277	$\text{K}_3[\text{Co}(\text{CN})_6]$
$^{103}\text{Rh}$	1/2	-0.852	100	$3.1 \times 10^{-5}$	$\text{RhCl}_3(\text{SMe}_2)_3$

$^{115}\text{Sn}$	1/2	-8.75	0.35	$3.5 \times 10^{-2}$	$\text{SnMe}_4$
$^{117}\text{Sn}$	1/2	-9.53	7.6	$4.5 \times 10^{-2}$	$\text{SnMe}_4$
$^{119}\text{Sn}$	1/2	-9.98	8.6	$5.2 \times 10^{-2}$	$\text{SnMe}_4$

<sup>a</sup> magnetogyric ratio ( $10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ )

<sup>b</sup> for equivalent numbers of nuclei at constant field

Quadrupolar nuclei are those with  $I > 1/2$ . They have non-symmetrical nuclear charge distribution. They often relax far more quickly than other nuclei and therefore can have very broad signals or might not be observed, and they can have the same effect on nuclei with which they are coupled. For this reason, usually  $^{35}\text{Cl}$  and  $^{14}\text{N}$  ( $I=1$ ) NMR are not possible due to excessive broadening.

### Spin-Spin Coupling

You may have already studied the coupling of  $^1\text{H}$  nuclei in organic chemistry courses. In this course you will be required to understand NMR coupling. The following

is a very brief introduction to the topic. If there is a proton ( $\text{H}_\text{A}$ ) which is close (i.e. fewer than 4 bonds away) in the molecule to another proton  $\text{H}_\text{B}$ , then the NMR spectrum of  $\text{H}_\text{A}$  will appear to be a doublet (two peaks of equal height). This occurs because the magnetic field around  $\text{H}_\text{A}$  is influenced by the spin of  $\text{H}_\text{B}$ . The neighboring proton  $\text{H}_\text{B}$  could be in a spin 1/2 or spin -1/2 state, causing the observed nucleus  $\text{H}_\text{A}$  to have two different energy levels. Therefore there will be two lines for the observed nucleus.

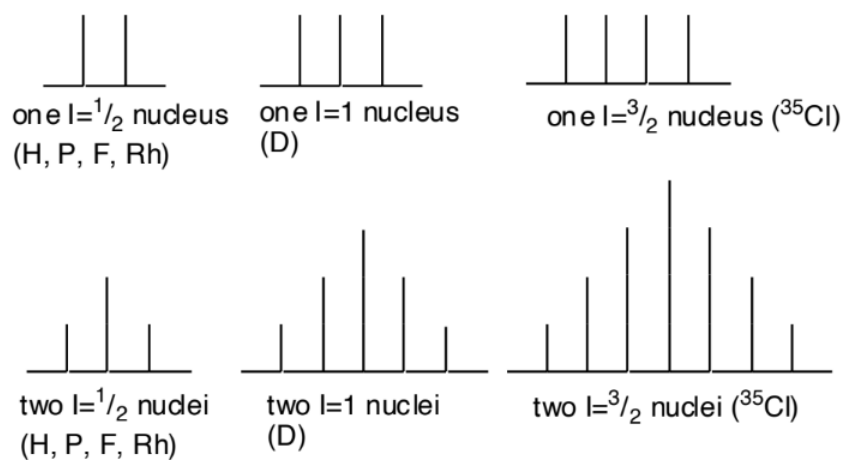
However, coupling of a proton  $\text{H}_\text{A}$  to a neighboring  $^2\text{H}$  (deuterium) atom ( $I = 1$ ) will generate three lines of equal intensity because the neighboring deuterium nucleus could be in 1, 0 or -1 spin states.

In order to predict the number of lines that the spectrum of a nucleus (let's call it A) will have, one has to know the number of nuclei (B) it is coupled to and the spin of those nuclei. We shall assume, for now, that the "other nuclei" are all equivalent to each other. We can then use the following rule: In general, for any nucleus A coupled to  $n_\text{B}$  equivalent neighboring nuclei B of spin  $I_\text{B}$ , the number of peaks in the NMR spectrum of the nucleus A is:

$$\# \text{ of peaks} = 2n_\text{B}I_\text{B} + 1 \quad (1.4.13)$$

Notice that the spin  $I_\text{A}$  of the nucleus we are observing does not appear in the equation. It doesn't matter what nucleus you are observing, the coupling pattern observed only depends on the isotope and number of neighboring nuclei.

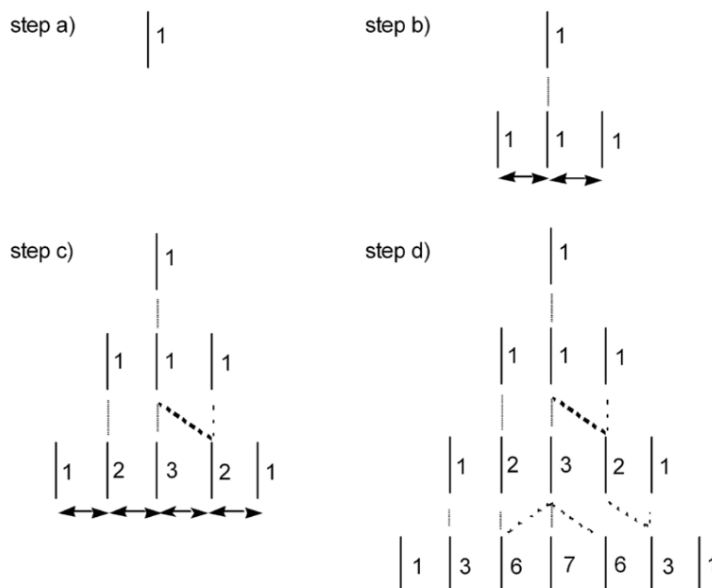
For example, coupling of a nucleus A to two equivalent neighboring  $^2\text{H}$  (deuterium) atoms ( $I = 1$ ) will generate five lines (# of peaks =  $2n_\text{B}I_\text{B} + 1 = 2 \times 2 + 1 = 5$ ). This answer is correct no matter what element nucleus A is (as long as it is NMR observable, of course).



**Scheme 2.** The NMR spectrum of nucleus A will look like this if the proton is coupled to.

Now that we know how to calculate how many lines there will be, how do we calculate how tall each line will be? Build a splitting tree, using the following steps. The process is illustrated in Scheme 3.

- Draw a vertical line for the observed nucleus. This represents what the spectrum would look like in the absence of splitting to any neighboring nuclei. Put a "1" beside the line.
- To represent splitting with the first neighboring  $B$ , draw  $2I_B + 1$  lines centered below the first line. This is row #2. The spacing between the lines represents  $J_{AB}$ , the coupling constant in Hertz (see double headed arrows in the diagram). Write a 1 beside each of these lines. Draw dashed lines from row one to the lines on row #2.
- To represent splitting with the second neighbor  $B$ , draw  $2I_B + 1$  lines below centered below *each* of the lines in row #2 and spaced  $J_{AB}$  apart. This is row #3. Note that some of the lines coincide. Draw dashed lines from the lines on row #2 to the corresponding lines on row #3. Write a number beside each of these lines, the number being the sum of the numbers from the lines in row #2 to which the line in row #3 is connected.
- Repeat this process until you have accounted for all of the neighbors.



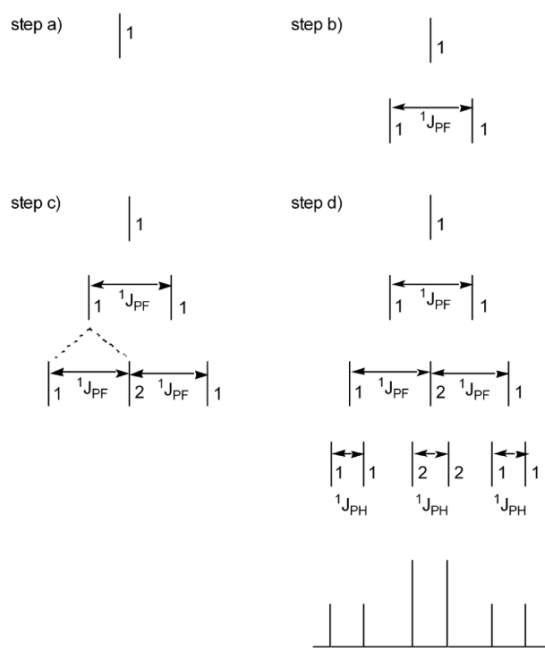
**Scheme 3.** What would the  $^1\text{H}$  NMR spectrum of  $\text{HCD}_3$  look like? The H is coupled to 3 equivalent nuclei of spin 1.

What if the neighboring nuclei are not all equivalent? For example, what if the observed nucleus A is split by *two* sets of nuclei B (total spin  $n_B I_B$ ) and C (total spin  $n_C I_C$ )? The number of peaks in the spectrum of A =  $(2n_B I_B + 1)(2n_C I_C + 1)$ .

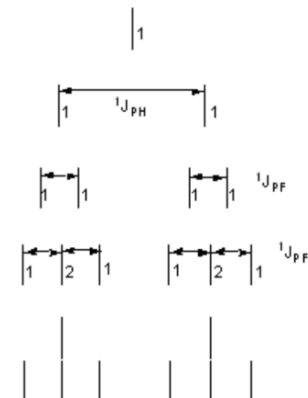
For example, the  $^{31}\text{P}$  NMR spectrum of  $\text{HPF}_2$  (F, P, and H have  $I = 1/2$ ) would have six peaks.

$$\# \text{ of peaks} = (2n_F I_F + 1)(2n_H I_H + 1) = (2 \times 2 \times \frac{1}{2} + 1)(2 \times 1 \times \frac{1}{2} + 1) = 3 \times 2 = 6 \quad (1.4.14)$$

In order to predict the intensities in the peaks, you have to draw another splitting tree, using the same rules as before. However, this time the lines might not overlap.



**Scheme 4.** The splitting tree for the  $^{31}\text{P}$  NMR spectrum for  $\text{HPF}_2$ , assuming  $^1J_{\text{PF}} > ^1J_{\text{PH}}$ . Note that we do the larger coupling first. Prediction: a triplet of doublets (td)



**Scheme 5.** The splitting tree for the  $^{31}\text{P}$  NMR spectrum for  $\text{HPF}_2$ , assuming  $^1J_{\text{PF}} > ^1J_{\text{PH}}$ . Note that we do the larger coupling first. Prediction: a doublet of triplets (dt).

If  $^1J_{\text{PF}} > ^1J_{\text{PH}}$  then some peaks will overlap and the # of peaks observed will be given by first formula above (answer = 4).

Coupling will **not be observed** if:

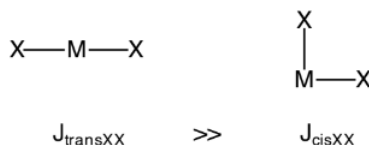
- the neighboring nucleus is too far away (4 bonds or more)
- the neighboring nucleus is NMR inactive ( $I = 0$ )
- the neighboring nucleus is NMR dilute (eg most C atoms are  $^{12}\text{C}$  ( $I = 0$ ), only very few are  $^{13}\text{C}$  ( $I = 1/2$ ), so in  $^{13}\text{C}$  NMR one doesn't see  $J_{\text{CC}}$  coupling).
- the neighboring nucleus is decoupled (such as  $^{31}\text{P}\{^1\text{H}\}$  NMR), or
- the neighboring nucleus is equivalent to the observed nucleus

Decoupling is used to simplify the spectrum if too much coupling is being observed. The nucleus which is decoupled is usually indicated by curly brackets. For example, a  $^{31}\text{P}$  NMR spectrum acquired with the hydrogen atoms decoupled would be referred to as a  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum.



Coupling constants can vary from very small (essentially 0 Hz) to very large (thousands of Hz). Coupling constants can also be negative, but that is a subject more appropriate for an advanced course. The relative size of the observed coupling constant can tell us about the relationship between the observed nucleus and the neighbor. The number of bonds between the observed nucleus and the neighboring nucleus is indicated by a superscript before the "J". For example,  $^3J_{HH}$  refers to the coupling constant between two protons which are three bonds apart.

Coupling between two atoms bound to a metal center is often particularly strong if the two atoms are trans (i.e.  $180^\circ$  apart) and much weaker if they are cis (i.e.  $90^\circ$  apart).



Coupling	J	Hz Range
$\text{CH}_a\text{H}_b$	$^2J_{HH}$	0 to 30
$\text{CH}_a-\text{CH}_b$	$^3J_{HH}$	6 to 8
$\text{CH}_a-\text{CR}_2-\text{CH}_b$	$^4J_{HH}$	0 to 1
$\text{C}_6\text{R}_4\text{H}_a\text{H}_b$ ortho	$^3J_{HH}$	6 to 10
$\text{C}_6\text{R}_4\text{H}_a\text{H}_b$ meta	$^4J_{HH}$	1 to 3
$\text{C}_6\text{R}_4\text{H}_a\text{H}_b$ para	$^5J_{HH}$	0 to 1
M-H	$^1J_{MH}$	40 to 1400
M-P (M=Si, Sn, Se, Te)	$^1J_{MP}$	-ve
M-P (M=Pt)	$^1J_{PtP}$	+2000 to +6000
$\text{P}_a-\text{M}-\text{P}_b$ trans	$^2J_{PP}$	+300 to +1300
$\text{P}_a-\text{M}-\text{P}_b$ cis	$^2J_{PP}$	-70 to +80

**Table:** Relative strengths of coupling constants.

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## 1.5: Experimental Techniques

### Filtration

The suction filtration apparatus that you will be using for many of the experiments in this course is illustrated on page 136 of the textbook.

### Cooling Baths

The cooling of flasks can be achieved by putting the flask into a cooling bath, which is a larger container partly filled with a cold liquid or slurry. The choice of coolant is determined by the temperature desired.

#### Caution

Dewar flasks are evacuated glass; if broken they implode and scatter broken glass everywhere - wear goggles.

- a) *Ice/water/salt*. Mix salt (NaCl is cheapest), ice, and a small amount of water in a beaker. The solution will settle around  $-5^{\circ}\text{C}$ .
- b) *Solvent/dry ice*. Place broken pieces of dry ice into a Dewar flask. Slowly pour the solvent onto the dry ice. Choose the solvent that will give you the desired temperature (see Appendix 8 in the textbook). If the dry ice pieces disappear after a while, add more pieces only one or two at a time. Never put solvent in the Dewar flask first and then add dry ice. The mixture will foam up and over the edges of the flask.
- c) *Liquid nitrogen*. The temperature of liquid nitrogen is  $-196^{\circ}\text{C}$ . Evacuate or flush the flask with nitrogen before placing the flask in a liquid nitrogen bath.

