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Chapter 4

Vacuum Line Techniques for Handling Air-Sensitive Organometallic Compounds

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Vacuum line techniques for handling air sensitive oganometallic compounds are described. The vacuum line is discussed in six sections: (i) the pumps and main traps, (ii) the main manifold with pressure gauges, (iii) work stations, (iv) the cryogenic traps and Toepler pump, (v) the inert gas purifiers and inlet system, and (vi) the specialty gas inlet system. Use of a swivel frit assembly in the synthesis of air sensitive compounds is described along procedures for the addition of gases, volatile and nonvolatile liquids and solutions to reaction mixtures. High temperature and pressure reactions are discussed in terms of the use of sealed NMR tubes and heavy walled reaction vessels. The procedure for molecular weight determination using the Signer method is also included.

Our research group carries out preparative chemistry in fume hoods, on bench tops, in high pressure (Parr) reactors, in glove boxes, in Schlenk tubes, and with cannulas and septa, just as other groups concerned with the synthesis and characterization of air-sensitive organo-transition metal compounds. In this article we attempt to describe the less common methods, procedures and the equipment, i.e. those associated with a vacuum line, which have evolved over the past fifteen years in the Bercaw group. Many of the techniques are taken from the literature and have been (hopefully) improved upon or modified for working with small amounts (50 mg - 35 g) of an organotransition metal compound. Others have evolved out of necessity, and, as far as we are aware, are not described elsewhere.

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The Vacuum Line

Most of the reaction chemistry that is done in our laboratory involves the use of vacuum lines, such as the one shown below in Figure 1. The use of a vacuum line offers two major advantages over more standard Schlenk techniques: hoses and rubber septa, which are more permeable to air and moisture, are completely excluded and quantitative manipulation of gases and volatile liquids can be performed conveniently. Although the construction of a vacuum line as complex as that shown involves a relatively large investment of time and money (ca. $15,000 in parts and labor), it becomes a permanent piece of equipment which is shared by two or three group members and used extensively on a regular basis. Moreover, it is often faster to assemble a complicated apparatus on the vacuum line, rather than at a Schlenk line, since many of the required components are permanently in place.

The vacuum line consists of six main sections: (i) the pumps and main traps, (ii) the main manifold with pressure gauges, (iii) the work stations, (iv) the cryogenic traps and Toepler pump, (v) the inert gas purifiers and inlet system, and (vi) the specialty gas inlet system.

Each vacuum line is equipped with two pumps which operate in series. A mercury diffusion pump, together with a mechanical fore pump, provide a residual pressure of $<10^{-4}$ torr, which is adequate for the syntheses that we undertake. Two traps cooled by large dewars filled with liquid nitrogen are placed, one before and one after the diffusion pump to protect the pumps from condensibles and the mechanical pump from mercury. The mechanical pump is exhausted to the hood. The residual pressure in the manifold is measured by the use of either a rotating McLeod gauge or a thermocouple gauge. The McLeod gauge provides the more accurate measurement of the residual pressure in the system, especially at pressures $<10^{-3}$ torr(1). Disadvantages with this gauge are that it needs to be regreased and cleaned regularly, and since it is slow, it is not as convenient when one is trying to locate a leak in the line. Although they periodically need to be recalibrated, the thermocouple gauges are relatively inexpensive and provide a continuous indication of residual pressures $>10^{-3}$ torr.

The main manifold of the vacuum line is kept evacuated and isolated from the work stations on the line by stopcocks which are lightly greased with Apiezon N Grease. There are two types of work stations: a standard Schlenk line section, consisting of vacuum and inert gas manifolds connected by three way stopcocks to standard taper 24/40 inner joints, and a high vacuum work station for working with smaller quantities of material or for accessing the cryogenic traps and Toepler pump section. The two manifolds of the Schlenk line work

