Pyrophorics (PYR) and Self-Heating Substances (and Mixtures)

H250 H251 H252

Examples: tert-Butyllithium, sec-Butyllithium, n-Butyllithium, DiethylZinc, Organoaluminium compounds (as Et₂Al, Et₂AlCl, EtAlCl₂, Me₃Al), Raney Nickel catalyst

Note: Before handling any pyrophoric material, researchers must also read and sign the “Quenching of Pyrophoric Materials” hazardous operation SOP

1. Purpose

This SOP covers the precautions and safe handling procedures for the use of Pyrophorics and Self-Heating Substances Chemicals, which include the following chemicals and their uses:

Note: All chemicals are to be used with Procedure 1: Transferring of liquid pyrophoric chemicals (as outlined in Section 12).

Note: A * next to chemical indicates that it is also an Acutely Toxic Chemical.

<table>
<thead>
<tr>
<th>CasNumber</th>
<th>Chemical_Name</th>
<th>Exhibit</th>
</tr>
</thead>
<tbody>
<tr>
<td>16750-63-3</td>
<td>2-Methoxyphenylmagnesium bromide solution</td>
<td>Exhibit 1</td>
</tr>
<tr>
<td>16750-63-3</td>
<td>2-methoxyphenylmagnesium bromide, 1.0 M solution in THF</td>
<td>Exhibit 1</td>
</tr>
<tr>
<td>7439-95-4</td>
<td>magnesium</td>
<td>Exhibit 1</td>
</tr>
<tr>
<td>829-85-6</td>
<td>Diphenylphosphine</td>
<td>Exhibit 1</td>
</tr>
<tr>
<td>598-30-1</td>
<td>SEC-BUTYLLITHIUM</td>
<td>Exhibit 1</td>
</tr>
</tbody>
</table>

Rev. Date: March 23, 2015
<table>
<thead>
<tr>
<th>Code</th>
<th>Substance</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1730-25-2</td>
<td>Allylmagnesium bromide 1.0 M in Diethyl Ether</td>
<td>Exhibit 1</td>
</tr>
<tr>
<td>10210-68-1</td>
<td>cobalt carbonyl*</td>
<td></td>
</tr>
<tr>
<td>7775-14-6</td>
<td>Sodium hydrosulfide</td>
<td></td>
</tr>
<tr>
<td>1907-33-1</td>
<td>Lithium tert-butoxide</td>
<td></td>
</tr>
<tr>
<td>865-48-5</td>
<td>Sodium-t-butoxide</td>
<td></td>
</tr>
<tr>
<td>865-33-8</td>
<td>potassium methylate</td>
<td></td>
</tr>
<tr>
<td>865-33-8</td>
<td>Potassium methoxide</td>
<td></td>
</tr>
<tr>
<td>1779-25-5</td>
<td>diisobutylaluminum chloride*</td>
<td></td>
</tr>
<tr>
<td>544-97-8</td>
<td>dimethylzinc (1.2 M in toluene)*</td>
<td></td>
</tr>
<tr>
<td>557-20-0</td>
<td>Diethyl zinc*</td>
<td></td>
</tr>
<tr>
<td>13716-12-6</td>
<td>Tri-tert-butylphosphine*</td>
<td></td>
</tr>
<tr>
<td>109-72-8</td>
<td>Butyl lithium*</td>
<td></td>
</tr>
<tr>
<td>21369-64-2</td>
<td>n-hexyllithium*</td>
<td></td>
</tr>
<tr>
<td>124330-23-0</td>
<td>Alane N, N-dimethylethylamine complex solution (0.5 M in toluene*)</td>
<td></td>
</tr>
<tr>
<td>1184-58-3</td>
<td>dimethylaluminum chloride 1.0 m in hexanes*</td>
<td></td>
</tr>
<tr>
<td>1184-58-3</td>
<td>Dimethylaluminum chloride*</td>
<td></td>
</tr>
<tr>
<td>594-19-4</td>
<td>tert-butyl lithium 1.7 M in pentane*</td>
<td></td>
</tr>
<tr>
<td>594-19-4</td>
<td>t-butyl lithium (1.7 M in pentane)*</td>
<td></td>
</tr>
<tr>
<td>557-20-0</td>
<td>diethylzinc*</td>
<td></td>
</tr>
<tr>
<td>594-19-4</td>
<td>tert-Butyllithium solution (1.7 M in pentane)*</td>
<td></td>
</tr>
<tr>
<td>96-10-6</td>
<td>Diethylaluminum chloride (0.9 M in PhMe)*</td>
<td></td>
</tr>
<tr>
<td>96-10-6</td>
<td>Diethylaluminum chloride solution 25 wt.% in toluene*</td>
<td></td>
</tr>
<tr>
<td>554-70-1</td>
<td>Triethylphosphine, 97%</td>
<td></td>
</tr>
<tr>
<td>136779-26-5</td>
<td>(-)-1,2-Bis(2S,5S)-2,5-dimethylphospholanoethane</td>
<td></td>
</tr>
<tr>
<td>42371-63-1</td>
<td>S-Alpine-Borane {-} (0.5 M solution in THF)</td>
<td></td>
</tr>
<tr>
<td>7397-46-8</td>
<td>Methoxydiethylborane</td>
<td></td>
</tr>
<tr>
<td>7439-95-4</td>
<td>Magnesium</td>
<td></td>
</tr>
<tr>
<td>7429-90-5</td>
<td>Aluminum powder</td>
<td></td>
</tr>
<tr>
<td>7397-46-8</td>
<td>diethylmethoxyborane</td>
<td></td>
</tr>
<tr>
<td>73624-47-2</td>
<td>R-Alpine-borane(r), (0.5 m in thf)</td>
<td></td>
</tr>
<tr>
<td>7429-90-5</td>
<td>Aluminium</td>
<td></td>
</tr>
<tr>
<td>122-56-5</td>
<td>tributylborane</td>
<td></td>
</tr>
<tr>
<td>122-56-5</td>
<td>tri-n-butylborane</td>
<td></td>
</tr>
<tr>
<td>591-51-5</td>
<td>phenyl lithium</td>
<td></td>
</tr>
<tr>
<td>75-24-1</td>
<td>trimethylaluminum</td>
<td></td>
</tr>
<tr>
<td>75-24-1</td>
<td>Aluminum trimethyl</td>
<td></td>
</tr>
<tr>
<td>1191-15-7</td>
<td>Diisobutylaluminium hydride</td>
<td></td>
</tr>
<tr>
<td>1191-15-7</td>
<td>Diisobutylaluminium hydride</td>
<td></td>
</tr>
<tr>
<td>1191-15-7</td>
<td>Diisobutylaluminium hydride solution (25 wt % in toluene)</td>
<td></td>
</tr>
</tbody>
</table>