#### Caution

Do not place a flask into a liquid nitrogen bath if the flask contains air or argon, because oxygen and argon have boiling points ( $-183^{\circ}\text{C}$  and  $-186^{\circ}\text{C}$ ) higher than that of liquid nitrogen. It is therefore possible to condense liquid oxygen or liquid argon in the flask. When that condensed gas later boils off, it will cause a very rapid increase in pressure and a possible flask explosion. Liquid oxygen could also react with organic materials in the flask.

## Removal of Solvent

When a method calls for the solvent to be removed, or the solution volume to be reduced, this can be achieved in a number of ways.

- a) *Evaporation by heating (not recommended)*: Heating the flask until the solvent is driven off is **NOT** an acceptable method because the residue will get hotter and hotter as the solution volume decreases. Eventually the residue will become dry and will overheat, possibly causing an explosive decomposition. Also, using a hot plate with an organic solvent could easily cause a fire.
- b) *Pump and Trap Method*. Set up a pump, a trap, two stopcock valves, and an adapter, all interconnected with thick-wall flexible tubing, as shown in the diagram below. The adapter to the flask contains a third stopcock valve. With all three valves closed, turn on the pump to evacuate the whole system. After a couple of minutes, place a Dewar flask around the trap and pour liquid nitrogen into the Dewar. Attach the sample flask (with a stir bar in it) to the adapter. Start the stirrer and then slowly open the adapter valve to evacuate the flask. The solution should froth up somewhat. If the solution froths up high enough to approach the adapter, then partially or completely close the adapter valve until the frothing settles down. If the flask becomes cool, warm it up to room temperature with your hands or a beaker of lukewarm water. If the evaporation takes a very long time, use warmer water. Because you are evacuating the flask, the flask may implode, especially if it is large, if it is damaged, or if it has a flat bottom. To decrease the risk, use a roundbottom flask (not an Erlenmeyer), tape up the flask with masking tape (if it is a large flask), and most importantly you must WEAR GOGGLES.

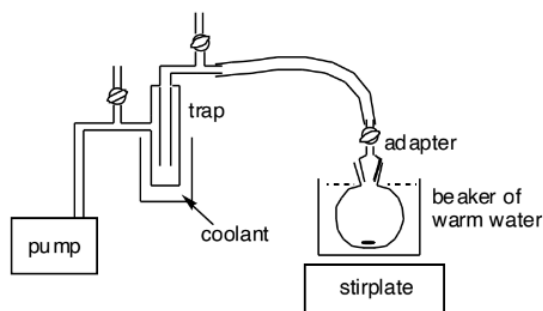


Figure 1. Experimental setup for removing solvent by 'Pump and Trap Method.'

c) *Rotary Evaporator*. You will be given instructions by the TA on the proper use of the rotary evaporator. note that you do not need to have a stir bar in the flask. The warnings about imploding flask\’s are the same for the rotary evaporator as for the Pump and Trap method.

### Manipulation of Air Sensitive Compounds

A compound can be “air-sensitive” for one or more of three reasons:

- it may react with  $O_2$  (e.g. Rh hydride complexes)
- it may react with water (eg. early transition metal alkyls)
- it may react with  $N_2$  (e.g. lithium metal)

In order to protect the compounds from “air”, one must use inert-atmosphere techniques. For most air sensitive compounds,  $N_2$  is not a problem. Because  $N_2$  is cheaper than argon, purified  $N_2$  is usually used as the inert gas under which air-sensitive compound manipulations are performed. For those few compounds which react with  $N_2$ , argon is used. One must also remove water/ $O_2$ / $N_2$  from the solvents and reagents one will use in all preparations and reactions.

The removal of air from a liquid is called degassing. This procedure replaces the air (but not the water) dissolved in the liquid with another gas. This can be achieved by either of two methods: bubbling and freeze-thaw.

- The bubbling method involves bubbling another gas (eg. nitrogen or argon) through the solvent for some time, in order to drive out the dissolved air. This technique is fairly effective, especially if the liquid is in air-free glassware such as a Schlenk tube (to be defined below). If the liquid is in an open container, the degassing effect will only be temporary; air will soon redissolve into the liquid. If the liquid is volatile, some of the liquid will be lost during the procedure.
- Freeze-thaw cycles are somewhat more time-consuming but can be quite effective. The technique (which will NOT be used in this course) involves putting the liquid in a Schlenk tube, closing the flask, freezing the liquid, evacuating the gas phase in the tube, replacing the gas phase with inert gas, and thawing the Schlenk tube again (while it is still open to the inert gas and a bubbler). A blast shield is a recommended precaution when using the freeze-thaw method because pump the liquid may expand as it thaws and this can sometimes cause the flask to burst at the bottom.

Water removal from solvents can be troublesome and time-consuming. Even traces of water in the solvent can destroy some water-sensitive compound. The traditional organic chemistry drying agents such as  $MgSO_4$  are not sufficient. Very strong drying agents such as  $CaH_2$ , elemental sodium/benzophenone ketyl, and Grignard agents are often used. This will not be required in this course.

Experimental manipulations of air-sensitive compounds can be performed in any of three different methods:

- Inert-atmosphere glove box* (otherwise known as “dry-box”). These boxes are very expensive, but can be quite effective and are operationally simple. The oxygen and water content in the gas phase inside such a box are continuously monitored can be kept below 1 ppm level. Experiments involving high or low temperatures inside a glove-box can be problematic, but with extra equipment can be done. Very little training is required.



Figure 2: An inert-atmosphere glove box (reproduced from <https://www.etelux-glovebox.com/prod...x-atmospheres/>)

b) *Gas/vacuum manifolds* and Schlenk-ware: A Schlenk tube is just a test-tube or flask designed for inert-atmosphere work. Often the top of the Schlenk tube is a ground-glass joint, and there is usually a side-arm with a stopcock on it. The gas/vacuum manifold has two long glass tubes (one containing an inert gas and 30 other containing vacuum) connected to several ports; each port has a length of flexible tubing attached to it. One normally attaches the other end of the flexible tubing to the sidearm of a Schlenk tube. By rotating the stopcock inside each port, one can supply either inert gas or vacuum to the Schlenk tube. Manipulation of air sensitive materials by these techniques requires much more training than a glove box, but offer a greater range of options, including high and low temperatures or deliberate addition of degassed water, or even dried oxygen. Filtrations, separations, and other procedures can be performed, but considerable training is required.

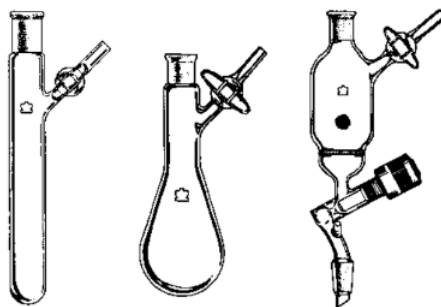


Figure 3: Two types of Schlenk tubes and a Schlenk filter (reproduced with permission from Kontes Glass Company).

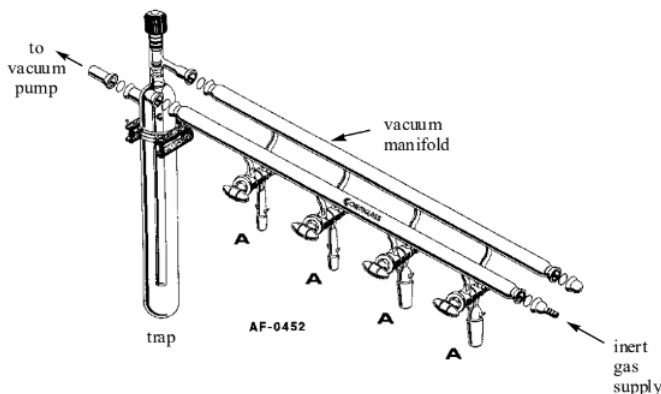


Figure 4: A gas/vacuum manifold. The attachment points for flexible tubing are indicated by the letter "A" (reproduced with permission from the ChemGlass Company).

c) Stand-alone glassware: This is the technique which will be used in this laboratory. It is effective for compounds which are only moderately air-sensitive. The technique is based upon the assumption that compounds in the solid state are much less air sensitive than they are in solution (this is generally true, but some compounds are quite air sensitive even as solids, and so other techniques would be preferable in those cases). In the technique, the solid reagents are placed, along with a stirbar, in standard taper/ground glass join glassware (such as a Schlenk tube) which is then flushed with a gas (either a reagent gas or an inert gas) to remove the air. Solvent is then added to start the reaction.

Alternatively, one can add the solvent and stir bar to an empty flask attached to a condenser and boil the solvent. The vapor of the boiling solvent displaces all of the air. Then the heat is removed briefly and solids are added. The disadvantage of this technique is that it requires the addition of solids to liquids that are close to boiling, and this can lead to bumping (an “eruption” of boiling liquid due to sudden boiling). To avoid being hit by bumping liquids: wear gloves, turn off the heat supply, keep the stirrer going at a high rate, do not place your face over the glassware while you are adding the solids, and never remove the condenser.

### Use and Care of Standard Taper Equipment

1. Standard taper glassware is expensive. The current cost of a single 24/40 outer joint is about \$12.00. A 500-ml three-necked flask with 24/40 joints costs over \$90.00.
2. Bare standard taper joints should not be attached to each other because the seal obtained is often poor, and the joints may freeze together thereby making them worthless. All ground glass surfaces should be greased (Lubriseal is satisfactory for most purposes) before they are connected. To make a good seal, the joints may be pressed firmly but gently together while turning one of them.
3. Assemblages containing standard taper joints are not as flexible as those employing corks and stoppers, so some care must be exercised in clamping the pieces to support bars in order to avoid strain. Pyrex glass will not bend appreciably at room temperature. Three-prong clamps are most convenient for clamping standard taper glassware because they may first be rigidly attached to a bar and finally gripped to the glassware by careful adjustment of the screws on either side of the prongs. The clamp prongs should be covered with rubber or other insulator to prevent contact between metal and glass.
4. Direct heating of a standard taper connection with a free flame should be avoided because it may melt out the grease and cause freezing of the joints.
5. If joints become frozen together, they may usually be separated by cautious warming with a heat gun or a soft flame (not allowed in this laboratory). However, if silicone grease has been used, this treatment may cause permanent freezing. Silicone grease should not be used unless it is specifically required. In cases where the joints are on equipment that has been heated during a reaction or distillation, it is best to separate the joints before the apparatus has cooled completely in order to prevent freezing. If you encounter frozen joints, ask for assistance from a TA.
6. In cleaning standard taper equipment, most of the grease may be wiped away with a cloth. If removal of the last traces is desired, the cloth may be moistened with a solvent such as hexane, toluene, ligroin or ether. **(CAUTION! Avoid free flames and spark sources!)**

### Cleaning Glassware

Laboratory glassware is more easily wetted by water than by the oily and tarry organic matter present in a newly soiled flask. Thus immediate rinsing with water may remove tar which would adhere tightly to the glass if the water were allowed to evaporate. Wash equipment as soon as it is empty.

Soap and detergent in combination with a brush, which may be bent judiciously so that it will reach certain otherwise inaccessible spots, are useful. Abrasive washing powder that will not scratch glass is very often helpful. If the tar is acidic, rinsing with sodium hydroxide solution may serve to loosen the tar. If it is basic, dilute hydrochloric acid may be helpful. Acetone, alcohol, or xylene, in small quantities, may dissolve a tar unaffected by other materials. Never heat a vessel over a flame while cleaning with these solvents. (Removal of seemingly intractable tars is best left to trained laboratory storeroom personnel.)

Glassware, if drained and left in the desk until the next week, will dry spontaneously. If it is needed dry sooner, it may be rinsed with acetone (5-10 ml) two or three times. Blowing nitrogen air into the vessel will then remove most of the acetone. Do not blow

air from the pressurized air supply into clean vessels, as oil droplets contained in the air supply will spray all over the inside of your clean glassware.

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## 1.6: Sources of Information

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1772 – present Chemical substances

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### CHEMnetBASE

Collection of searchable major chemical reference works, including: CRC Handbook of Chemistry & Physics, Dictionary of Commonly Cited Compounds, Dictionary of Drugs, Dictionary of Food Compounds, Dictionary of Inorganic and Organometallic Compounds, Dictionary of Marine Natural Products, Dictionary of Natural Products, Dictionary of Organic Compounds, Polymers: A Property Database, Properties of Organic Compounds, and Combined Chemical Dictionary.

### Merck Index: an encyclopedia of chemicals, drugs, and biologicals

The Merck Index contains over 11,000 entries (referred to as monographs) mostly for single substances and related compounds (isomers, salts, etc.). Some families of natural products and biological substances are included as well. Data provided include: chemical, generic, and brand names; CAS (Chemical Abstracts Service) registry numbers; physical data and literature references; structures and stereochemistry; toxicity; and information on therapeutic and non-medicinal uses. The Merck Index Online also includes sections on: organic name reactions, and additional tables. The Merck Index can be searched by structure with installation of a free ChemDraw plug-in available on the structure search page.

### CRC Handbook of Chemistry and Physics

2022-2023 (103rd ed.) The CRC handbook that started it all - over 100 years old and the most important data handbook for major areas of Chemistry and Physics.

Print copy at Shields Reference QD 65 C4. Reference

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5. Norman, N. C. *Periodicity and the p-block elements*
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## 2: The Alane-Amine Adduct (C<sub>2</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>2</sub>N-AlH<sub>3</sub> (Experiment)

This experiment is adapted from the textbook (pages 47-53).

### Safety Notes

1. Both lithium aluminum hydride ("LAH," formula LiAlH<sub>4</sub>) and the alane-amine complex are highly moisture sensitive and react violently with water.
2. Throughout this experiment, be extremely mindful of the direction of air flow and monitor the bubblers to ensure that the pressure remains positive but modest. A rapid flow through the bubbler may result in the loss of the oil and the potential for a loss of integrity in the system.
3. Whenever positive pressure is placed upon a flask or is likely to result from a reaction (any gas evolution), a vent must be present in the form of a needle or cannula except in the case of momentary transitions.
4. **In no scenario should vacuum be applied to a flask that still has a vent to the atmosphere. This may result in loss of product, fire, or explosion.**
5. Every flask must be secured by a clamp at all times that it is in use. The flasks being used are pear-shaped Schlenk flasks, most stable and durable for vacuum, but largely impossible to safely secure in the appropriate orientation without a clamp.
6. For the second day of the experiment, students must wear a Bulwark FR laboratory coat (obtained from the dispensary for the day) and flame-resistant gloves.

### Day 1 - Practice using a Schlenk manifold system

The compounds used in this experiment are not necessarily more sensitive than those in the other air-free experiments; however, their interaction with the atmosphere is potentially more violent and noticeably more dangerous. To address this increased risk, this short experiment is prefaced with direct experimental technique practice.