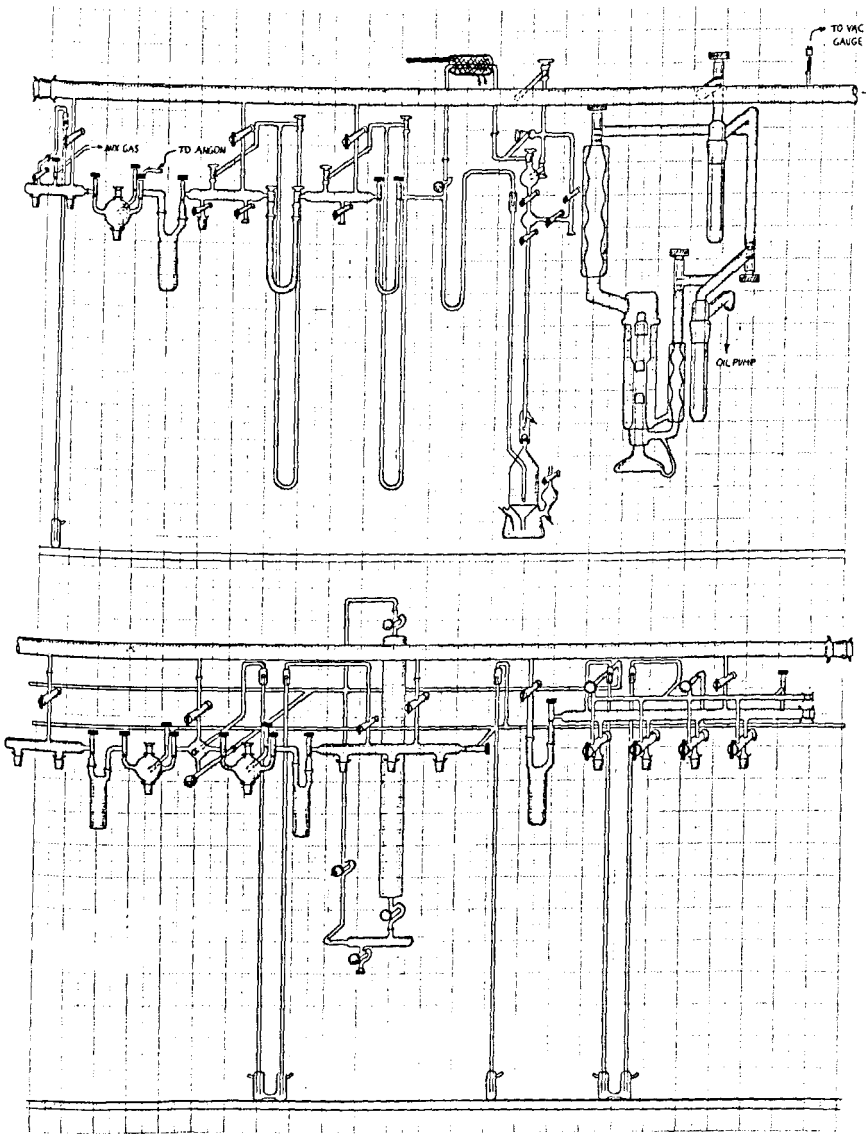

Figure 1. Diagram of a Bercaw group vacuum line (courtesy of Dr. Dean M. Roddick).

station are equipped with mercury bubbler/manometers, which serve two general purposes: (i) to provide a rough measure(2) of the amount of gas that is admitted to a manifold and (ii) to provide an exit when the pressure in the manifold is excessive. Gas is exited from the bubbler into tygon tubing affixed to a hood exhaust. A separate mechanical pump for the vacuum manifold of the Schlenk line work station is used for several of our lines, allowing two people to work simultaneously at the line without interfering with each other. The vacuum manifold is also connected (via a large stopcock) to the main manifold of the high vacuum line, so that access to high vacuum is still possible. Similarly, the inert gas manifold is connected (via a stopcock and manifold) to the specialty gas section of the main line. Large capacity, removable traps, affixed to the end of the vacuum manifold by means of O-ring joints, are used to collect the large volumes of solvent which are removed in vacuo from reaction mixtures. The standard taper 24/40 outlets may be fitted with butyl rubber tubing with an outer joint. Thus, the Schlenk line may be operated with its own rough pump in a conventional mode, or, when connected to the main vacuum and specialty gas system, more like the work station described below.

The high vacuum work station is the heart of the line. It consists of two main 24/40 standard taper inner joints connected via teflon needle valves(3) to (i) the high vacuum manifold, (ii) the inert gas manifold, (iii) the specialty gas manifold, (iv) each other, (v) manifolds leading to large volume, removable traps, (vi) outlets on these smaller manifolds for admitting gases from bulbs or lecture bottles or solvents, reagents, etc. from flasks or calibrated volumes, and (vii) at the right to the cryogenic traps and Toepler pump system. The large number of connections provided to these ports presents a design problem, which we have solved by incorporating 100 ml flasks as connectors. Glass strain at the connections is thus relieved by spreading out the area of the glass seals. Moreover, the flasks serve as splash guards and provide easy access for cleaning through their stoppered 14/20 standard taper outer joints at the top. The entire work station, as well as most of the other manifolds, Schlenk line, bubblers, etc. are interconnected and connected to the line via O-ring joints for easy removal when cleaning.

The cryogenic trap section of the line consists of one more large capacity, removable trap, and three U traps leading to the inlet of the Toepler pump. These traps can be used to separate volatile materials on the basis of differing vapor pressures, as is performed routinely for boranes, phosphines, etc. on lines similar in design to this section of the vacuum system. Normally, we use these traps to assure complete removal of solvent and other liquid nitrogen condensable compounds from noncondensables such as CO, H_2, CH_4 and

N_2, which are quantitatively collected by the Toepler pump. Needle valves are used to allow only small pressures of gas to flow into the Toepler pump, in order to prevent damage from a "mercury hammer"(4). The pressure is indicated by manometers at one or two points along the manifolds connecting the traps. These manometers are also useful in measuring out known amounts of reagents or gases into calibrated bulbs, which may be attached to outlets along the manifolds. The Toepler section consists of the pump, several precalibrated volumes separated by 2-way, oblique bore stopcocks, an outlet for attaching a gas infrared cell, mass spectrometry sample bulbs, etc., a stopcock to the main high vacuum manifold, and a recirculating manifold(5), a section of which is packed with CuO that may be heated to 320°C (vida infra). The CuO section of the tube is wrapped, along with a glass tube to hold a 360°C thermometer, with heating tape which is connected to a Variac transformer, then encased in thermal insulating material. The inlet tube of the Toepler pump and the first, tubular calibrated volume of the pump are positioned parallel to each other so that a section of meter stick may be taped into place. Thus, when the Hg level is allowed to rise to a mark above the top valve assembly, the inlet tube functions as the Hg column of a manometer for reading the pressure in the calibrated volumes.(6) The Toepler pump cycle is automated by using the mercury as a switch alternately connecting the common lead to the top lead (which activates the solenoid valve to open the lower chamber to a mechanical pump) and the lower lead (which activates the solenoid valve to open the lower chamber to a slow, filtered air lead. The Toepler pump control box is assembled at Caltech and is comprised of a 6.3 V transformer (e.g. Triad F 14X), a relay (e.g. PB KRP11AG), a thermal delay relay (e.g. 6N02), a 2 ohm 10 W resistor, five female AC plugs, chassis mount (for the mechanical pumps, diffusion pump heater, CuO tube heater, etc.), five tineon lamps, 125 V, 0.3 W, five SPST 10 A power switches, a fuse holder, an amphenol 5 pin hex chassis mount female connector (to receive male connector with wires from alligator clips attached to leads on Toepler pump), a 6 foot power cord, 3 wire, number 16 or larger, and two 4 pin terminal strips all contained in an aluminum chassis with cover plate (3X5X10).(7)