Rev. Date: March 23, 2015
If you have questions concerning the applicability of any recommendation or requirement listed in this procedure, contact the Principal Investigator/Laboratory Supervisor or the campus Chemical Hygiene Officer at ucbcho@berkeley.edu.

2. Physical & Chemical Properties / Definition of Chemical Group

Pyrophoric materials can ignite spontaneously (within 5 minutes) on contact with air, moisture in the air, oxygen, water, or other chemicals with reactive hydroxyl groups. Most pyrophorics may also be classified as water reactives. However, not all water reactives are pyrophoric. The reaction rates of pyrophorics with air is in the order Rate_{SOLID} < Rate_{LIQUID} ≤ Rate_{GAS}.

Pyrophoric solids generally smolder before igniting; pyrophoric liquids generally ignite immediately on exposure to air; pyrophoric gases may form jet fires if escaping from a vessel following a mechanical failure.

As most pyrophorics react violently with water, water should not be allowed to contact pyrophoric materials.

Pyrophorics must be handled under an inert atmosphere that rigorously excludes air/moisture.

3. Potential Hazards and Toxicity

Many pyrophorics are supplied as solutions in flammable solvents such hexane. The hazards of the mixture, the pyrophoric and the solvent, should be considered together and procedures for safe handling should reflect the hazard properties of both solvent and solute. Most of these materials are toxic and may cause damage to the liver, kidneys, and central nervous system. Safe use requires assessing all potential hazards.

As defined by the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), pyrophorics and self-heating substances are designated by one or more of the following H codes:

- **Pyrophorics**
  - H250 Catches fire spontaneously if expose to air

- **Self-Heating Substances**
  - H251 Self-heating; may catch fire
  - H252 Self-heating in large quantities; may catch fire

4. Engineering Controls

The following is the set of engineering controls required when handling pyrophoric materials:

- Work under an inert atmosphere (e.g., argon, nitrogen) using a Schlenk line, in a glove box, vacuum manifold, or any enclosed inert environment.
- Use a clean fume hood, preferably with the sliding sash windows or a glove box.

Rev. Date: March 23, 2015
• If procedure is done in the fume hood, use the sash as a safety shield. For hoods with a horizontal sliding sash, position the sash all the way down, stand behind the sliding windows and reach around to perform the manipulations required. For hoods with vertical sliding sash, keep the sash as low as possible.
• Face shields are to be used when there is no protection from the hood sash or when the hood sash is open.
• Keep the materials under inert atmosphere when not in use.
• Remove any flammables (squirt bottles containing solvents, oil baths) and combustibles (Kimwipes, paper towels) from the area that will be used for the quenching.