#### Glassware maintenance

Schlenk flasks are stored in the oven at ~120° C to drive off any moisture that may cling to the surface or within the pores of the glass, itself. At the beginning of class, the flasks and stopcocks should be in the oven. Remove them with heat-resistant gloves and set them on a non-plastic surface to cool. Once they are still warm but safe to touch (this should take only 2-3 minutes), the stopcock must be lubricated with vacuum grease and placed in the valve, then secured with a metal clip. Rotate the stopcock repeatedly to ensure the most complete coverage of grease, then wipe any excess from the surface of the glassware. Note that excessive grease will work its way into the channel and may contaminate either the hose or the interior of the flask.

When a flask is no longer needed, it needs to be disassembled and cleaned thoroughly. Use paper towels to remove the majority of the vacuum grease from the valve joint and stopcock, then wash everything with soap and water. Rinse with tap water, then deionized water. At this point, be prepared to wash a second time or rinse with acetone, depending on the nature of any suspected persistent materials still clinging to the flask. The final rinse should be deionized water, then the glass pieces must be placed back in the oven to dry for the next lab.



Figure 1 - Alane Schlenk Diagram. 1) Rheostat for heating element 2) oxygen scraper 3) drying column 4) valve to isolate columns 5) three-valve Schlenk manifold 6) first bubbler 7) second bubbler and final  $N_2$  valve. Clear hose on the right connects to solvent trap for vacuum line.

### Purging the atmosphere of a flask

Any fresh flask connected to a Schlenk line via hose has likely been exposed to atmosphere to some degree. Before an empty flask can have any sensitive materials transferred into it, the interior must be purged. The flask should have a fresh septum covering any openings, rolled down over the edge and secured with a zip-tie or rubber band about the septum lip. **Any time a flask is going to be placed under positive pressure from any source, the septa must be secured in this fashion.** The pressure required to cause a septum to pop out of a machined glass neck is surprisingly small. Connect the hose to the stem and turn the manifold's valve to vacuum. At this point, open the valve on the flask's stem. The sound of the pump will change as the pressure spikes and is drawn down. The perturbation of the idle noise is a good indicator of the status of the pressure. Once most of the atmosphere has been removed, slowly turn the manifold valve to the nitrogen line to re-fill it - this only takes a few seconds. Pull vacuum again and refill with nitrogen three times total. Once complete, it is generally best to close the valves until the follow-up operation is ready.

Each time the purge-fill cycle is performed, the original atmosphere is removed in percentages. It can never be perfect, but if the pressure in the flask drops from 760 torr to 76 millitorr (not unreasonable with a moderate strength pump), then the oxygen in the flask has been reduced by four orders of magnitude, or 0.01% of its original. Two more identical cycles should reduce the oxygen to negligible levels.

### Removing solvents with a syringe

Solvents isolated from atmosphere have a few challenges to address. First, their containers are sealed, so solvent removal must come with a similar volume displacement. Second, the syringe itself can be a source of contamination. Needles used for this purpose tend to be long and quite bent.

Before placing a syringe into a sealed solvent container, the needle end should be placed into a hose connected to the manifold with a positive nitrogen flow. At this point, the plunger should be drawn in and pushed downward 3-5 times. Finally, pull the plunger back to fill it with nitrogen, then place the needle on the septum and pierce it. Once punctured, press the plunger to add the nitrogen in the syringe to the head space (air above a solvent) of the container. At this point, place the point of the needle into the solvent and bend needle so that the syringe faces upwards, then draw the plunger back until the desired quantity is obtained. Pull the tip of the needle out of the solvent and draw in around 1-2 mL of vapor from the bottle to shield the solvent from atmosphere for transport and draw the solvent fully into the syringe. At this point, the needle is ready to be withdrawn and placed through the receiving vessel's septum for dispensing. When drawing solvent up, the syringe should point upwards and when dispensing it should point downward.

## Transferring solvents with a cannula

Transferring liquids from one sealed vessel to another requires the use of a cannula, or a two-ended needle. Like Schlenk flasks, it should be stored in the oven to keep it dry between periods, but is always purged of air inside it before any transfer is performed.

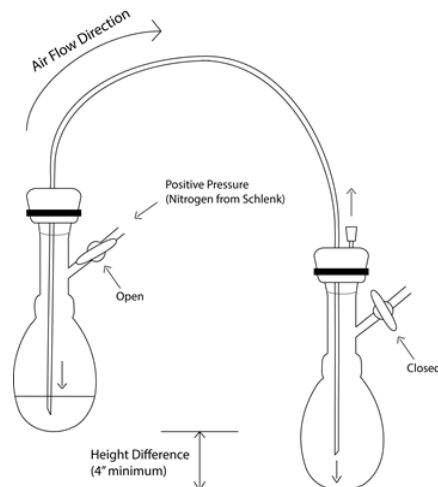


Figure 2 - Basic Cannulation diagram for transfer. Note that both flasks must be secured with clamps.

First, both flasks should be already sealed with septa secured with zip-ties. Only the flask serving as the source is connected to the Schlenk manifold by hose. Positive nitrogen pressure is placed on the source flask, the pierce the source flask's septum with first end of the cannula. Once the cannula is inserted, the other end acts as a vent for the pressure in the first flask, preventing backflow of atmosphere. The cannula remains above the solvent in the head space at this point, so that only gasses are passing through it. Next, pierce the second flask with the other end of the cannula. Now the nitrogen flow is entering the first flask, going through the cannula, and entering the second flask. At this point, pierce the septum of the receiving flask a second time with a small needle to allow the pressure to vent. Observe the bubbler and note whether the speed of the bubbling has decreased now that there is a second path for the nitrogen gas. Once this step is reached, the first end of the cannula can be placed into the liquid to be transferred. The transfer itself may happen slowly or rapidly, depending on the needs of the reaction. If no liquid has transferred after ~30seconds, then the pressure may need to be increased by closing off the vent at the end of the bubbler system. If the pressure in the system is too high, this may put strain on the system and risk popping a septum that has been insufficiently secured, ruining the efforts to keep the solvent or solution isolated. If the bubbler valve was closed for this transfer, be certain to open it immediately upon the transfer's completion, but to do so very slowly. With rapid pressure changes, the oil in the bubbler may be either ejected or drawn into the manifold itself, and both of these negatively impact the integrity of its ability to maintain an inert atmosphere. This is also the reason why vacuum is not used on the receiving flask to accelerate the transfer – it is certain to overpower the nitrogen pressure and draw in atmosphere through the bubbler system after sucking the oil into the manifold.

After the transfer is complete, the steps are undone in the reverse order. The vent needle is removed, first. The cannula is withdrawn from the receiving flask. The cannula is withdrawn from the original flask. Then the nitrogen pressure is disconnected from the flask. At this point, the cannula itself should be mostly dry on the inside, but should not be re-used without careful consideration regarding contamination. A clean solvent transfer followed by a solution of that solvent is a non-issue, but a solution cannot be followed by a clean solvent while retaining the expectation of cleanliness.

When done using a cannula, rinse it with deionized water, flush it out with air pressure, and replace it in the oven to keep it dry. When not in use, cannula are generally stored in a twisted loop. Your TA can demonstrate this.

## Reducing solvent volume under vacuum (solvent trap use)

One of the most common uses for the vacuum access on a Schlenk manifold is to use the reduced pressure to help a volatile solvent evaporate. This is significantly simpler than the other operations. However, it must be ensured that the solvent trap is prepared. The trap is a large two-piece glassware assembly that looks like one of the bubblers on a larger scale. The two pieces are joined at a ground-glass joint that must be lubricated with vacuum grease to maintain a seal while preventing the joints from fusing. These two pieces may be separate when you arrive, requiring greasing and assembly. A dewar of appropriate size for the trap should be half-filled with liquid nitrogen, and secured about the trap itself with cotton insulation wrapped around the top to minimize temperature loss. This functions to condense any gasses drawn into the manifold by the vacuum system and prevent them from entering the

pump itself. Gasses that pass through the trap successfully end up in the oil of the vacuum pump and then being exposed to the heat that the pump's operation creates – this is a danger if the gas is flammable, as most organic solvents are. In addition, the gasses that enter the oil are also expelled from the pump by evaporation, resulting in the rapid spread of any smells they may have and the potential dissemination of inhalation-based health risks. If the trap is exposed to atmosphere, liquid nitrogen is capable of condensing gaseous oxygen into liquid oxygen, a dangerous and explosive liquid. It is for this reason that the manifold must never be exposed to atmosphere while the trap is up (connected and sealed) and cooled, and vacuum must never be drawn on a solvent without the trap being up.

A flask sealed with a secured septum is connected to the manifold by one of the hoses. The manifold is turned to vacuum and the valve on the flask is opened. The solvent may begin to boil, but the volume of the flask should be selected to prevent this from posing any danger of contamination by bumping. Alternately, the valve on the flask can be to shut off access to the vacuum line for a few seconds at a time to let the liquid and vapors equilibrate, temporarily ending the boil. The solvent boiling away should condense in the trap, eventually causing any solute to precipitate out, and eventually leaving only dry materials in the flask. Note that evaporation is a highly endothermic process, so it is common for flasks to frost over and retard the evaporation. This is most commonly overcome either with body heat from a gloved hand, a heat gun, or with a bath of room temperature water.

When you are finished with air-sensitive operations for the day, the dewar must be moved aside and allowed to evaporate and the trap must be taken down (disconnected). Any condensed solvent in the trap must be disposed of in an appropriate manner. If the trap is going to be left down, then the vacuum grease should be wiped away from both parts of the joint to avoid dust from building in the grease and damaging its ability to seal. Otherwise, an empty trap can be stored up so long as it is secure.

## Day 1 Tasks

1. Draw 5 mL of ether from a sealed container via syringe and place it into flask 1.
2. Cannulate that ether from flask 1 to flask 2.
3. Evaporate the ether from flask 2.

**Repeat 3 times for each member in the group, or until confident. It is not enough to feel adequate in skill for these operations. The safety of multiple people rests upon each student's ability to perform this experiment to the safest degree possible.** That being said, once the safety and purpose aspects are understood, each of these operations can be easily summarized as a bullet point list.

Additional time can be spent practicing entering and exiting the glove bag to be prepared for the difference in tactile sensation and simple ability to grip and hold objects.

## Day 2

### Step 1: Purification of $\text{LiAlH}_4$ in dry diethyl ether

**Safety Note:** For this portion of the experiment, a fire-resistant laboratory coat is required and flame-resistant gloves are strongly recommended. This expectation does not relax until all products and waste are quenched.

Lithium aluminum hydride is both moisture and oxygen sensitive. Trace access to water or oxygen results in the formation of aluminum and aluminum oxide impurities which must be removed.

A pear Schlenk flask (**PS1**) with a side-arm is pre-prepared with approximately 100 milligrams of  $\text{LiAlH}_4$  weighed and sealed with a septum. A second septum must be prepared with a filter cannula assembly already pierced. The RBF will be prior purged and filled with nitrogen, but the septa must be switched to give access to the filter cannula. This will require positive nitrogen pressure at all points in time to prevent backflow of water vapor into the vessel, utilizing the neck as a vent during the exchange, then the cannula as vent after the switch.

Additionally, a second pre-weighed flask (**PS2**) must be prepared with 10 mL dry diethyl ether and chilled with an ice bath. Separately, an additional bath of water at room temperature water should be prepared before beginning this step. **PS1** should be transferred into the ice bath immediately before the solvent transfer. Use the filter cannula to slowly transfer the cold, dry ether into the flask with the LAH, watching for clear reactions and signs of temperature change. Once the ether has been transferred and the solution stirred for 10 minutes, use the filter cannula to transfer the solution from **PS1** to **PS2**. Disconnect the filter cannula from **PS2** and place it under vacuum to reduce the volume of solvent, eventually resulting in the rapid crystallization of the now purified LAH. A lukewarm water bath will prevent the flask from icing over by functioning as a heat source for the evaporation. Once set up, the crystallization step in **PS2** requires minimal supervision.

**PS1** still contains the filter cannula, but now also contains impurities removed from the LAH. Among these impurities may be elemental aluminum as well as unreacted LAH, both of which require careful quenching. The crystallization in **PS2** provides an opportunity to deal with these remnants.

### General Procedure for quenching metal hydrides:

The flask must be placed into an ice bath and given positive nitrogen pressure with a vent, then treated dropwise with protic solvents from a syringe in the following sequence of increasing reactivity:

1. Isopropyl Alcohol: 2 mL
2. Methanol: 2 mL
3. Water: 2mL

Remove from ice bath and allow to reach room temperature before exposing the flask to the atmosphere. At this point, the metal hydride has been rendered into a less reactive form and is ready to be disposed of in the appropriate hazardous waste container.

Once quenched, the resulting solution (or suspension) should be placed into the appropriate container and the flask cleaned and placed in the oven for future use.

Once the recrystallized LAH has had sufficient time to dry (<5 minutes after last visible solvent has evaporated), secure and double-check the seals on the sidearm and septum, and disconnect it to weigh for yield, taking care to utilize a carrier for the distance and handling it with caution. Once this is obtained, recalculate the amount of triethylammonium chloride which will be required for the reaction.



Formula weights - LAH: 37.95 g/mol Triethylammonium chloride: 137.65 g/mol

At a 1:1 stoichiometric ratio, this means that if the LAH yield was a perfect 100 mg (2.64 mmol) after purification, 362.7 mg (2.64 mmol) of the salt would need to be prepared for the reaction. On this scale, the salt should be easy to weigh for the near-exact ratio.

### Step 2: Formation of alane complex with amine

Reconnect **PS2** to the Schlenk line and purge it with nitrogen, then dissolve the recrystallized LAH in 5 mL of dry tetrahydrofuran (THF) by syringe while keeping the flask cold with an ice bath.

Weigh out the precise amount of triethylammonium chloride required for the recrystallized LAH and place it into a pear Schlenk flask (**PS3**) and purge the atmosphere. With a syringe, add 5 mL of dry THF and swirl until dissolved, then draw the solution up into the syringe for the addition into **PS2**. Once this transfer is complete, **PS3** needs to be briefly rinsed with toluene (3x 5mL) to remove traces of THF and any remaining salt.

While stirring and cold, add the triethylammonium chloride solution dropwise. The addition should be spaced across a minimum of 5 minutes. Remove the syringe and allow the reaction to continue for 20 minutes under positive nitrogen pressure from the Schlenk line with a needle to vent the surplus nitrogen as well as the hydrogen gas being formed. After 20 minutes, remove the needle, then shift the flask from positive nitrogen pressure to vacuum to reduce the volume, switching the ice bath for the unheated warm-water bath.