The two working inert gases, dinitrogen and argon, are taken from 1A cylinders through regulators, copper tubing and metal to glass seals and passed through purifiers before they enter the vacuum line. Two large capacity columns (Figure 2), one filled with MnO supported on vermiculite(8), the other with 4Å molecular sieves, remove dioxygen and water, respectively. Periodically (approximately annually) the oxidized MnO (of empirical formula Mn_3O_4) needs to be reduced. Reduction is accomplished conveniently by passing

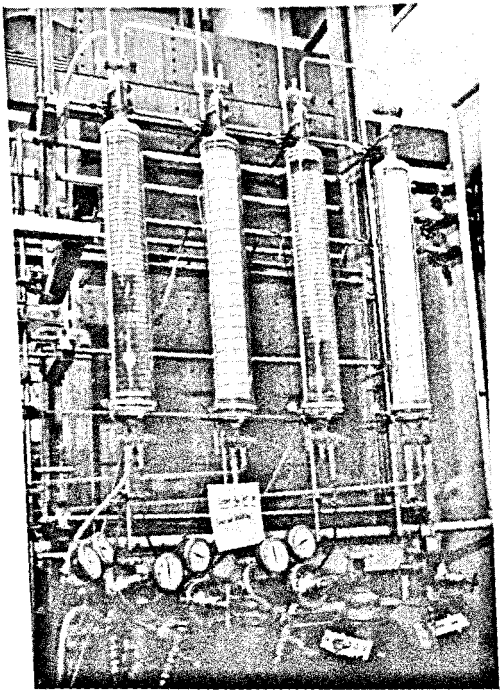

Figure 2. MnO/vermiculite and molecular sieve columns for argon (left) and dinitrogen (right) purification.

dihydrogen (hood exhaust) through the column while heating to 300-350°C. The column filled with molecular sieves is normally regenerated at the same time by passing dinitrogen at approximately 250°C. The columns may be heated using commercially available heating tape, or by wrapping the inner column with nichrome wire. Strips of asbestos tape on the sides, one next to the glass column, the other over the nichrome wire are essential to hold the wire in place. The asbestos tape is wetted to adhere it to the column and wire. The resistance of the wire is chosen to maximize the power at 120 V and 5 A, the maximum settings for a standard Variac transformer. The glass outer jacket of the column reduces the cooling effects of drafts. Wrapping the outer jacket with aluminum foil(9) during this process further increases the heating efficiency. The normal working inert gas, Ar, is transferred through glass tubing to the Ar manifold of the two working stations. A mercury bubbler is connected to this manifold and the Hg level and regulator set to maintain ca. +50 torr Ar pressure without continual bubbling. The dinitrogen is usually transferred through glass tubing to the specialty gas manifold described below. N_2 is the inert gas of choice when working with an apparatus cooled near liquid nitrogen temperature(10).

A smaller, all-in-one column, filled with MnO/vermiculite (lower half) and molecular sieves (upper half) is used for purifying specialty gases such as dihydrogen, dideuterium, and carbon monoxide(11). This apparatus is attached to the vacuum line near the inert gas manifold, as shown in Figure 1. It is a good working practice to leave the column filled with the last specialty gas used, with a label indicating the column contents. Replacing the gas by evacuating the column packed with vermiculite and molecular sieves is quite time consuming.

Solvent Pots and Their Use

When using a vacuum line, solvents are introduced by vacuum transferring from a solvent pot into the reaction flask. To prepare a solvent pot, the solvent is rigorously dried by refluxing over an appropriate drying agent in a solvent still. Drying agents such as "titanocene"(12) or sodium and benzophenone (for preparation of Na/benzophenone-ketyl) and a stir bar are added to a large round bottomed flask (~ 500 ml). The flask is then attached to a 180° needle valve adapter, which consists of a 24/40 standard taper inner joint, straight needle valve and 24/40 standard taper outer joint as shown in Figure 3. With exclusion of air, solvent is transferred from the solvent still to the solvent pot (transfer is facilitated greatly by evacuating the solvent pot first(13)). The solvent pot is then degassed by attaching to the high vacuum line