5. Personal Protective Equipment
At a minimum, the following PPE must be worn at all times.

  **Eye Protection**
  A. ANSI Z87.1-compliant safety glasses with side shields, or chemical splash goggles.
  • Ordinary prescription glasses will NOT provide adequate protection unless they also meet ANSI standard and have compliant side shields.
  B. If the potential for explosion/splashing exists, and adequate coverage is not provided by the hood sash, a face shield should be worn.

  **Skin Protection**
  A. Flame-resistant lab coat (Nomex IIIA, NFPA 2112) should be worn when working with pyrophoric and self-heating materials.
  B. Gloves are required when handling hazardous materials. Refer to the specific chemical SDS for information on glove selection.
  C. Long pants, closed-toe/closed-heel shoes, covered legs, and ankles. Cotton-based, non-synthetic clothing should be worn.

6. First Aid Procedures and Medical Emergencies

*In the event of an injury, notify your supervisor immediately and EH&S within 8 hours. Follow up with a call to 510-642-6060 to report the incident.*

⚠ **Go to the Occupational Health Facility (Tang Health Center, on campus); if after hours, go to the nearest emergency room (Alta Bates, 2450 Ashby Ave in Berkeley); or**

⚠ **Call 911 (from a cell phone: 510-642-3333) if:**
  • it is a life threatening emergency; or
  • you not are confident in your ability to fully assess the conditions of the environment and/or the condition of the contaminated/injured person, or you cannot be assured of your own safety; or
  • the contaminated/injured person is not breathing or is unconscious.

*Please remember to provide a copy of the appropriate manufacturer SDS (if available) to the emergency responders or physician. At a minimum, be ready to provide the identity/name of any hazardous materials involved.*

**In case of skin contact**
If skin contact occurs, and/or skin or clothing are on fire, immediately drench in the safety shower with copious amounts of water for no less than 15 minutes to remove any remaining contaminants. If possible to do so without further injury, remove any remaining jewelry or clothing.
In case of eye contact
Rinse thoroughly with plenty of water using an eyewash station for at least 15 minutes, occasionally lifting the upper and lower eyelids. Remove contact lenses if possible.

If swallowed
Do NOT induce vomiting unless directed otherwise by the SDS. Never give anything by mouth to an unconscious person. Rinse mouth with water.

Needle stick/puncture exposure
Wash the affected area with antiseptic soap and warm water for 15 minutes. For mucous membrane exposure such as eyes, mouth and/or nose, flush the affected area for 15 minutes using an eyewash station.

If inhaled
Move into fresh air.

7. Special Handling and Storage Requirements
Pyrophoric reagents can be handled and stored safely as long as all exposure to atmospheric oxygen and moisture or other incompatible chemicals is avoided. Never leave a container with a residue of a pyrophoric material open to the atmosphere.
Lab-specific information on handling and storage may be included in Section 12 - Protocol/Procedure section.

Working Alone
The UC Berkeley Office of Environmental Health and Safety specifies not to work with pyrophorics alone or during off hours, when there are few people around to help.

Handling Pyrophoric Liquids
Users should read and understand the Aldrich Technical Information Bulletin, No. AL-134; there are many detailed handling recommendations that are not presented in this SOP.

- There are two basic techniques to transfer pyrophoric liquids: the syringe and the cannula needle (over-pressure transfer). The syringe should only be used for small quantities (less than 20 mL) as described in No AL-134. To conveniently transfer 20 mL or more of reagent, the cannula technique is recommended.
- These reagents can be handled safely in the laboratory, if proper techniques are used. A Schlenk line in a fume hood with inert gas flow will be necessary. The Aldrich Sure/Seal™ Packaging System provides a convenient method for storing and dispensing air-sensitive reagents. Most researchers only need to use small quantities, so the syringe method is more convenient. Be cautious with the use of the plastic syringe as the rubber gasket may swell up leaving you with a syringe of pyrophoric liquid. Start with small quantities, until you are proficient with the method.
- Pyrophoric solids should be transferred under an inert atmosphere in a glove box.
- Pyrophoric gases must be handled in compliance with the California Fire Code, Chapter 41.

Storage of Pyrophoric Materials

- Keep the material under inert atmosphere when not in use.
- Use and store minimal amounts of pyrophoric chemicals. Store pyrophoric materials as recommended in the SDS or product guidance. Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name and hazard warning in English.
- Inert gas-filled desiccators or glove boxes are suitable storage locations for most materials. Do not store pyrophoric chemicals with other flammable materials or in a flammable liquids storage cabinet.
• If pyrophoric materials are received in specially designed shipping, storage or dispensing container (such as the Aldrich Sure/Seal packaging system), ensure that the integrity of that container is maintained.