Seal a third pear Schlenk flask (**PS3**) and purge the atmosphere in the flask as listed above, then syringe 5 mL of dry toluene into the flask. Once the alane-amine product in **PS2** has dried, check the seals on both flasks and prepare to cannulate the toluene from **PS3** to **PS2**. Once the toluene has been transferred, swirl the flask gently to maximize exposure to the solvent. The remaining LiCl salt impurities produced by the reaction should be almost entirely insoluble, allowing for a simple separation of product by tilting the flask to isolate the remaining solids from the tip of the cannula. Any remaining solids should be free-flowing to ensure no product remains trapped beneath the secondary products. Tilt **PS2** to decant the solution from the remaining solids, establishing maximum separation. Cannulate the product in the toluene solution from **PS2** back into **PS3**. The product should now be isolated. In most scenarios, a solid phase yield would be required, but for safety and simplicity, assume that the reaction is qualitative (100% yield).

### Step 3: Spectroscopy

At this point, carefully double-check the seals and disconnect the flask to transfer your product to the glove-bag to collect portions for spectroscopy (see page 22). You will collect an IR and  $^1\text{H}$ -NMR spectrum for your product.

Once in the glove bag, dilute 0.1 mL of the product solution with 0.9 mL of deuterated toluene in an NMR tube. Once capped, seal the tube with parafilm.

Prepare a sample for infrared spectroscopy similar to a Nujol mull. You will not have your product in the solid state, so as the sample should contain no more than a few milligrams of the alane-amine adduct, use a small droplet of the toluene solution in the center of the first plate. Surround your sample with small amounts of mineral oil and press the salt plates together as normal. The mineral oil will provide sufficient insulation to inhibit the reactivity of the product to allow the spectrum to be obtained.

Once quantities of the alane product have been extracted for both spectroscopy techniques, the remaining product needs to be quenched as a reactive metal hydride.

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2: The Alane-Amine Adduct ( $\text{C}_2\text{H}_5)(\text{CH}_3)_2\text{N-AlH}_3$  (Experiment) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

### 3: $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ and $\text{NiCl}_2(\text{dppe})$ (Experiment)

#### Introduction

**This experiment is from the textbook (pages 85-92).** Further information and background information can be found there. The experiment is copied here verbatim for ease of use during lab.

#### Notes

The adapter on the right arm of the 3-neck flask is not necessary. Just replace it with a plug. Allow a TA to assist in transferring the ammonia. Do this before adding the dry ice. The oil in the bubbler may suck back when you add the dry ice. If that happens, disconnect the bubbler.

Add the  $\text{NH}_4\text{Br}$  slowly, or the  $\text{NH}_3$  will bubble up too vigorously.

Don't try too hard to extract hard crude product from the flask. The flask would probably break and it is expensive.

Leftover product should be given to the TA.

#### Safety Precautions

Be sure to use a fume hood for this experiment. ***Do not inhale ammonia fumes!!***

Read all the safety warnings in the text for this experiment.

Ni complexes are carcinogens.

#### Waste disposal

Sodium metal waste should be disposed of as described in the text. Anhydrous isopropanol will be available for disposal. Ask your TA what to do with the alkane that was used to prepare the sodium. Place the remaining waste in the experiment 8 waste container.

#### Spectra

1. Acquire the  $^1\text{H}$  NMR spectrum of dppe in  $\text{CDCl}_3$ . Acquire the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of dppe. To get a good  $^{31}\text{P}$  spectrum, use 40-50 mg of material dissolved in about 0.5 mL of  $\text{CD}_2\text{Cl}_2$ . Get at least 256 scans, which takes about 10 min. We use the same solvent ( $\text{CDCl}_3$ ) for both the  $^1\text{H}$  NMR and the  $^{31}\text{P}\{^1\text{H}\}$  NMR.
2. Acquire the IR spectrum of dppe.
3. UV-Vis measurements of  $\text{NiCl}_2(\text{dppe})$ . A spectrum in the range of about 320–800 nm should be measured in dichloromethane solution.
4. Acquire the  $^1\text{H}$  NMR spectrum of  $\text{NiCl}_2(\text{dppe})$  in  $\text{CDCl}_3$ . Also acquire the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum

#### Experiment

#### Safety Precautions

Liquid ammonia is a very volatile, irritating, and toxic material; all operations involving it must be conducted in a hood. Wear rubber gloves whenever handling liquid  $\text{NH}_3$ . Although ammonia has a low boiling point ( $-33^\circ\text{C}$ ), its heat of vaporization is sufficiently high that it can be dispensed into the reaction flask without external cooling. Solutions of sodium in liquid ammonia are so reducing that they carbonize Teflon-coated stir bars; it is therefore necessary to use a glass-covered stir bar. The large amount of  $\text{NH}_3$  gas evolved during the operation serves as a protective atmosphere so that it is not necessary to flush the reaction with  $\text{N}_2$ .

#### Sodium-Liquid $\text{NH}_3$ Solution

Equip a 500-mL three-neck round-bottom glass with a glass covered magnetic stir bar (**Caution: Rapidly agitated glass stir bars tend to break though round bottom flasks**). Attach a dry ice condenser to the central neck, attach the condenser to a bubbler (see Fig. 8-1), but leave one neck unstoppered for now. Lubricate all joints with silicone grease.

The next step is to put liquid  $\text{NH}_3$  into the flask. Ammonia cylinders contain a mixture of liquid gas, and which of these comes out of the cylinder depends on how the cylinder is oriented. The larger  $\text{NH}_3$  cylinders usually are fitted with a goose neck educator



tube as shown in Figure 8-2. With the cylinder tipped and the outlet of the main valve pointing upward, the educator tube will be immersed in the liquid  $\text{NH}_3$ . (Smaller cylinders without educator tubes may simply be tipped at a greater angle.) In this way, liquid  $\text{NH}_3$  is dispensed from the cylinder directly into the reaction flask. This procedure is by far the best way to obtain the 200mL needed for the reaction flask. This procedure is by far the best way to obtain the 200mL needed for the reaction. (Do *not* try to obtain the liquid  $\text{NH}_3$  by cooling the gas with a dry ice condenser. This latter method will condense enough water from the air to spoil the reaction in the next step.) We use an additional 3-neck flask to distill liquid ammonia in 2018 spring. (Reaction without distillation failed. Possibly due to water in liquid ammonia.)



Figure 8-1  
Three-neck flask equipped with a dry ice condenser.

Delivery of the liquid  $\text{NH}_3$  from the cylinder may be accomplished through a rubber tube inserted into the open neck of the flask. After positioning the cylinder as shown in figure 8-2, open the main valve (*Remember*, this is only an on off valve). Regulate the flow of liquid  $\text{NH}_3$  by adjusting the needle valve. Introduce approximately 200mL of liquid  $\text{NH}_3$  into the flask, after the  $\text{NH}_3$  has been added to the reaction flask, close the needle valve and main valve on the  $\text{NH}_3$  cylinder, and stopper the third neck of the flask. The ammonia that remains in the transfer tube should be allowed to evaporate in the hood.

Charge the condenser to *one-quarter* full with 95% ethanol and then cautiously add pieces of dry ice. The dry ice condenser prevents the loss of very volatile solvents so long as their boiling points are greater than  $-78^\circ\text{C}$ , which is the sublimation point of the solid carbon dioxide. Do not allow the ethanol to spill into the reaction flask. During the course of the reaction, an insulating coating of ice should be allowed to accumulate on the outside of the reaction flask. Monitor the amount of dry ice in the condenser and add more than necessary.

Weigh out 2.3g (0.1mol) of solid in the following way. Remove a piece of sodium from the oil in which it is stored, and use a paper towel to soak up most of the oil that remains on the sodium lump. Do not use sodium that has developed a thick white coating of  $\text{NaOH}$ ; instead, choose a piece that appears grey. On a paper towel, cut the sodium into small pieces and weigh the sodium by adding the pieces to a tared beaker containing heptane or similar nonvolatile alkane. It is important that you accurately weigh out the  $\text{Na}$ , but it is not important that this amount be exactly 2.3 g. Adjust the amount of the other reagents in accordance with the amount of  $\text{Na}$  used. Remove one of the stoppers on the three-neck flask and add 2.3g (0.1mol) of the freshly cut sodium metal. Replace the stopper. After approximately 10 min, the sodium dissolves completely to give a deep blue solution, which should be used immediately in the next step.

Dispose of any unwanted sodium scraps by adding them to a small beaker an anhydrous isopropanol, which reacts with sodium to form  $\text{H}_2$  and  $\text{NaOC}_3\text{H}_7$ . After the sodium has completely reacted, the alcohol solution may be washed down the drain with a flush of water. Do *not* discard sodium metal in a waste basket or sink.

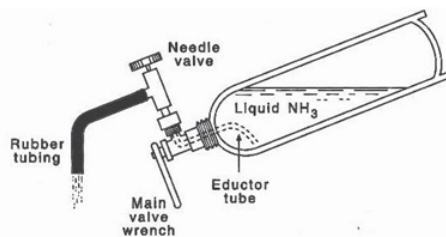


Figure 8-2  
Dispensing  $\text{NH}_3$  from a cylinder.

### 1,2-Bis(diphenylphosphine)ethane, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (dppe)

Add 13.1g (0.05mol) of solid triphenylphosphine to the Na-NH<sub>3</sub> solution. The addition should be done in five portions over the course of a few minutes to minimize the frothing of the reaction. The solution changes from blue to the red-orange color characteristic of the NaPPh<sub>2</sub>. By gripping the necks of the flask, *gently* swirl the solution to dissolve any sodium that has deposited on the upper walls of the flask. After 30 minutes, cautiously add 4.9g (0.05mol) of dry NH<sub>4</sub>Br to the reaction mixture with stirring. Prepare a solution of 2.47g (0.025mol) of 1,2-dichloroethane in 20mL of anhydrous ether. Add this solution to the orange NaPPh<sub>2</sub> solution and allow the mixture to stir for at least 10 minutes. Finally, remove the dry ice condenser, and allow the resultant pale orange mixture to evaporate quickly – simply leave the flask unstoppered in the hood until the next laboratory period.

To work up the reaction, add 100mL of water and 75mL of dichloromethane to the flask; stir the mixture well to dissolve most of the solid. Pour the two-phase mixture into the separatory funnel. Rinse the reaction flask with some additional dichloromethane and add this washing to the separatory funnel; drain the organic (lower) phase into a 250-mL round-bottom flask and dilute it with 100mL of 95% ethanol. Concentrate this solution on a rotary evaporator to a total volume of about 75mL. Filter off the colorless microcrystals (see Figure 13.1), wash them with a little ethanol, and allow them to air dry. Recrystallize the product by dissolving it in dichloromethane and, if necessary, filtering the solution to remove any solids. Dilute the dichloromethane solution with an equal volume of 95% ethanol and concentrate the mixture to about one-third its volume in a rotary evaporator. Collect the resulting crystals by filtration. Record the melting point.

### Dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II), NiCl<sub>2</sub> (dppe)

Prepare a solution of 0.320g (1.34mmol) of NiCl<sub>2</sub> · 6 H<sub>2</sub>O in 50mL of 95% ethanol. To this green solution add 0.54g (1.34mmol) of dppe. After the mixture has stirred for a few minutes, the product is fully formed and can be collected by filtration. Wash the orange solid with 20mL of diethyl ether to remove unreacted dppe. Record the infrared (IR) spectrum of the product as Nujol mull (see Experiment 19) and the proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectrum in CHCl<sub>3</sub> or CDCl<sub>3</sub> (consult your instructor). Integrate the NMR peaks due to the CH<sub>2</sub> and C<sub>6</sub>H<sub>5</sub> groups (see Experiment 7).

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3: Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> and NiCl<sub>2</sub>(dppe) (Experiment) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

## 4: Metal-Metal Quadruple Bonds (Experiment)

### Synthesis of Chromium (II) Acetate

#### Safety Precautions

This procedure requires the use of concentrated (12 M!)  $\text{HCl}_{(\text{aq})}$  which is corrosive, causes burns and releases  $\text{HCl}$  gas, which is also toxic and corrosive and causes burns. Care must be taken that this material is kept in the hood at all times.

The addition of  $\text{HCl}$  to  $\text{Zn}$  metal produces  $\text{H}_2$  gas which is *extremely flammable*, odorless, and colorless. The gas produced by the reaction must be vented into the hood, and there are to be absolutely no Bunsen burners or sparks of any kind during this experiment.

Chromium (III) is toxic and an irritant, so this material is not to be allowed in the sinks or the drains. The chromium (II) produced by this experiment is a strong reducing agent, and so must be treated with caution. If it will reduce oxygen, it will reduce you, too. Do not pour this waste down the drain, there will be a specially labeled waste container instead.

As always, goggles **MUST** be worn in the lab at all times. You only have two eyes and they are not replaceable. Also, because of the toxicity and reactivity of the chemicals used in this experiment, it is strongly advised to wear gloves whenever handling any chemical and good chemical hygiene (common sense) is expected at all times.

#### Handling Chemicals

It is important to remember that **chromium (II) is very sensitive to oxygen**, so the reaction must remain under inert gas at all times. This reaction also produces a lot of  $\text{H}_2$  gas, and you must be careful to make sure that the gas has somewhere to go. Otherwise your glassware may decide to fly apart, and aside from ruining your experiment, it could create a serious accident. Even with venting, enough pressure may build inside the flask to make connections pop loose, so be sure to **secure any attachments to your flasks with rubber bands**.

Because of the sensitivity of chromium (II), all solvents and reagents (15mL DI water, 32 mL conc.  $\text{HCl}$ , 25mL saturated  $\text{NaOAc}$  solution) must be thoroughly degassed by bubbling  $\text{N}_2$  through them for at least 30 min. **Do not use tap water, or dissolved  $\text{O}_2$  in the liquid will destroy your product.**

#### Procedure:

We will be using a Schlenk line in this experiment, so you need to make sure that the line is ready before you begin working. The line itself should resemble Figure 3, but you will want to have your TA show you what needs to be done if you don't already know. You should have  $\text{N}_2$  flowing through the gas side of the Schlenk and the vacuum pump should also be ready before you begin.

Find a 250 mL Schlenk flask and clamp it into position in an empty pan on top of a magnetic stir plate. Add to it a magnetic stir bar, **22.6 g**  $\text{Zn}$  metal, **13.7 g**  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , and **15 mL** of degassed, deionized water. Connect a 50 mL pressure equalizing addition funnel, and close the free neck with a glass stopper. *Don't forget to grease all the ground glass connections!* It should look like the setup in figure 1. Connect the apparatus to the Schlenk line with a thick Tygon hose, then evacuate the apparatus and refill it with  $\text{N}_2$ . Repeat this step several times, or some  $\text{O}_2$  will remain in the flask. With  $\text{N}_2$  flowing through the flask from the sidearm, pour **32 mL** degassed, concentrated  $\text{HCl}_{(\text{aq})}$  into the addition funnel.