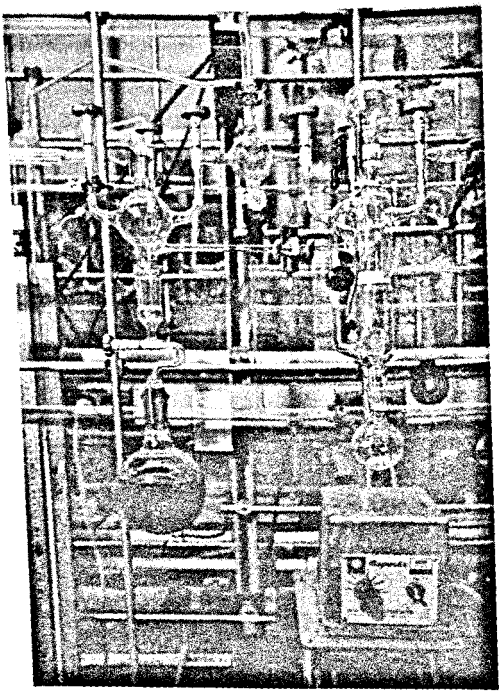

Figure 3. High vacuum line work station with solvent pot (left) and swivel frit assembly (right).

and, while stirring at room temperature, pumping on the solvent through a -196°C trap for a couple of minutes. To transfer solvent from the pot into a reaction flask, the entire assembly interconnecting the two is completely evacuated. Cooling the reaction flask with either a dry ice/ethanol bath (-78°C) or with liquid nitrogen (-196°C) and slowly opening the needle valve of the solvent pot while stirring magnetically causes solvent to transfer into the flask. The rate of transfer will depend on: (i) the vapor pressure of the solvent, (ii) the residual pressure in the manifold and the temperature of the solvent pot. Keeping a room temperature(14) water bath under the solvent pot will facilitate the transfer.

Swivel Frit Assemblies and Their Use

Preparative synthesis on a vacuum line is carried out primarily using a swivel frit assembly. Although they may be constructed in virtually any size, a typical frit assembly has 14/20 standard taper joints and can accommodate up to approximately 10-15 grams of solid. A diagram of an apparatus of moderate size is shown below in Figure 4. A quick opening teflon valve or a stopcock is centered in the pressure-equalizing side arm, to isolate one side of the frit from the other. An adapter consisting of a 14/20 standard taper inner joint, right angle teflon needle valve and 24/40 standard taper outer joint, is used to attach the assembly to a port of the working section of the vacuum line. In a typical experiment, one of the round bottomed flasks is charged with solid reagents (these are loaded in the inert atmosphere glove box if they are air sensitive), and a magnetic stir bar is placed in both flasks. The joints of the frit and the needle valve are greased lightly with Apiezon H grease(15) and are secured with springs or rubber bands. With the teflon needle valve tightly closed, the assembly is removed from the glove box and attached to the vacuum line at one of the ports of a working station via 24/40 standard taper joint, lightly greased with M or H grease. The system is evacuated, first up to the teflon needle valve of the adapter, then including the entire frit assembly. An appropriate solvent is then transferred into the reaction flask following the procedure described above.

Adding Reagents to the Reaction Flask of the Swivel Frit Assembly

Condensable Gases. To add a desired quantity of a condensable gas, a a gas bulb of known volume is normally used. The working section, gas bulb and connection to the gas supply, manometer(16) and frit assembly are all evacuated (see Figure 1). If the frit assembly contains solvents or volatile materials, the lower flask is cooled to -78°C or -196°C before evacuation. The frit assembly

is then isolated from the ensuing procedures by closing the needle valve of the adapter. Gas is admitted to the desired pressure calculated using the simplified expression of footnote 6. The stopcock of the calibrated bulb is closed and the gas remaining in the manometer and the rest of the working section is removed by evacuation by condensing it back into its storage bulb or evacuating the system through a removable trap(17). The working section is then isolated from the vacuum manifold by closing the stopcock to the main manifold, and the gas in the bulb is condensed into the reaction flask by cooling to -196°C. If the gaseous reagent has been purified by freeze-pump-thaw cycles prior to use and is stored in a -196°C trap, the desired quantity of gas can be admitted into the manifold and calibrated gas bulb by removing the liquid nitrogen coolant and slowly warming to room temperature until the desired quantity has been admitted to the manifold. The need for a calibrated gas volume can be eliminated by determining the volume of the manifold and using it as the calibrated gas volume, although a manometer correction must then be applied to account for the increase in volume with increase in pressure.

Volatile Liquids. Volatile liquids can be added to a reaction flask of a frit assembly by either of two methods, depending on the quantity of liquid being added and its vapor pressure at room temperature. The first method is analogous to that used for gaseous reagents, and thus is suited to small amounts of very volatile compounds. The liquid to be added is rigorously dried, degassed and stored (in vacuo) in a solvent container such as a round bottomed flask with adapter consisting of a standard taper inner joint, 180° teflon needle valve and 24/40 standard taper outer joint. The liquid is then admitted into a calibrated gas bulb and condensed into the frit assembly as described above for a gaseous reagent. For larger amounts of liquids, a graduated volume(18) attached to an adapter consisting of a standard taper inner joint, 180° teflon needle valve and 24/40 standard taper outer joint is useful (Figure 5). The desired amount of liquid is vacuum transferred into the graduated volume. Once this is accomplished and the manifold is evacuated (either by condensing any residual vapor back into the solvent container or into a -196°C trap), the liquid is then vacuum transferred into the reaction flask of the frit assembly. For storing liquids which are low boiling (just above room temperature) or which are not compatible with Apiezon greases, a solvent container such as that shown in Figure 6 is convenient to use. This container is similar in design to that described later in the section on thick-walled reaction vessels except that it is constructed from standard wall thickness glass tubing. The liquid to be stored is first

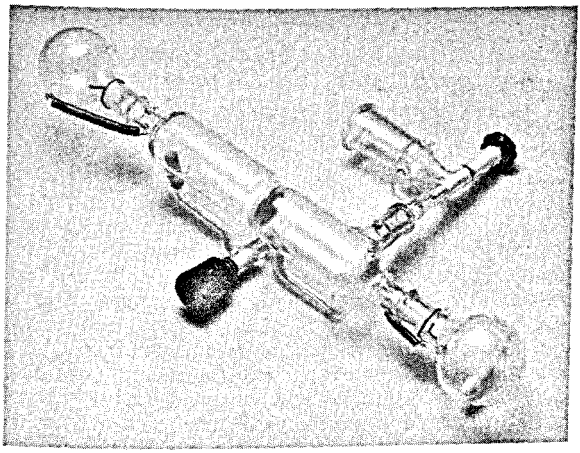

Figure 4. Swivel frit assembly.