• Take extreme care to prevent containers of pyrophorics from leaking or breaking. Secondary containment is required for storing and transporting pyrophoric materials. The use of corrosion and shatter-resistant containers is encouraged.

• Ampules must be stored and transported in secondary containers (even in glove boxes). Take extreme care while handling ampules outside of the glove box, keep in mind that these glass containers are very fragile.

• Ensure that a sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.

• For extended storage of unused pyrophorics, use the solid plastic cap, or equip the bottle with an Oxford Sure/Seal valve cap, or transfer the reagent to a suitable storage vessel.

Disposal of Pyrophoric Reagents

• Never leave a container with a residue of a pyrophoric material open to the atmosphere.

• Any unused or unwanted pyrophoric materials must be destroyed by following the specific destruction procedure(s) included in your “Hazardous Operation SOP – Quenching od Pyrophoric Materials”. As an alternative to quenching, remember that pyrophoric chemicals can be disposed of as hazardous waste.

• The empty container should be rinsed three times with an inert dry COMPATIBLE solvent. The rinse solvent must be transferred in and out of the container under an inert atmosphere using the syringe or cannula technique.

• After the empty container is triple-rinsed, it should be left open in back of a hood or ambient atmosphere at a safe location overnight.

• Solvent rinses should be disposed of as hazardous waste.

• DO NOT use water to extinguish a pyrophoric chemical fire as it probably will enhance the intensity of the fire.

8. Chemical Spill and Managing Any Subsequent Fire

Pyrophoric Spill Response

• In the case of a spill, announce the situation loudly in the immediate area and have any nearby persons move to a safe location.

• Immediately eliminate/remove all nearby ignition sources.

• If spill occurs in a fume hood, cover with Met-L-X, dry sand, or other non-combustible material, close the hood sash and if present, press the red purge button.

• If a spill occurs outside a fume hood, cover with Met-L-X, dry sand, or other non-combustible material, and stand away from the spill.

• Locate and have a proper fire extinguisher (dry chemical-based) ready in case of ignition/fire.

• Use clean, non-sparking tools to collect absorbed material and place into loosely-covered metal or plastic containers ready for disposal.

• Do not use combustible materials (paper or cloth towels) to clean up a spill, as these may increase the risk of igniting the reactive compound.

• If you cannot assess the situation well enough to be sure of your own safety, do not approach the spill.

• Keep others from entering contaminated area (e.g., use caution tape, barriers, etc.).
• Report the spill to 510-642-3073.

**Pyrophoric Fire Response**

• Call **911** (from a cell phone: **510-642-3333**) for emergency assistance and for assistance with all fires, even if extinguished.

• If the spill ignites, and if you are trained and you feel comfortable to do so, consider extinguishing the fire with an appropriate fire extinguisher. Only dry chemical fire extinguishers should be used (classes ABC or D). Do not use a CO₂ extinguisher.

• A can of Met-L-X or dry sand in the work area, within arm’s reach, might be helpful to extinguish any small fire as it can smother the flames.

• Do not use water to extinguish a pyrophoric chemical fire as it may enhance the intensity of the fire. An exception to this would be in the case of skin contact or ignited clothing/skin. In these cases rinsing any unreacted chemical off is of primary importance.

*Be AWARE*: Small flames at the tip of the needles can be produced – always expect this to occur, and do not panic. The can of Met-L-X/sand is in the hood to quickly extinguish those small flames.

Carbon Dioxide, Foam, Halon, and Fire blanket are **UNSUITABLE** for extinguishing metal alkyl fires.

9. **Cleaning and Decontamination**

Lab-specific information on decontamination may be included in the Protocol/Procedure section.

• Wearing proper PPE, laboratory work surfaces should be cleaned at the end of each work day.

• Dispose of contaminated materials in accordance with hazardous waste disposal guidelines referenced below

• Clean all equipment before removing from a designated area.

10. **Hazardous Waste Disposal**

Label Waste

Label all waste containers. See the EH&S Fact Sheet, “Hazardous Waste Management” for general instructions on procedures for disposing of hazardous waste.

Dispose of Waste

• Dispose of regularly generated chemical waste within 6 months.

• Call EH&S with questions.