When you have finished setting up the reaction, cool the flask with a bath of ice and water, then begin stirring. The  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  should dissolve to give a dark green solution. Once the mixture has had time to cool and the  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  has dissolved, check to make sure that the flask is open to the  $\text{N}_2$  line (**very important!**). If it is, begin dripping the  $\text{HCl}$  into the solution. You should see a very vigorous and exothermic evolution of  $\text{H}_2$  gas, and after a few minutes, the reaction will start to turn very bright blue.

While the reaction is running, you will need to setup another apparatus. This one will be a 3-neck round bottom flask (1L), a second addition funnel, another magnetic stir bar, 2 glass stoppers and gas inlet. Connect the addition funnel to the middle neck of the flask, the gas inlet to one side neck and glass stoppers in the open joints. The apparatus should look like figure 2. Connect the gas inlet to the Schlenk line with a length of Tygon hose. Evacuate and refill the flask with  $\text{N}_2$  several times, then close it off from the Schlenk line.

After all of the  $\text{HCl}$  has been added to the reaction flask, you will notice that the evolution of gas begins to slow down. When the evolution is complete or close to completion, replace the addition funnel with a rubber septum (with  $\text{N}_2$  flowing through the flask),

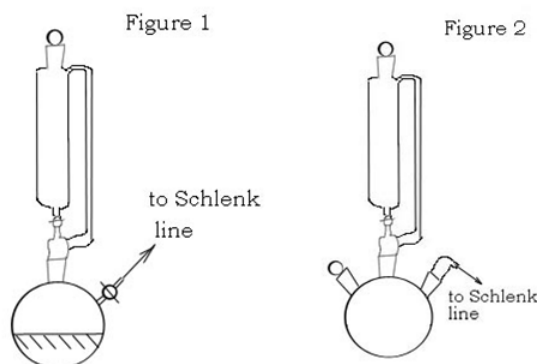
and replace the glass stopper on the side of the 3 neck flask with a rubber stopper as well (don't forget the  $N_2$ !!). You are now ready to transfer the solution to the empty flask. This will be done with a cannula, which is a very long, double ended needle. Poke the cannula through the rubber septum of the reaction flask and allow  $N_2$  to flow through it for a few seconds. You will then poke the other end of the needle through the rubber septum on the empty flask. Lower the end of the needle into the reaction mixture, and clamp the whole flask higher than the receiver. Use a lab jack to support the raised flask, and make sure the receiving flask is resting on something secure. To get the solution to siphon into the empty flask, quickly turn the Schlenk key of the empty flask past the vacuum position, but beware that dissolved  $HCl$  and  $H_2$  will try to bubble out from the solution! If you're not sure about this step, find your TA.

Once all of the  $CrCl_2$  solution has been transferred to the receiving flask, it should be open to the  $N_2$  line if it's not already and you are done with the reaction flask. Cannulation won't transfer everything, so some excess  $Zn$  and a little bit of solution will remain behind – this is OK. Dispose of the solids and liquid properly, and make sure that all of the equipment is clean for the next group. Your TA will know where to dispose of the waste. While you're at it, you may want to observe how quickly your  $CrCl_2$  changes back to green! This is an indication of how careful you need to be with your experiment. If you observe this color change during the next few steps, you probably let air into your flask and you should talk to your TA. Be sure to clean the cannula and flask with water right away (regular distilled water is fine this time) because you will reuse it in the following step.

With  $N_2$  flowing through the flask, open the glass stopper on the addition funnel and pour in **25 mL** of degassed, saturated sodium acetate solution. Start the magnetic bar stirring and slowly add the sodium acetate solution. You will begin to see a dark precipitate which is  $Cr(O_2CCH_3)_2$ . We now need to isolate the precipitate, and this will be accomplished by using a Schlenk filter, shown in Figure 4.

Evacuate and fill the both sides of the Schlenk filter several times, then with  $N_2$  flowing through the flask, replace the glass stopper with a rubber septum. While the reaction vessel is open to the  $N_2$  line, poke the *clean* cannula through the rubber septum. Allow  $N_2$  to flow through for a few seconds, and then insert the free end of the needle through the septum of the filter. Your setup should resemble Figure 5. Cannulate the solid and the liquid into the top of the filter, then have your TA show you how to use the Schlenk filter. Remove as much of the liquid as you can with the vacuum pump, then collect the solids. Measure IR spectrum of the product with the solid.

In your report, you should include the IR spectrum for the product, as well as the yield. Also, be sure to include an analysis of how the two chromium atoms are interacting using literature references that are not included in Experiment 11 in your lab manual.



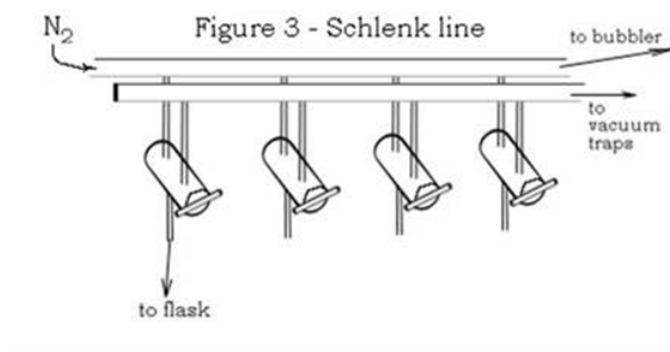


Figure 4 Schlenk filter

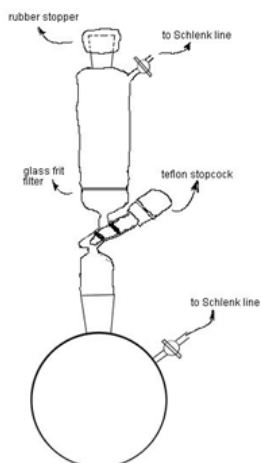
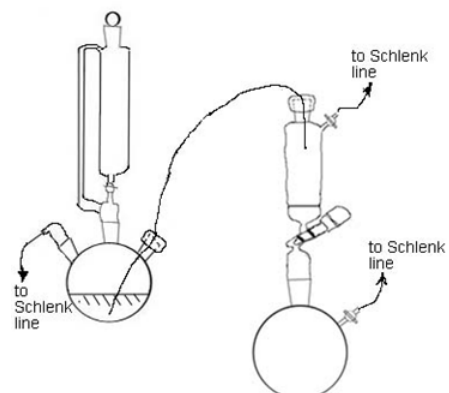


Figure 5 Schlenk filter setup



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## 5: The Paramagnetic Complex $\text{Mn}(\text{acac})_3$ (Experiment)

### Introduction

**This experiment is from the textbook (pages 117-130).** Further information and background information can be found there. The experiment is copied here verbatim for ease of use during lab.

### Notes

1. The molar amount for  $\text{KMnO}_4$  is incorrect. Instead of 0.027 mol it should say 0.023 mol.
2. Near the top of page 126, the instructions state that you should dry the crystals of  $\text{Mn}(\text{acac})_3$  for at least 30 minutes. Dry them for longer than that if possible.
3. The normal chemical shift of  $\text{CHCl}_3$  is 7.26 ppm. In the presence of a paramagnetic complex it is shifted upfield.
4. The magnetic susceptibility balance (MSB) we use is slightly different from the Gouy balance used in the lab manual. With the MSB, you need to weigh the empty tube and then the filled tube (filled to 2.5 to 3.5 cm).
5. Because we are using an MSB instead of a Gouy balance, some of the questions do not apply. Please ignore Report question #1 and Problems #2, 5 and 10.
6. There is an error on page 122 in footnote "a" of the table. The number should be  $-13 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ . Also be careful when reading the table. For example, the entry for  $\text{acac}^-$  is  $-52 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ .
7. The equation for calculating the susceptibility is explained in the manual for the magnetic susceptibility balance. The equation is:

$$\chi_g = \frac{C_{bal} \times l \times (R - R_0)}{10^9 m} \quad (5.1)$$

$$\chi_m = \chi_g \times M \quad (5.2)$$

$C_{bal}$  = balance calibration constant =  $1.006 \text{ cm}^2$

$l$  = sample length (cm)

$m$  = sample mass (g)

$R$  = reading for tube plus sample

$R_0$  = reading for empty tube

$M$  = molar mass of  $\text{Mn}(\text{acac})_3$

8. An alternative, and very accurate, method for determination of the magnetic susceptibility is the Evan's Method, based on  $^1\text{H}$  NMR. A special NMR tube is needed to carry out this measurement. It is based on the chemical shift difference between pure  $\text{CDCl}_3$  and a  $\text{CDCl}_3$  solution of a known amount of the dissolved paramagnetic  $\text{Mn}(\text{acac})_3$ .



### Safety Precautions

Read all of the safety warnings in the text for this experiment.

Chloroform may be a carcinogen. Therefore **do not touch, inhale or ingest chloroform**. Use chloroform in a **fume hood**. **Wear gloves** which are resistant to chloroform (see chart earlier in this manual). The Viton and Silver Shield gloves are not disposable.

### Waste disposal

All solid waste should be collected in the Experiment 12 solid waste container. Collect the filtrate in the Experiment 12 liquid waste container.

### Experiment

### Safety Precautions

Potassium permanganate is a strong oxidant. If you spill some on your skin, wash it off immediately with large amounts of water.

### Tris(acetylacetonato)manganese(III), $\text{Mn}(\text{acac})_3$

In a 250-mL beaker, prepare a solution of 3.75g (0.0237mol) of potassium permanganate,  $\text{KMnO}_4$ , and 75mL of distilled  $\text{H}_2\text{O}$ . Warm the stirred solution to  $80^\circ\text{C}$  on a hot plate to dissolve all the solid. Then cool the solution to room temperature by packing the beaker with ice. When the solution has cooled, stir it rapidly and slowly add 17mL (16.6g, 0.166mol) of acetyl acetone in several aliquots over a few minutes. (If you add the acetyl acetone too quickly, the solution will generate large amounts of foam that may overflow the flask.) Note the color change. After the addition is complete, boil the solution for 5 minutes, and then chill the beaker in ice. Collect the shiny brown-black crystals on a coarse fritted filter (see Figure 13-1) and wash them three times with 10-mL portions of distilled water. Dry the crystals thoroughly by pulling air through the frit for at least 10 minutes. If possible, dry the crystals under vacuum for at least 30 minutes.

### Measurement of Magnetic Susceptibility by the Evans Method

Weigh a clean and dry NMR tube (5-mm outer diameter) on an analytical balance to the nearest 0.1mg (or the nearest 0.01mg if possible). Add between 2 and 5mg of  $\text{Mn}(\text{acac})_3$  to the NMR tube; this amount of  $\text{Mn}(\text{acac})_3$  is less than what is needed to cover the bottom of the tube. Reweight the NMR tube to determine exactly the amount of solid added.

If you will be using a NMR spectrometer equipped with an electromagnet, carry out the following procedure. Into the NMR tube, place a sealed capillary that contains pure chloroform,  $\text{CHCl}_3$  (the capillaries that can be made by syringing  $\text{CHCl}_3$  into a melting point capillary, and then sealing the open end in a flame). Make sure to insert the capillary so that the end filled with solvent is resting on the bottom of the NMR tube. With a syringe, add exactly 0.70mL of  $\text{CHCl}_3$  to the NMR tube. Cap the tube and shake gently to dissolve the  $\text{Mn}(\text{acac})_3$  completely. When the solid is completely dissolved, record the NMR spectrum of the solution (see your instructor for directions concerning the use of the NMR instrument). There should be two peaks near  $\delta 7$ : One of the two peaks is due to the  $\text{CHCl}_3$  in the capillary and the other due to the  $\text{CHCl}_3$  that has been paramagnetically shifted by the dissolved  $\text{Mn}(\text{acac})_3$ . Determine the chemical shifts of these two peaks, and measure the separation between them in hertz. For example, if the spectrometer frequency is 100MHz and the two peaks are 0.3ppm apart, then the separation is  $0.3 \times 100 = 30\text{Hz}$ . The magnetic susceptibility of your sample can be determined from the weight of your sample, the volume of  $\text{CHCl}_3$  used, the chemical shift difference  $\Delta\nu$  between the two peaks. And radio frequency used. Use Eq. with  $Q=1$ .

If you will be using a NMR spectrometer equipped with a superconducting magnet, carry out the same procedure except use deuterated chloroform ( $\text{CDCl}_3$ ) both in the capillary and as the solvent to dissolve the  $\text{Mn}(\text{acac})_3$ . The measurement is conducted the same way; the only difference is that the two peaks near  $\delta 7$  are due to the small (about 0.1%) residual amounts of  $\text{CHCl}_3$  in the  $\text{CDCl}_3$  solvent. Determine the magnetic susceptibility of your sample from Eq 10 with  $Q=2$ .

### Measurement of Magnetic Susceptibility by the Gouy Method

Scratch a horizontal line on the Gouy tube about 2cm from the top, if this has not already been done. For the weight measurements, the tube should always be filled to this line. To remove paramagnetic impurities from the tube, clean it with Nochromix cleaning solution (do not use chromic acid, which will add paramagnetic impurities!). Thoroughly rinse the tube with water and acetone, and dry it in the oven. Do not wipe the tube with a dry towel; this gives the tube a static charge that significantly affects the weighings.

Weigh the empty tube on the chain with the field off. With the field on, weigh the tube again. Although “pure class” is diamagnetic, paramagnetic impurities may cause the tube to be attracted by the field rather than repelled. The difference between these two weighings, on minus off, is and will be used to correct for the magnetism of the tube when the sample is weighed in the tube. It is necessary to maintain the same magnetic field for all measurements when the field is on. With electromagnetics this will require a constant electric current (and therefore field). Because the current will decrease as the coils begin to heat, the current will have to be adjusted frequently. Current regulators are available that will conveniently provide this control.

To correct for the magnetism of air when it is displaced by the sample, the volume occupied by the air must be determined. Fill the tube to the line with water at the existing temperature, the volume ( $V$ ) may be calculated. The volume susceptibility of air is  $0.029 \times 10^{-6}$ .