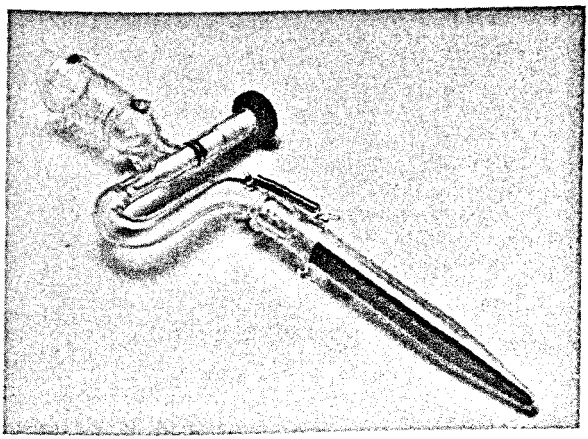

Figure 5. Graduated volume for addition of volatile liquids to reaction flasks.

purified by the appropriate means and then vacuum transferred into the container for storage under vacuum.

Solutions and Non-Volatile Liquids. In many instances, it is desirable to add a solution (such as a commercially available solution of a Grignard or alkyl-lithium reagent) or a non-volatile liquid such as dimethylphenylphospine to a reaction flask. This addition to the reaction flask of the swivel frit assembly can be accomplished in the following manner: under an argon counterflow, the teflon plug from the right angle teflon needle valve of the adapter(19) is removed. A syringe attached to a length of polyethylene tubing (approximately six inches in length) is inserted into the needle valve and degassed by drawing argon through the syringe several times. Filled with argon, the syringe is disconnected from the tubing. The syringe is inserted into the reagent container (usually stored under an inert atmosphere and capped with a sure-seal top or a septum) and the desired volume drawn out. The syringe is then reattached to the tubing and the solution syringed into the reaction mixture. The teflon plug is then fit back into the adapter, leaving the reaction vessel open to the mercury bubbler/manometer. This same technique can be used for non-volatile liquids , which have been previously degassed and are stored under an inert atmosphere.

Filtering Using a Swivel Frit

When working up a reaction mixture, an unwanted solid (salt, etc.) often needs to be removed from a solution of the desired product. Alternatively, the product of a reaction might be insoluble directly from the reaction mixture. In either case, a filtration is required. There are two general ways in which to do this; both rely on differences in pressures to drive the filtering process. The first method is especially convenient when filtering a hot solution. The entire frit assembly is filled with argon. Prior to filtration, the valve of the side arm is closed and the assembly is inverted. A slight vacuum is pulled on the bottom flask causing the solution to pass through the frit. When a cold solution is to be filtered, a different approach is taken. The entire frit assembly is cooled by "swabbing" the outside with a dry ice/ethanol slush(20). Inverting the frit assembly with the stopcock along the side arm closed and admitting a partial atmosphere of argon into the top half of the frit assembly will facilitate the process. A little forethought when assembling the frit, flasks and needle valve adapter (i.e. which side to put the needle valve adapter on) will save time later.

Washing a Solid on a Frit

To wash a solid which has been collected on a frit, the flask containing the wash solvent (the filtrate in the receiving flask or fresh solvent from a solvent pot attached at a nearby port of the working section) is cooled with a dry ice/ethanol slush bath and then degassed. After closing the valve of the sidearm along the side of the frit assembly, the slush bath is replaced with a warm water bath and the top flask is cooled by "swabbing" with slush. Condensation of the wash solvent occurs on the upper half of the frit and upper flask the percolator action of the solvent effectively washes the solid. The resultant solution is forced back into the bottom flask by replacing the warm water bath with a slush bath. The valve of the side arm should be closed during this process.

Procedures for Carrying Out Reactions in an NMR Tube

We routinely use high field NMR spectrometry to screen reactions, to characterize compounds and to measure reaction kinetics. By working in a sealed NMR tube it is possible carry out reactions involving very air sensitive materials an volatile reagents, as well as those which require conditions of high temperature or moderate pressure (0 - ca. 3 atm). The procedure for assembling the reagents for a reaction in a sealed NMR tube is described below for the reaction of $(C_5Me_5)_2ScCH_3$ with 2-butyne. In the inert atmosphere glove box, an NMR tube(21) fused to a small diameter standard wall pyrex tube and then to a 14/20 standard taper outer joint is charged with a known amount of the solid starting material. The NMR tube is then attached to a calibrated gas volume such as the one shown in Figure 7. Deuterated solvent (approximately 0.5 ml) is added either in the glove box or by vacuum transferring from a NMR solvent pot on the vacuum line. The NMR tube is then evacuated while cooling at -78°C, and the stopcock separating the NMR tube from the calibrated volume above is closed. 2-butyne (which has been dried over 4 A molecular sieves) is freeze-pump-thawed on the vacuum line, and a specified pressure is admitted to the manifold and gas volume above the NMR tube. Residual 2-butyne is returned to the storage to its storage container by cooling. The known amount of 2-butyne in the gas volume is then condensed into the NMR tube (-196°C). The tube is now sealed with a cool flame of a glass blowing torch while maintaining cooling (-196°C) of the lower half of the tube. Sealed NMR tubes should be allowed to warm behind proper shielding in a fume hood, since condensed O_2 or excess pressure can lead to an explosion. If the tube is to be heated in the NMR probe, pre-testing of the tube strength by heating briefly at at least 20°C higher temperature than the probe is highly recommended. If volatiles are