To determine the calibration constant for the apparatus, fill the dry tube to the line with the solid standard. The largest source of error in the Gouy method is inhomogeneously packed sample tubes. To minimize this problem, the sample should be finely powdered (use a mortar and pestle) and introduced into the tube in small portions. After each addition, firmly tap the tube on the hard surface. Careful packing of the tube will require 20-30 minutes. Weigh the tube with the magnet off and again with the magnet on, using the same current as used previously. After each weighing of a solid sample with the field on, measure the temperature between the poles of the magnet. The difference in these two weighings (on minus off) is designated  $\Delta$  and is a measure of the magnetic susceptibility of both the sample and the tube. From the magnetic susceptibility of both the sample and the tube. From the magnetic susceptibility per gram of the standard ( $\chi$ ), the mass in grams of the standard ( $m$ ), and the values of  $\delta$ ,  $\Delta$ , and  $V$ , the calibration constant ( $\beta$ ) may be calculated

$$(\chi)(m) - (0.029 \times 10^{-6})V = \beta(\delta - \Delta) \quad (5.3)$$

For calibration, either  $\text{HgCo}(\text{NCS})_4$  or  $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$  where  $\text{en}=\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , has provided to be very satisfactory. These compounds may be prepared easily in high purity, are stable, are not hygroscopic, and pack very well. The susceptibility per gram of  $\text{HgCo}(\text{NCS})_4$  at  $20^\circ\text{C}$  is  $\chi=16.44 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ . The susceptibility obeys the Curie-Weiss law with  $\theta = -10\text{K}$ . The relatively high susceptibility of this compound sometimes causes the sample tube to cling to one of the poles of the magnet. This problem can be avoided by carefully positioning the sample tube midway between the poles. On the other hand, or  $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$  is rarely drawn toward a pole because of its lower susceptibility. Its values  $20^\circ\text{C}$  is  $\chi=11.03 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ . It, too, obeys the Curie-Weiss law with  $\theta = 43\text{K}$ .

After the values of  $\beta$  is obtained, the sample tube is cleaned and dries. The same procedure is repeated for the determination of the unknown,  $\text{Mn}(\text{acac})_3$ . The empty tube is weighed with the field on and off to obtain  $\delta$ . Then the tube is carefully packed with finely powdered  $\text{Mn}(\text{acac})_3$ . The filled tube is then weighed with the field on and off to obtain  $\Delta$ . These measurements will then permit the calculation of  $\chi$  and the molar susceptibility  $\chi_M$ .

Summarized below are the measurements that must be made first on the standard and then on the unknown:

- A. Weight of the empty tube, field off \_\_\_\_\_ g
- B. Weight of the empty tube, field on \_\_\_\_\_ g
- C. Weight of the tube filled to line with water, field off \_\_\_\_\_ g
- D. Weight of the tube filled to line with solid, field off \_\_\_\_\_ g
- E. Weight of the tube filled to line with solid, field on \_\_\_\_\_ g
- F. Temperature during measurements above \_\_\_\_\_ g

As given, these weights are related to the terms in Eq. 12.3 in the following manner:

$$V = \frac{(C - A)}{d} \quad (5.4)$$

*d is the density of water (g/mL) at ambient temperature*

$$\Delta = B - A \quad (5.5)$$

$$\delta = E - D \quad (5.6)$$

$$m = D - A \quad (5.7)$$

To determine the reproducibility of your value, repeat the evaluation for  $\chi$  for  $\text{Mn}(\text{acac})_3$  at least one more time by emptying and repacking the tube and then making the necessary weighings.

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5: The Paramagnetic Complex  $\text{Mn}(\text{acac})_3$  (Experiment) is shared under a [CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/) license and was authored, remixed, and/or curated by LibreTexts.



## 6: B- Synthesis of Synthetic Opal (Experiment)

### Introduction

Consult the publication [Jiang, P., Bertone, J.F., Whang, K.S., Colving, V.L., Single-Crystal Colloidal Multilayers of Controlled Thickness. \*Chem. Mater.\*, 1999, 11, 2132-2140.](#) for background and synthetic procedure.

### Materials:

- 4 disposable 20 mL screw cap vials (glass)
- 4 glass pipettes (3x1 mL, 1x5 mL)
- 4 micro stir bars
- 4 glass microscopy slides (cut to 1cm x 7.5cm) – **NOT DISPOSABLE**. Clean for re-use.
- disposable cuvette for UV/vis spectroscopy
- Sample holders for electron microscopy digital or cell phone camera (bring own)
- flash drive (bring own);
- Image J program: <http://imagej.nih.gov/ij/download.html>

### Chemicals:

- Tetraethoxysilane (TEOS), Alfa Aesar (99+%)
- Absolute (200% proof) ethyl alcohol (Koptec)
- Concentrated ammonium hydroxide solution (EM Science, 28.0~30.0%)
- Deionized water (18 MΩ)



### Safety Precautions

Perform experiment on bench top. Measure concentrated ammonia in fume hood. Avoid eye contact with tetraethoxysilane.

### Waste disposal

Use the containers provided.

Table 1. The amounts of chemicals used in different samples

Sample Number	1	2	3	4
Volume of TEOS (mL)	0.76	0.76	0.76	0.76
Mass of TEOS (g)	0.71	0.71	0.71	0.71
Volume of ammonium hydroxide (mL)	1.33	1.33	1.33	1.33
Mass of ammonium hydroxide (g)	1.20	1.20	1.20	1.20
Volume of deionized water (mL)	0	0.40	0.75	1.30
Mass of deionized water (g)	0	0.40	0.75	1.30
Volume of ethyl alcohol (mL)	17.91	17.51	17.16	16.61
Mass of ethyl alcohol (g)	14.13	13.82	13.54	13.11

### Day 1

**Synthesis of colloidal SiO<sub>2</sub> particles.** For each experiment the necessary amounts of dehydrated ethanol, ammonium hydroxide, and deionized water (18 MΩ) were first mixed in the reaction vial. Then add the TEOS quickly and with mild stirring. The solution was colorless and transparent. Continue to stir the solution with magnetic stir bar for 1 h. The final appearance of the solution is white milky. The amounts of chemicals used in different samples are shown above in **Table 1**, while the concentrations of TEOS,

$\text{NH}_3$ , and  $\text{H}_2\text{O}$  in the ethanol solution are shown below in **Table 2** (assuming that the total volume is the sum of volumes of each chemicals).

Table 2. The concentrations of TEOS,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  in the ethanol solution

Sample Number	1	2	3	4
Concentration of TEOS (mol/L)	0.17	0.17	0.17	0.17
Concentration of $\text{NH}_3$ (mol/L)	1.0	1.0	1.0	1.0
Concentration of $\text{H}_2\text{O}$ (mol/L)	2.4	3.5	4.5	6.0

**Growth of  $\text{SiO}_2$  Colloidal Crystal.** Transfer 10 mL  $\text{SiO}_2$  nanosphere solution into a new scintillation vial and insert a glass slide (1cm x 7.5cm) in upright position. Let the solvent evaporate naturally in fume hood to produce films on the microslide.

**SEM sample preparation.** Transfer ~3 mL  $\text{SiO}_2$  nanosphere solution into a disposable 15mL centrifuge tube and then centrifuge at 6000 rpm for 5 min. **Be sure to balance your samples before centrifugation.** Discard the colorless supernatant in the waste container. Disperse the white precipitate in ~3 mL ethanol and centrifuge again. Then discard the colorless supernatant and disperse the white precipitate in ~12 mL ethanol. These solutions will be used for UV-Vis measurement later. Pick one sample solution and dilute it tenfold. Place 5  $\mu\text{L}$  onto a clean glass slide and examine it after evaporation. A faintly visible ring signifies that the concentration is appropriate. A clearly visible ring or series of rings indicates the concentration is too high. Transfer 5  $\mu\text{L}$  diluted solution to a silicon wafer. The uncovered silicon wafer with sample is then oven dried for at least one day.

## Day 2

**SEM measurement.** In Chemistry 0011 at 6 pm or 10 am. Please bring your own flash drive. From SEM images the size of  $\text{SiO}_2$  nanoparticles is obtained for the picked sample.

**UV-Vis spectra for  $\text{SiO}_2$  nanosphere solution.** The UV-Vis spectra for the  $\text{SiO}_2$  nanosphere solutions above are recorded by using the disposable cuvette. Use a cuvette filled with ethanol to record the background.

**$\text{SiO}_2$  colloidal crystal:** Place the glass slide with the  $\text{SiO}_2$  colloidal crystal into the spectrometer to record the transmission spectrum for the range from 350 nm to 1000 nm. Use an uncoated glass slide to record the background. The absorption of the glass slide corresponds to the size of the  $\text{SiO}_2$  nanoparticles (Glass slides and  $\text{SiO}_2$  do not absorb visible light.)

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## 7: F- Preparation of Ferrocene $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ (Experiment)

### Introduction

Consult the following publication for background information and history: Rausch, M., Vogel, M., Rosenberg, H. Ferrocene: A Novel Organometallic Compound. *J. Chem. Ed.* **1957**, 34, 266-272.

Recent commentary on history of ferrocene structure determination: Seeman, J. I., Cantrill, S. Wrong but Seminal. *Nature Chem.* **2016**, 8, 193-200.

### Synthesis requires the following chemicals:

- 4 g of KOH
- 12 mL of 1,2-dimethoxyethane (glyme)
- 1.3 g Iron(II) chloride tetrahydrate
- 7 mL DMSO
- 1.0 mL cyclopentadiene (obtained by thermal cracking of dicyclopentadiene with storage at ca.  $-78^\circ\text{C}$ )
- 20g ice
- 9 mL 12 M HCl
- 0.70 mL Acetic anhydride
- 0.20 mL 85% Phosphoric acid
- 1.0 mL ice cold water
- 3 M NaOH
- 1mL Dichloromethane
- Diethyl ether
- t-Butanol
- 300 mg Alumina

### Equipment required:

- Mortar and pestle
- 2 Stir bars (1" and ¼")
- 100 ml 3-neck RBF
- 3 14/20 septa
- 5 mL
- dropping funnel (~10mL, 14/20 joint)
- bubbler
- 250 mL beaker
- 25 mL beaker
- 600 mL beaker
- Hirsch funnel
- Filter paper
- Adapter
- Filter flask
- Watch glass
- 2 crystallization dishes
- 2 Melting point tubes
- 10 mL round bottom flask
- pH paper
- column
- Alumina
- Stir/hot plate and heating (water bath)

## Safety Precautions

### Perform experiment in fume hood.

DMSO, DCM,  $C_5H_5$ , and  $Et_2O$  are all **volatile and have noxious vapors. Avoid inhalation.**

DMSO is **easily absorbed through the skin.**

KOH is hygroscopic and **extremely corrosive**. Handle with caution. Grind KOH in fume hood, inhalation of powder is dangerous.

HCl is a **strong acid and corrosive**.

## Waste disposal

Use the containers provided. Needles should be disposed of in the sharps container.

## Procedure

### Part A: Synthesis of Ferrocene (Day 1)

Set up a 100-mL three neck (14/20) round bottom flask (RBF) with a stir bar. Attach septa on the two side necks. Use a mortar and pestle to grind 4.0 g of KOH into a powder. Do this in the fume hood to avoid breathing in powders. KOH is hygroscopic – work fast! Use a powder funnel to pour the KOH into the RBF. Add 12 mL of 1,2-dimethoxyethane through the funnel to wash the remaining KOH down. Replace the powder funnel with a dropping funnel. Seal the flask with a septum and purge it with nitrogen and use a needle as a vent. After about 10 minutes, add 1 mL of cyclopentadiene with syringe while stirring. The solution should turn pink. If the solution turns black or green, it means that small amounts of the cyclopentadiene anion has oxidized. With stirring, wait approximately 5 min then insert a venting needle into the septum to release the pressure. After the pressure has been released, remove the needle.

While the solution is stirring, pulverize 1.3 g of  $FeCl_2 \cdot 4H_2O$  and dissolve in 6 mL DMSO in a flask. Transfer to the dropping funnel. Rinse flask with ~1mL DMSO to get quantitative transfer. While stirring, add the  $FeCl_2 \cdot 4H_2O$  at a rate of ~20 drops per minute. After addition of  $FeCl_2 \cdot 4H_2O$  is complete, allow reaction to stir for an additional 30 minutes.

In a 250 mL beaker, prepare 20g of ice and 9 mL of 12M HCl. Transfer a small amount to a 25 mL beaker to use to wash the reaction flask. Stop the reaction, disconnect the dropping funnel and carefully pour the reaction mixture into the HCl-ice slurry. Use the additional HCl-ice slurry in the 25 mL beaker to carefully rinse the RBF out and add this to the beaker. Stir until the mixture is dissolved and the excess potassium hydroxide is consumed. It is essential that this mixture remains near 0 °C during and after this addition. Add more ice to the solution as needed.

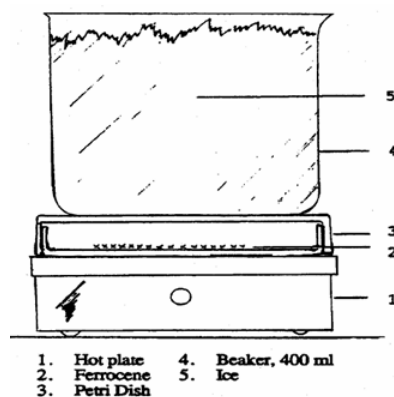
Set up the filtering apparatus with a Hirsch funnel, filter paper, adapter, and filter flask. Filter the beaker contents and collect the precipitate (ferrocene). Wash the ferrocene with three portions of 10mL of water. Spread the ferrocene out on a watch glass and let it dry until the next lab.

### Part B: Purification of Ferrocene (Day 2)

Ferrocene is a crystalline, diamagnetic material that is extremely stable to air, moisture and light. It is moderately to extremely soluble in practically all-nonpolar or weakly polar solvents. It may be purified by sublimation.

Weigh and take a melting point of the dried crude ferrocene. [NOTE: All melting points must be taken in melting point tubes sealed off with parafilm. Ferrocene sublims below its melting point and would be lost from an unsealed tube.]

Sublimation may be conducted in a 100 x 15 mm culture dish as shown in the figure below. Transfer ferrocene to the "bottom" of the culture dish to cover the center of the dish to a thickness of about 5 mm. Cover with the larger half of the culture dish and place it on a variable temperature hot plate. Slowly raise the temperature until the ferrocene sublims to the upper half of the dish. The sublimation will proceed slowly. Cooling the top culture dish by placing a beaker filled with ice water on top of it will facilitate the sublimation (WARNING: Slide the beaker off the top of the culture dish. Lifting it may lift the upper culture dish off and cause it to fall or disturb the sublimed ferrocene resulting in a loss of ferrocene.) Remove the dish from the heat, allow it to cool and recover the sublimed ferrocene. This procedure may be repeated several times until all the ferrocene is purified. Do not heat over 100 °C. To prevent sublimated ferrocene fall of when trying to recover them, when there is a layer of ferrocene on the top of the culture dish, students can take it off an dput another upper culture dish on top, Repeat this until no orange product on the bottom.



Determine the melting point of each batch of ferrocene sublimed. Place the final product in a weighed vial, determine the yield and report this along with the melting point. Calculate and report your actual percent yield. The melting point should equal or exceed 171 °C (lit., 173- 174 °C).

### Part C: Synthesizing Acetylferrocene & Chromatography

You will acetylate ferrocene using phosphoric acid and acetic anhydride and determine the number of products with thin layer chromatography. If we don't have enough ferrocene, scale down every reagent based on the ferrocene that will be used in this part.

Prepare a 65 °C water bath and preheat a 10 mL round bottom flask with a stir bar. Add 1.0 mmol of ferrocene, 0.7 mL of acetic anhydride and 0.2 mL of 85% phosphoric acid. If you do not add the reactants in this order, you will successfully decompose the ferrocene. Close the round bottom with a septum and insert a venting needle. Warm the solution with stirring until the ferrocene dissolves, and then heat the solution for 30 minutes. Thoroughly cool the round bottom in an ice bath and then carefully add 0.5 mL of ice water to the mixture with stirring. Add drop wise 3 M aqueous sodium hydroxide solution until the solution pH is neutral (somewhere between 20-30 drops). Collect the product in a filter funnel and wash the solids with water. Press the product with filter paper to get it as dry as possible. The crystals air dry. Take a yield and melting point of the crude product.

### Part D: Procedure for TLC & Column Chromatography

You will determine the distribution of products in your acetylation reaction using thin-layer chromatography.

Prepare solutions of your sublimed ferrocene and dried acetylation product by placing a few (5 to 10) drops of methylene chloride,  $\text{CH}_2\text{Cl}_2$ , in two small vials. Add a small amount (one spatula-tip full) of ferrocene to one vial and acetylation product to the other vial. The solution should be concentrated enough so that a dark spot is clearly visible on the TLC plate after application. If you are unable to see spots on the TLC plate, add more sample to the solutions and try again (You can use the same TLC plate, just apply the more concentrated solution directly on top of where you applied the first sample.)

The goal of this portion of the experiment is to determine the best hexane to ethyl acetate ratio that most effectively separates the various ferrocene products. The principle applied here is the separation of products as a function of solvent polarity.

Begin by testing product separation with pure solvent (hexane or ethyl acetate). Once you have obtained those results, decide on whole number ratios of solvent mixtures and test those in the same way (i.e. 1:4 hexane to ethyl acetate). TLC plates may be obtained from the dispensary and you will use micro-capillary tubes as applicators. Put a piece of filter paper in a small jar with lid as shown in the Figure and carefully pour in the solvent. Be certain that the solvent level is below the point where you spot the TLC plate. Draw a line to mark the starting solvent on the TLC plate, then use the capillary to spot the TLC plate slightly above the solvent line. Carefully place the spotted TLC plate into the solvent jar and place a lid on top. Let the plate develop in the solvent until the product spots are within 1 cm from the top of the plate. If you leave the plate in the solvent for too long, the spots will collect at the top of the plate and you will have no useful observations. Sketch each chromatogram results in your lab notebook along with a note of which solvent ratio you used for that plate. Once you obtain a TLC plate of good separation (no smearing of spots, no spot overlap etc.), calculate the ratio to front ( $R_f$ ) value for each spot.

At this point you would then perform column chromatography with your TLC determined solvent ratio in order to collect your isolated products and determine their purities and yields. Unfortunately, time constraints in 124L do not leave enough time for you to do this. But please make note in your lab report, how you would perform such an experiment and what you would do to determine purity and yield of your separated products.

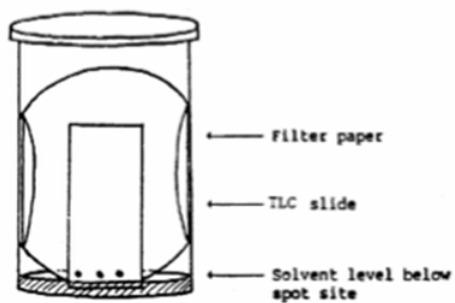


Figure 3. Apparatus for the Separation of Acetylation Products using TLC

7: F- Preparation of Ferrocene  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$  (Experiment) is shared under a [CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/) license and was authored, remixed, and/or curated by LibreTexts.

## CHAPTER OVERVIEW

### 8: H- Wilkinson's Catalyst (Experiment)

[8.1: Part A- Synthesis of Wilkinson's Catalyst](#)

[8.2: Part B- Homogeneously-Catalyzed Hydrogenation of an Alkene](#)

#### Homogeneous Catalysis Introduction

A catalyst is "a substance which when added to a reaction mixture changes the rate of attainment of equilibrium in the system without itself undergoing a permanent chemical change." (Reference: Sharp "Penguin Dictionary of Chemistry" 1981) A catalyst increases the rate at which the system reaches equilibrium but it does not change the equilibrium itself, because it also increases the rate of the back reaction to an equal extent. The following related terms also need to be defined:

- catalyst precursor* = a compound or complex which undergoes a reaction to produce the active catalyst.
- autocatalyst* = a reaction product which is a catalyst for the same reaction
- inhibitor* = a compound which will slow down or stop a reaction
- substrate* = molecule upon which the catalyst acts
- % conversion = % of the substrate which has been converted to product
- turnover number* (TON) = moles of product per mole of catalyst (unitless)
- turnover frequency* (TOF) = moles of product per mole of catalyst per hour (units are  $\text{h}^{-1}$ )

A *homogeneous catalyst* is a catalyst which is in the same phase as the substrate. A homogeneous catalyst could be an organic molecule, a salt, or a transition metal complex. The solution does not have to be homogeneous in order for the catalyst to be homogeneous. For example, homogeneous hydrogenation involves two phases; hydrogen is in the gas phase and the catalyst and substrate (an olefin) are in the liquid phase. Therefore, although the system is technically heterogeneous, the catalyst is a homogeneous catalyst.

Although heterogeneous catalysts have been the historical favorite in industry, homogeneous catalysts have a number of advantages (Table 1). They are used in many industrial processes.

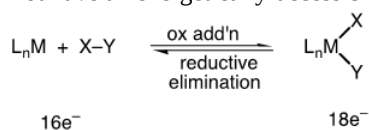
Table 1. Comparison of homogeneous and heterogeneous catalysis.

Heterogeneous	Homogeneous
Simple to prepare	Complicated synthesis
Very stable	Less stable
No solvent restrictions	Solvent restrictions
Easy to separate from products, solvents	Difficult to separate
Difficult to characterize	Simple to characterize (NMR, X-ray)
Only surface atoms used	All metal atoms used
Poisons easily	Somewhat more resistant
Low selectivity	High and tunable selectivity
Empirical matching of catalyst and substrate	Catalyst design

The mechanism of a homogeneously-catalyzed reaction is usually a cycle consisting of several steps, each of which can also occur as a stoichiometric reaction. For transition metal complexes, the most common primary steps are oxidative addition, reductive elimination and insertion.

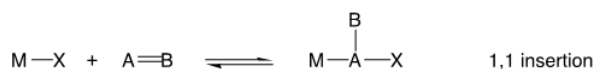
During the *oxidative addition* of a molecule X-Y (e.g.  $\text{H}_2$ ,  $\text{HCl}$ ,  $\text{RS-SR}$ ,  $\text{Br}_2$ ,  $\text{R-I}$ ) to a metal fragment  $\text{L}_n\text{M}$ , the metal oxidation number is increased by two units, the X-Y bond is cleaved, and new M-X and M-Y bonds are formed. The electron count at the metal goes up by two units. Therefore oxidative addition is not possible if the metal already has 18 valence electrons or if it does

not have an energetically-accessible oxidation number two units above the present number.

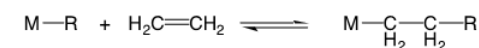
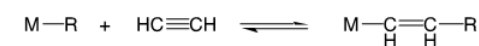
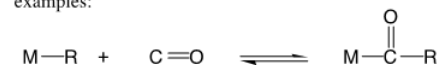


*Reductive elimination* is the opposite of oxidative addition. During the reductive elimination of a molecule X-Y from a metal fragment  $L_nM(X)(Y)$ , the metal oxidation number is decreased by two units, the M-X and M-Y bonds are cleaved, and a new X-Y bond is formed. The electron count at the metal goes down by two units. Therefore reductive elimination is not possible if the metal does not have an energetically-accessible oxidation number two units below the present number.

In an *insertion reaction*, an unsaturated molecule  $A=B$  inserts into a metal-ligand bond M-X (where X is an anionic ligand). The bond order of the A-B bond decreases by one unit (i.e. a double bond goes to a single bond, a triple bond goes to a double bond). There are two possible geometries of insertion: 1,1-insertion and 1,2-insertion. You can predict which would happen by looking at how the molecule would bind to the metal as a ligand. 1,1-insertion usually happens if the molecule  $A=B$  would bind end-on to the metal (for example, carbon monoxide). 1,2-insertion usually happens if the molecule  $A=B$  would bind side-on to the metal (for example, an alkene).



examples:

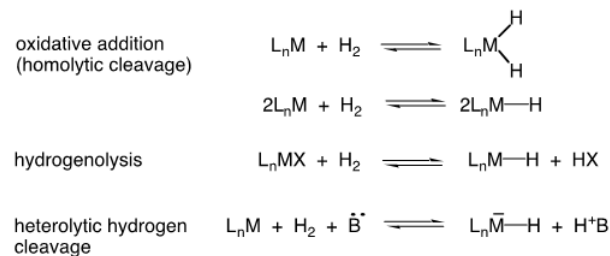


These simple steps (and a few others) are combined in a catalytic cycle. However, it can be extraordinarily difficult to figure out the catalytic cycle for a given catalytic reaction. A common technique is to try to observe the individual steps as stoichiometric reactions and then pose a catalytic cycle as a hypothesis; the mechanism must be consistent with the observed kinetics. However, even after all that work, the mechanism may only match the observations for one substrate, one temperature and one solvent. Changing to another substrate, temperature or solvent may cause an entirely different mechanism to take over.

Another complication is the fact that any species which can be observed by spectroscopy during catalysis may actually be a species which is not in the catalytic cycle. If the species is so stable that it can be observed, it is probably so stable that it cannot be a part of a rapid catalytic cycle.

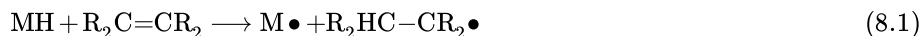
## Homogeneous Hydrogenation

Hydride ligands are of paramount importance to homogeneous hydrogenation. Hydrogen gas ( $H_2$ ) doesn't react with alkenes at room temperature without a catalyst. Metal complexes activate the hydrogen by forming hydride complexes, which then transfer hydrogen to the alkenes. The hydride complexes can be formed by oxidative addition of  $H_2$ , hydrogenolysis, or heterolytic activation.

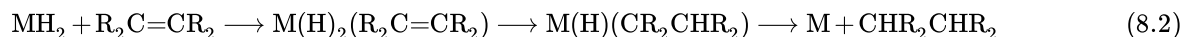




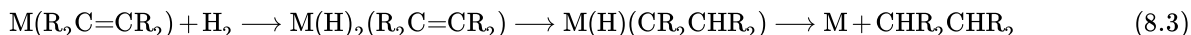
Another necessary step is transfer of the hydrogen from the metal to the alkene. This can happen in several ways, the most common of which are hydrogen atom transfer, the hydride pathway and the unsaturated pathway. The latter two routes differ only in the sequence of hydrogen and alkene binding to the metal.



*H atom transfer (radical hydr.)*

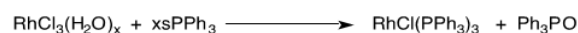


*Hydride Pathway*

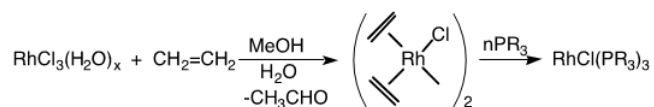


*Unsaturated Pathway*

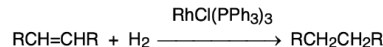
In 1964 Wilkinson and Coffey independently and nearly simultaneously discovered a remarkable homogeneous olefin hydrogenation catalyst, chlorotris(triphenylphosphine) rhodium(I), which is now commonly called "Wilkinson's catalyst". The simplest preparation of this complex is the direct reaction of rhodium chloride with triphenylphosphine, although with other phosphines this route does not work well.



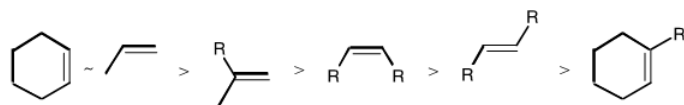
or:



This catalyst was the first to be able to rapidly hydrogenate unconjugated alkenes and alkynes at extremely mild conditions (1 atm of  $\text{H}_2$  and at room temperature). The hydrogenation is usually performed in benzene with a polar cosolvent like ethanol. The polar solvent might facilitate migratory insertion, which is rate limiting.



The reactivity of olefins is primarily determined by steric factors, although some olefins like ethylene and 1,3 butadiene are very slowly reduced under ambient conditions and can act as powerful competitive inhibitors.

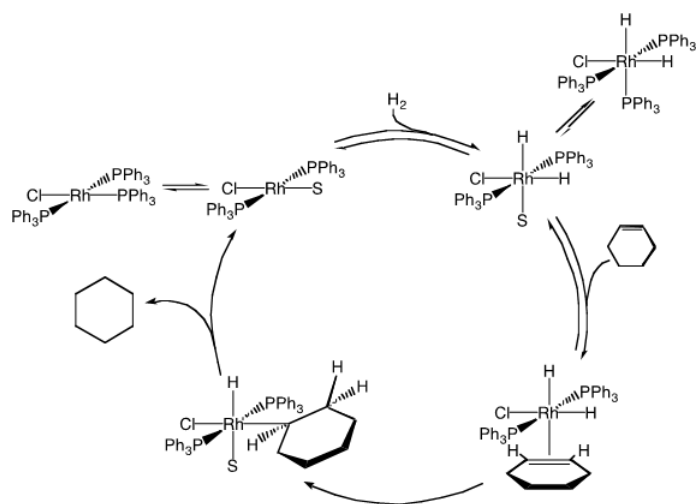


The complex slightly dissociates in solution, and this is thought to be important to the mechanism.



The mechanism for the hydrogenation of cyclohexene is shown below ( $\text{S}$  = solvent), but note that the mechanism for the hydrogenation of styrene is different, and yet another mechanism is involved in the hydrogenation of ethylene.

Note that according to this mechanism Wilkinson's catalyst should actually be called "Wilkinson's catalyst precursor".



**Source:** Szafran, Z.; Pike, R. M.; Singh, M. M. *Microscale Inorganic Laboratory*, John Wiley: 1991.

#### References:

Young, J. F.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* (1965) 131.

Brown, J. M.; Lucy, A. R. *J. Chem. Soc., Chem. Commun.* (1984) 914.

Halpern, J. *J. Mol. Catal.* (1976), 2, 65, (1977-78), 3, 403.