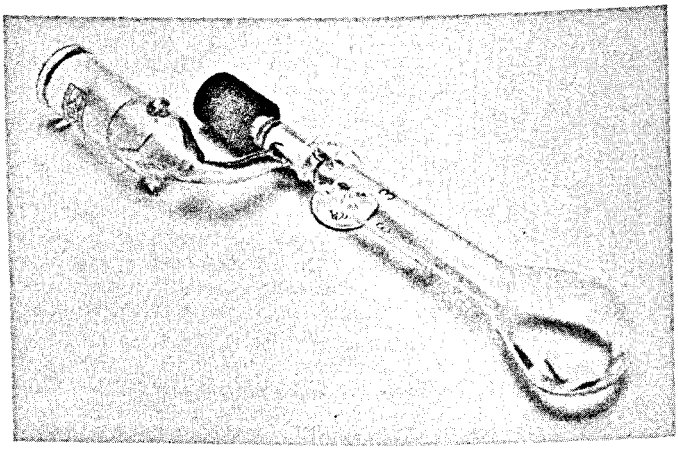

Figure 6. Container for volatile reagents.

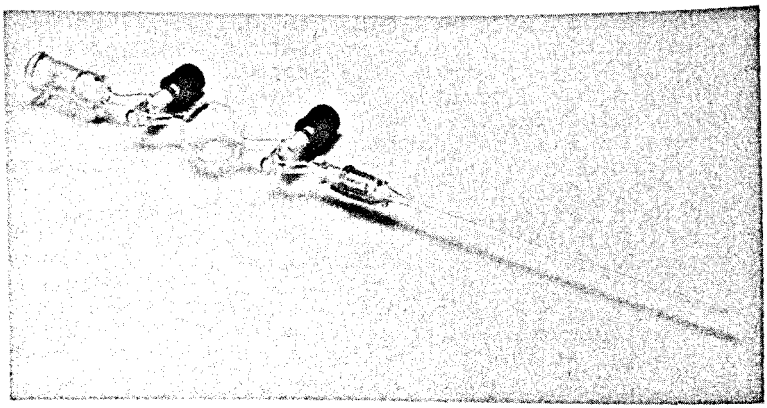

Figure 7. NMR sample tube attached to calibrated gas volume assembly.

condensed into an NMR tube which exhibit greater than one atmosphere vapor pressure at the temperature of the probe, a preliminary calculation should be done to determine what the actual pressure inside the NMR tube will be during the experiment. For pressures approaching or greater than five atmospheres, use of medium walled or thick walled NMR tubes is recommended.

Thick Walled Reaction Vessels

Many of our reactions are carried out at high temperatures and/or moderate pressures (1-7 atm). A convenient way to do this type of reaction is to use a thick-walled reaction vessel, shown in Figure 8. Solid starting materials are added in the inert atmosphere glove box; solvents and gases are added on the vacuum line as described above. The glass vessel can then be heated in an oil bath for the appropriate length of time. Once the reaction is completed, excess pressure is released, for example by cooling the vessel and carefully venting it through a trap cooled at -196°C. The solution is transferred to a swivel frit assembly for work up, using either an inert atmosphere glove box or a syringe attached to polyethylene tubing, following the procedure described above for adding solutions to the swivel frit assembly. The second method is much quicker and is suited to solutions of thermally sensitive, moderately air sensitive compounds.

Use of a Toepler Pump

To quantify the amount of a noncondensable(22) gas such as H_2, CO, CH_4, or N_2 liberated during a reaction, a Toepler pump is employed. The basic operating principle of a Toepler Pump is the use of a mercury piston which is pushed up the upper cylinder by atmospheric pressure admitted to the lower chamber, and allowed to fall as the lower cylinder is evacuated. These procedures are alternated by the relay/control mechanism described earlier, and the gas collected on each cycle is trapped by a one way, float valve in the upper calibrated volumes. Our pumps use a a simple stainless steel ball bearing seated into a spherically ground portion of the valve. Toepler pumps of several different designs are commercially available; ours are of a hybrid design and are constructed in the Caltech glass shop. If the volume of the upper cylinder is 500 ml and the volume being pumped (the cryogenic traps, manometers, manifolds etc. back to the reaction flask is 1500 ml, 75% of the residual gas of the sample being collected will be left behind on each cycle. Thus, many cycles will be needed to reduce the amount of residual gas to a negligle value ($(0.75)^n \longrightarrow 0$, where n is the number of Toepler pump cycles). An indication of the amount of residual gas is provided by the size of the bubble formed when the

mercury approaches the upper valve. The pressure in the calibrated volume should be measured occasionally (by allowing the Hg level to rise to the mark above the valve). When no difference is detected from reading to reading, gas collection may be stopped.