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## 8.1: Part A- Synthesis of Wilkinson's Catalyst

### Safety Precautions

1. All parts of this experiment must be performed in the fume hood, except the gas chromatography.
2. Take care when adding solids to hot liquids; the liquids may "bump" (boil over violently).

### Note

1. Solutions or solids containing rhodium should not be discarded. They should be put into the bottle in the fume hood labeled "rhodium for recycling."
2. Don't use a septum that someone else has already used. Recycling septa is not wise because the leaks caused by damaged septa could cause the loss of expensive catalyst.
3. Review the sections on air sensitive compounds in this manual before you attempt this experiment.

In a fume hood, place a magnetic stir bar and 12 ml of absolute (100%) ethanol in a 25 mL round-bottom flask fitted with a 14/20 ground glass joint. Attach the condenser to the flask and the water lines to the condenser. Heat the flask in a sand bath on a hotplate so that the ethanol reaches boiling. Turn off the heat and wait till the boiling ceases. Add 450 mg of triphenylphosphine through the condenser. Use a stir rod to push most of the phosphine down the condenser. When almost all of the phosphine is dissolved, add 75 mg (0.36 mmol) of rhodium trichloride hydrate by the same method. Flush down any solids stuck on the condenser wall with up to 4 ml of ethanol. Resume the heating and refluxing.

During the reflux time, prepare the standard filtration apparatus (see Introduction) with a Hirsch funnel. After 30 min of reflux, red crystals should be observed in the flask. Turn off the heat. Suction filter the hot solution, then wash with ether (3 x 1 mL) and leave the solid to dry on the funnel without turning off the suction.

The filtrate (the liquid which passed through the filter) may contain extra rhodium, which should be recycled. Pour this into the bottle in the fume hood labeled "rhodium for recycling."

Report the theoretical, observed, and percentage yields. Acquire the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the complex in  $\text{CDCl}_3$ . Warning: Chloroform may be a carcinogen. Therefore do not touch, inhale or ingest chloroform. Use chloroform in a fume hood. Wear gloves which are resistant to chloroform (see chart earlier in this manual). The Viton and Silver Shield gloves are not disposable.

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## 8.2: Part B- Homogeneously-Catalyzed Hydrogenation of an Alkene

### Safety Precautions

1. All parts of this experiment must be performed in the fume hood, except the gas chromatography.
2. Take care when adding solids to hot liquids; the liquids may "bump" (boil over violently).

### Note

1. Solutions or solids containing rhodium should not be discarded. They should be put into the bottle in the fume hood labeled "rhodium for recycling."
2. Don't use a septum that someone else has already used. Recycling septa is not wise because the leaks caused by damaged septa could cause the loss of expensive catalyst.
3. Review the sections on air sensitive compounds in this manual before you attempt this experiment.

You will hydrogenate two samples of cyclohexene. For the first sample, you will follow this procedure:

Place 10 mL of toluene and a stir bar into a Schlenk tube which is attached to an oil bubbler (see the Figure below). Degas the solvent by bubbling hydrogen through it for 10 min. With the H<sub>2</sub> still flowing, add 25 mg of RhCl(PPh<sub>3</sub>)<sub>3</sub> (you will have to temporarily remove the septum). Stir vigorously until the catalyst is dissolved. Slowly add 1 mL of freshly distilled cyclohexene using a 1 mL calibrated pipet. Note the time the cyclohexene was added. Continue the vigorous stirring and H<sub>2</sub> flow, making sure that the needle tip is almost touching the stir bar. After 20 minutes take a tiny sample of the solution and analyze it by GC (note the time the sample was taken). Continue the hydrogen bubbling through the remaining solution. After the solution has turned completely yellow (and at least 30 minutes after your previous sample was taken), stop the H<sub>2</sub> supply and the stirring, note the time again, and analyze the solution again. Report all color changes during the reaction.

Analyze the solutions by gas chromatography (the TA will instruct you on the proper conditions).

Pour the solutions into the bottle in the fume hood labeled "rhodium for recycling."

For the second sample, you will modify the procedure in one of the following ways.

- a) Use double the quantity of catalyst precursor, or
- b) Use double the quantity of cyclohexene, or
- c) Add 1 mL of an alcohol, or
- d) Add 1 mL of an amine, or
- e) Add 80 mg of PPh<sub>3</sub>.

For GC samples. A ~100 times dilution is needed for best results. Dilute 1 drop of toluene solution from Schlenk tube with 2mL acetone. Put the diluted solution into GC vials with a syringe with a **filter**! (4 GC vials and 4 filters are need for each group.)

Choose only one of these options. Make sure that you have not chosen the same option as the other group(s) doing this experiment today.

You may perform the hydrogenation of the second sample of cyclohexene simultaneously with the first sample, or with a gas splitter. You will need to confirm that the alcohol or amine, if you use them, do not have similar retention times to cyclohexene or cyclohexene. If the retention times are similar, then you will have to choose a different alcohol or amine.

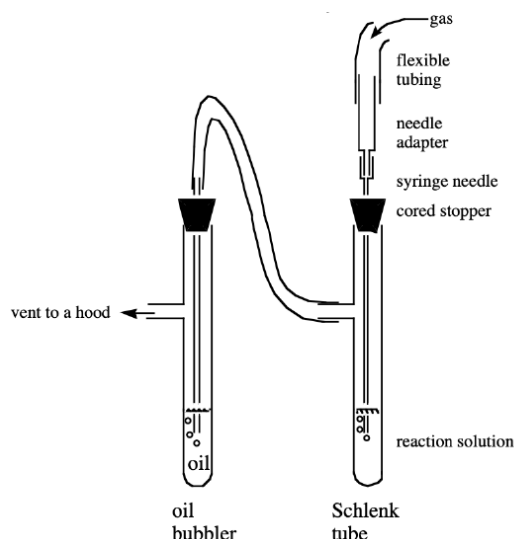


Figure: How to bubble a gas through a solution of an air sensitive compound.

## Calculations:

First calculate the % conversion of cyclohexene to cyclohexane.

$$\% \text{ conversion} = \frac{\text{moles alkane}}{\text{moles of alkene originally used}} \times 100\%$$

Assuming there has been no loss of material, then:

$$\% \text{ conversion} = \frac{\text{moles alkane}}{\text{moles alkane} + \text{moles alkene}} \times 100\%$$

where “moles alkane” and “moles alkene” refer to the quantities of these species present at the time the sample was injected into the GC.

Because the areas of the alkane and alkene peaks are proportional to the number of moles of alkane and alkene:

$$\text{area of alkane peak} = C_{\text{alkane}} \times n_{\text{alkane}}$$

$$\text{area of alkene peak} = C_{\text{alkene}} \times n_{\text{alkene}}$$

Assuming that the proportionality constants C (called “calibration constants”) are equal, then:

$$\% \text{ conversion} = \frac{\text{area alkane}}{\text{area alkane} + \text{area alkene}} \times 100\%$$

Based upon the GC trace for the sample taken after 20 minutes, calculate the % conversion of the cyclohexene from the integration of the GC peaks. Using the % conversion and the original number of moles of cyclohexene, calculate how many moles of cyclohexane were produced. From that answer, determine the TON and TOF. Repeat these calculations for the sample which had a longer time to react.

$$\text{TON} = \frac{\text{moles product}}{\text{moles of catalyst}}$$

$$\text{TOF} = \frac{\text{moles product}}{(\text{moles of catalyst}) (\text{reaction time})} = \frac{\text{TON}}{\text{reaction time}}$$

## Waste disposal

Solutions potentially containing rhodium are *not waste*. Similarly the products, after they have been analyzed and graded, are not waste. The solutions and products should be placed into the bottle in the fume hood labeled “rhodium for recycling.”

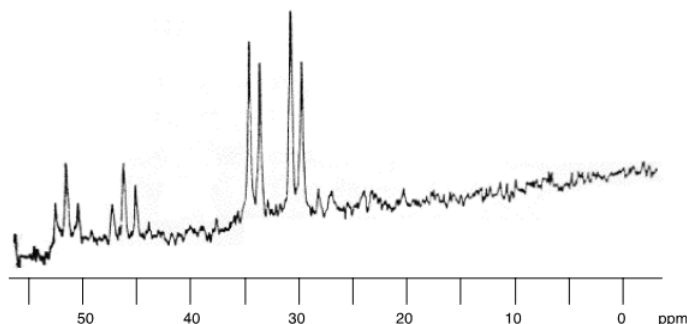
All clean organic solvents, containing no metals or corrosive compounds, should be collected in the organic waste container. All waste triphenylphosphine must be disposed of in the Experiment H waste container.

## Problems

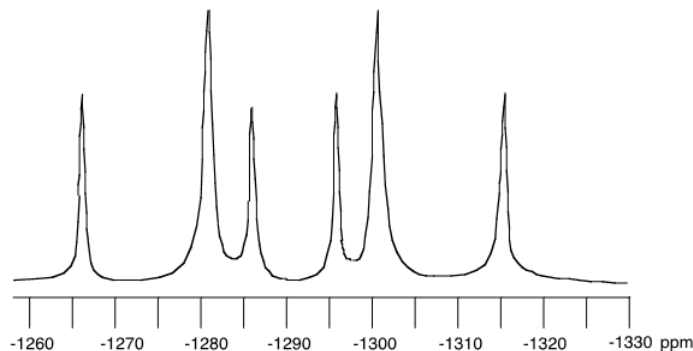
1. The  $^{31}\text{P}\{^1\text{H}\}$  NMR and  $^{103}\text{Rh}$  NMR spectra of  $\text{RhCl}(\text{PPh}_3)_3$  in  $\text{CD}_2\text{Cl}_2$  are shown in Figures 1 and 2. Using splitting trees, explain the observed coupling. Compare the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shown below to the one you acquired. If they are different, explain why (you may ask your TA to help you on this last point).
2. If you bubble  $\text{H}_2$  through a solution of  $\text{RhCl}(\text{PPh}_3)_3$  in  $\text{CD}_2\text{Cl}_2$ , you get a pale yellow solution which has the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra shown in Figures 3 and 4. Using splitting trees, explain the observed coupling (for the  $^1\text{H}$  spectrum, don't try to explain the fine structure on the hydride peaks; the resolution is insufficient to resolve the details). What is the formula and structure of the product? Would you get this pattern with any isomer of the product? Compare the  $^1\text{H}$  NMR chemical shift of the hydride ligands in this complex to the chemical shift of pure  $\text{H}_2$  gas in solution (4.6 ppm in  $\text{CD}_2\text{Cl}_2$ ). Explain the difference in the chemical shifts in terms of the bonding in the complex.
3. When  $^{31}\text{P}$  NMR spectra are obtained, proton decoupling is used. Why? What would the  $^{31}\text{P}$  NMR spectrum of a simple phosphine (such as  $\text{P}(\text{CH}_3)_3$ ) look like with and without proton decoupling?
4. The area under a peak in a gas chromatogram depends on the amount of compound present and the response of the detector to that compound. A Flame Ionization Detector (FID) burns the compound as it comes out of the column, and detects it by measuring the conductivity of the flame. We have neglected the possibility that cyclohexene and cyclohexane may have different responses. How could one correct for this problem? Why isn't it necessary in our experiment?
5. Compare the conversions, TONs and TOFs for the two samples and the two reaction times. How did conversion, TON and TOF vary with time? How did the "altered procedure" affect conversion, TON, and TOF. Speculate on a reason for any changes observed.
6. If you were asked, as part of a research project, to optimize the rate of hydrogenation of cyclohexene, what parameters or conditions would you adjust? Describe why each parameter could potentially increase the hydrogenation rate.

## Spectra

1. Acquire the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of your sample of  $\text{RhCl}(\text{PPh}_3)_3$ .



**Figure 1.** The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{RhCl}(\text{PPh}_3)_3$  in  $\text{CD}_2\text{Cl}_2$ . (Heaton et al., *J. Chem. Soc., Dalton Trans.* (1992), 2533)



**Figure 2..** A simulation of the  $^{103}\text{Rh}$  NMR spectrum of  $\text{RhCl}(\text{PPh}_3)_3$  (1 ppm = 9.45 Hz) based on published data. (data from T. H. Brown and P. J. Green., *J. Am. Chem. Soc.*, (1969) 91, 3378, and T. H. Brown and P. J. Green., *J. Am. Chem. Soc.*, (1970) 92, 2359)

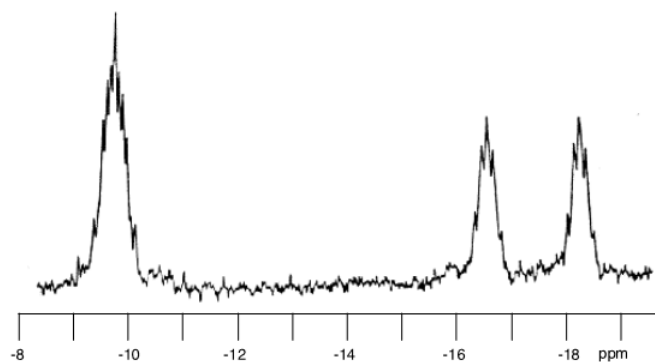


Figure 3. The  $^1\text{H}$  NMR spectrum of the compound obtained by bubbling  $\text{H}_2$  gas through a solution of  $\text{RhCl}(\text{PPh}_3)_3$  in  $\text{CD}_2\text{Cl}_2$ . (Heaton et al., *J. Chem. Soc., Dalton Trans.* (1992), 2533)

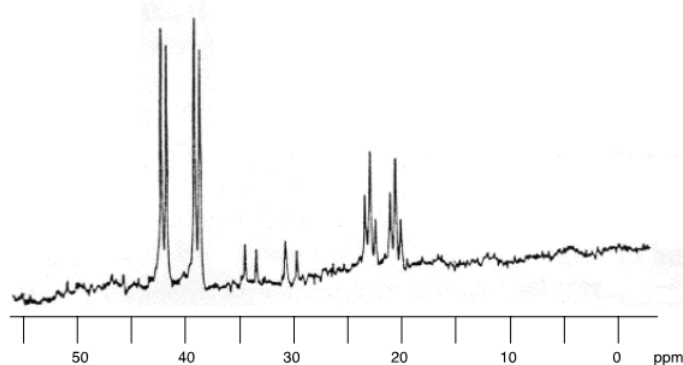


Figure 4. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the compound obtained by bubbling  $\text{H}_2$  gas through a solution of  $\text{RhCl}(\text{PPh}_3)_3$  in  $\text{CD}_2\text{Cl}_2$ . Note that a small amount of  $\text{RhCl}(\text{PPh}_3)_3$  remains in solution. (Heaton et al., *J. Chem. Soc., Dalton Trans.* (1992), 2533)

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