To separate (hot CuO) combustible gases(23) from noncombustibles, the sample is first collected and the total amount of gas is measured. The stopcock leading back to the cryoscopic traps is closed, the stopcocks opening the pathway around the recirculating manifold section are opened. The teflon needle valve leading back to the last trap is opened only slightly so that excessive pressures of gas are prevented from building up at the inlet of the Toepler pump. The gas mixture is now circulated by the Toepler pump through the heated CuO section (320°C), the trap cooled to -196°C and back into the calibrated section, etc. until all H_2 is oxidized to H_2O and CO is oxidized to CO_2, both of which are trapped out at -196°C. By closing the stopcock immediately above the last section of the calibrated volume, the residual, noncombustible gas (N_2 and/or CH_4) may be collected and its pressure determined. By periodically repeating these procedures it can be determined if more cycles through the CuO tube are required. The residual gas is measured and analyzed by infrared spectroscopy, gas chromatography or mass spectrometry by withdrawing a sample into a gas ir cell or gas sample bulb attached to the port at the top of the Toepler pump section of the vacuum line. The residual N_2/CH_4 is pumped out of the calibrated volumes. The trap at -196°C is warmed to -78°C by replacing the liquid nitrogen with a dry ice/ethanol in the dewar surrounding it, and the CO_2 is now collected by the Toepler pump. The amount of CO_2 is, of course, the same as the amount of CO in the original sample. The difference is the amount of H_2, now as H_2O in the -78°C trap, in the original sample. Thus, by applying Dalton's Law of Partial Pressures, one can easily quantitatively determine the composition of H_2/CH_4, H_2/N_2, CO/CH_4, CO/N_2, CO/H_2, $CO/H_2/CH_4$, and $CO/H_2/N_2$ binary and tertiary mixtures, and if coupled with mass spectrometry to quantify the proportions of methane in N_2, $CO/H_2/CH_4/N_2$ quaternary gas mixtures.

Molecular Weight Determination for Non-Volatile Organometallic Compounds

Of all the methods that are available for determining the molecular weight of an organometallic compound, the most straightforward is undoubtedly that developed by Signer(24). This method is based on the simple idea that the vapor pressure of an ideal solution is proportional to the concentration of the solute (Raoult's Law). The major advantages of this technique is that it does not require any sophisticated equipment, only about 0.05 g of the unknown compound are needed and it can be suited to

extremely air sensitive compounds with the adaptations described below. The limitations of this method are that the sample must be stable in solution at room temperature for 3-7 days and the accuracy of this method is ±10% at best. The molecular weight apparatus consists of two graduated capillary tubes (approximately 10 ml in volume, constructed from sections of a Mohr pipet) each sealed to a round bulb. The two bulbs are connected to a short glass tube with solvent seal connectors. In the middle of the glass tube, there is a stopcock through which the entire assembly can be evacuated. A diagram of the apparatus is shown in Figure 9 . The procedure for determining the molecular weight of an unknown air sensitive compound is outlined below.

In the glove box, 0.010-0.015 g of the standard (azobenzene or ferrocene are good choices) is carefully weighed out (± .1 mg) and placed in one bulb. Similarly, an amount of the unknown is accurately weighed out and placed in the other bulb. A solvent which is very inert toward the sample (benzene, cyclohexane, tetrahydrofuran) is added (ca. 0.5-0.8 ml) to each bulb and the apparatus is assembled. The bulbs are cooled to -78°C, and the apparatus is evacuated on the vacuum line. The assembly is then allowed to come to room temperature and placed (with the solvent in the bulbs) in a location free from drafts, away from direct sunlight or room light (a cardboard box or large pot work nicely). The volume change should be periodically monitored by tilting the assembly so that the solutions flow into the volumetric portions of the apparatus. The volume of each solution will change by transfer of solvent vapor until the vapor pressures of the two solution equilbrate, usually requiring 3-7 days. The experimental molecular weight is determined by the following relationship:

$$MW_X = \frac{(mg_X)(MW_S)(ml_S)}{(mg_S)(ml_X)}$$

where mg_X = weight of unknown in mg
mg_S = weight of standard in mg
MW_X = molecular weight of unknown
MW_S = molecular weight of standard
ml_X = volume of standard solution
ml_S = volume of unknown solution

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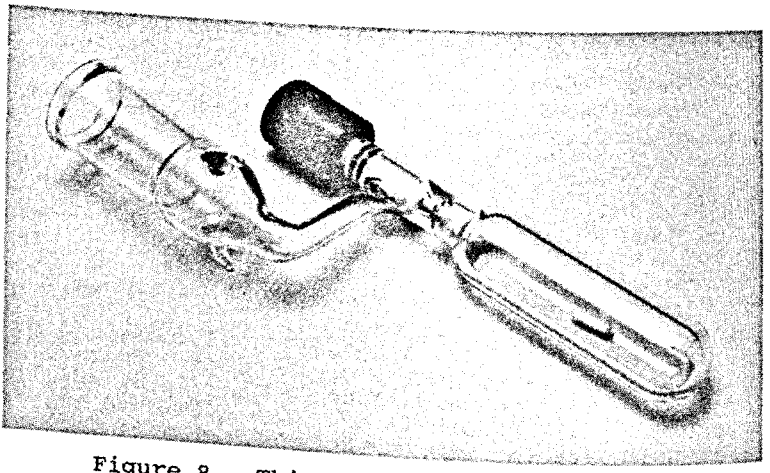

Figure 8. Thick walled reaction vessel.

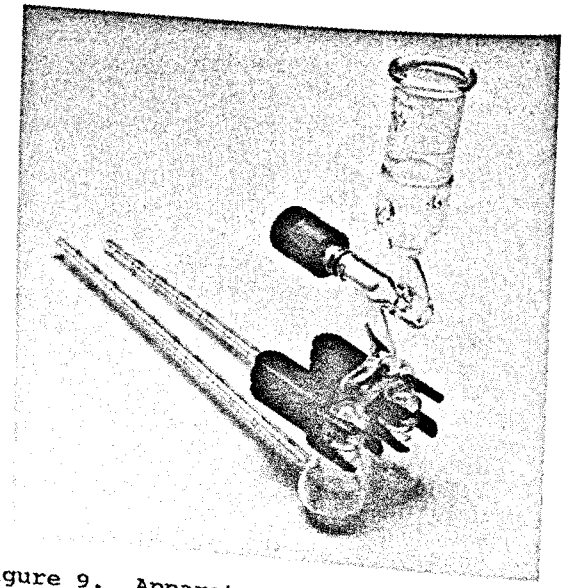

Figure 9. Apparatus for molecular weight determination.

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REFERENCES AND FOOTNOTES

1. Because it operates with a Hg column, the McLeod gauge does not read the partial pressure of mercury (ca. 10^{-3} torr) which continually fills those portions exposed to liquid Hg.
2. The accurate measurement of pressure requires use of a manometer. The bubbler is less accurate since the level of the pool of mercury at the base varies slightly as the column height varies.
3. Our group has invested heavily in Fischer Porter brand 4 mm needle valves. These provide fine control when they are opened, and are thus preferable for those sections of the system where control is needed, for example, for solvent removal and at the points of entry to the cryogenic trap and Toepler section. In recent years less expensive, but equally effective teflon needle valves have become available.
4. The base of the Toepler pump and the bases of the mercury bubblers should be placed in plastic cups and secured with plaster of paris to a depth of 3 or 4 inches. Thus, mercury spillage is avoided is the glass base is broken.
5. The pathway of this recirculating section should have as little volume as possible out of the circuit, since gases must flow freely to prevent them from "hiding in corners" from the reactive CuO.
6. A simplified ideal gas formula is used to calculate the mmols of gas in the volumes: n (mmols) = p (torr)·V (ml)/1.85 X 10^4 at 23.5°C.
7. The circuit diagram is available on request.
8. Brown, T. L.; Dickerhoof, D. W.; Bafus, D. A.; Morgan, G. L. Rev. Sci. Instruments 1962, 33, 491-492.
9. Care should be taken not to allow the aluminum foil to contact the electrical leads!
10. Since Ar has only ca. 100 torr of vapor pressure at liquid nitrogen temperature, a dangerous buildup of liquid Ar will occur if the pressure of Ar exceeds this value while a trap, flask, NMR tube, etc. is being cooled with liquid nitrogen. Similarly care must be taken to not allow the pressure to exceed one atmosphere when cooling a part of the line with N_2 as the inert gas.
11. The purity of commercially available carbon monoxide (e.g. Matheson) is normally sufficient for our experiments.
12. Marvich, R. H.; Brintzinger, H. H. J. Amer. Chem. Soc., 1971, 93, 2046-2048.
13. For solvent pots of greater than 500 ml in volume, it is recommended that they be taped or otherwise treated to prevent flying glass should the flask implode. This advisory note applies whenever large glassware is evacuated.

14. Heating the solvent pot above room temperature will only slightly increase the rate of transfer, and has the undesirable effect of causing solvent condensation along the path of the transfer.
15. Thicker Apiezon H grease is used to compensate for the poorer fit of standard taper joints and to reduce the amount of solvent wash out. The joints are greased only along the top half of the ground glass section to minimize contamination from grease; however, we have never noted deleterious effects of Apiezon greases on our compounds.
16. If the high vacuum working station is used the bubbler/manometer may be accurately used as a manometer since the pools of Hg are interconnected (see Figure 1).
17. If a very reactive, noxious or poisonous reagent is used, the residual reagent should be trapped out into one of the removable traps, and the reagent should be carefully transferred to the fume hood where it is allowed to warm slowly.
18. A section of a Mohr pipet or graduated centrifuge tube sealed to a 14/20 standard taper outer joint have proven to be quite satisfactory.
19. Caution: the reaction flask may be cooled only to -78°C; cooling to liquid nitrogen temperature will lead to dangerous buildup of liquid Ar. If the reaction flask must be cooled to liquid nitrogen temperature, N_2 should be used as the inert gas and great care must be exercised to avoid condensation of liquid nitrogen.
20. Care should be taken to avoid cooling the teflon valves. The much different coefficients of thermal expansion for teflon and glass results in leakage when the valve is cooled much below room temperature.
21. We have found that Wilmad (507 pp) NMR tubes provide adequate resolution for routine high field NMR spectra.
22. A noncondensable gas is operationally defined as one that has more than ca. 0.01 torr pressure at liquid nitrogen temperature.
23. Care should be taken to avoid O_2, even in small amounts, as a component of these gas mixtures. An explosive mixture with H_2, CO or CH_4 could easily be produced and detonated by sparks at the electrodes of the relay or on contact with the hot CuO.
24. E.P. Clark, Ind. Eng. Chem., Anal. Ed. 1941, 13, 820..

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