11. **Safety Data Sheet (SDS) Location**

SDS can be accessed online at [http://ucmsds.com](http://ucmsds.com)
### 12. Protocol/Procedure for: Pyrophoric Chemicals

<table>
<thead>
<tr>
<th>Preparation</th>
<th>List any other particular preparation requirements needed for this procedure (e.g., location of spill kit or keep water or ignition sources away from procedure area)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• Know the location of the nearest fire extinguisher, eyewash, and safety shower before beginning work.</td>
</tr>
<tr>
<td></td>
<td>• Have a small can of Met-L-X or dry sand in the work area, within arm’s reach.</td>
</tr>
<tr>
<td></td>
<td>• Solvents must be dry.</td>
</tr>
<tr>
<td></td>
<td>• Glassware must be dry before using. Either “flame” dry or dry in an oven at a minimum temperature of 100°C for at least two hours.</td>
</tr>
<tr>
<td></td>
<td>• Remove all other flammable/combustibles materials from the hood to reduce the hazard in case of a fire. Make adjacent lab workers aware that you will be working with pyrophoric chemicals.</td>
</tr>
</tbody>
</table>

**Procedure**

1. Transferring of liquid pyrophoric chemicals

**Appendix**

Comprehensive List of Pyrophoric Chemicals.
1. Transferring of liquid pyrophoric chemicals

This procedure is to be used for up to 150 mL or less of liquid pyrophoric material as supplied in the reagent bottle. The reaction vessel can hold more than 150 mL of total solution (up to 3 L) but no more than 150 mL of liquid pyrophoric as supplied in the reagent bottle.

Conduct in a clean fume hood with the sash closed using the Schlenk techniques, or an inert atmosphere glove box. If using outside an inert atmosphere glove box, ensure the receiving vessel is dry and a blanket of inert gas is kept over the air sensitive chemicals. When dispensing 20 or more than 20 mL of liquid pyrophoric use a cannula system with a volumetric addition funnel.

**Eye Protection:** Wear fitted safety goggles or safety glasses with side shields.

**Face Protection:** Face shields are to be used when there is no protection from the hood sash or when the hood sash is open.

**Hand Protection:** Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Wash and dry hands after use.

**Hand Protection for indirect contact with pyrophoric material** (closed-system procedures such as transfers via syringe or cannula): Use nitrile gloves of at least 10 mil thickness (double-glove if 5 mil thickness).

**Hand Protection for direct contact with pyrophoric material** (open system procedures such as spill handling, wiping of residual pyrophorics): Provide for adequate employee hand protection by evaluating any additional risks via a hazard assessment and provide the

<table>
<thead>
<tr>
<th>Procedure/Use</th>
<th>Scale</th>
<th>Engineering Controls/Equipment</th>
<th>PPE (eye, face, gloves, clothing)</th>
<th>Procedure Steps and Special Precautions for this Procedure</th>
</tr>
</thead>
</table>
| 1. Transferring of liquid pyrophoric chemicals | This procedure is to be used for up to 150 mL or less of liquid pyrophoric material as supplied in the reagent bottle. The reaction vessel can hold more than 150 mL of total solution (up to 3 L) but no more than 150 mL of liquid pyrophoric as supplied in the reagent bottle. | Conduct in a clean fume hood with the sash closed using the Schlenk techniques, or an inert atmosphere glove box. If using outside an inert atmosphere glove box, ensure the receiving vessel is dry and a blanket of inert gas is kept over the air sensitive chemicals. When dispensing 20 or more than 20 mL of liquid pyrophoric use a cannula system with a volumetric addition funnel. | **Eye Protection:** Wear fitted safety goggles or safety glasses with side shields. **Face Protection:** Face shields are to be used when there is no protection from the hood sash or when the hood sash is open. **Hand Protection:** Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Wash and dry hands after use. **Hand Protection for indirect contact with pyrophoric material** (closed-system procedures such as transfers via syringe or cannula): Use nitrile gloves of at least 10 mil thickness (double-glove if 5 mil thickness). **Hand Protection for direct contact with pyrophoric material** (open system procedures such as spill handling, wiping of residual pyrophorics): Provide for adequate employee hand protection by evaluating any additional risks via a hazard assessment and provide the | General Considerations:
The reagent can be dispensed using a syringe for small quantities (<20 mL) or double-tipped needle - cannula method for larger quantities (≥20 mL). The needle should be no larger than 16 gauge, inserted through the hole in the metal cap.

It is recommended to use the plastic syringes and needles only once; the rubber gasket of a plastic syringe may swell up leading to a jammed syringe.

The plastic cap on the reagent container is to be replaced after each use.

Draw the syringe plunger slowly, checking for leaks. If the syringe is pulled too hard, the pyrophoric liquid can come out the back of the syringe onto the researcher. Orient the syringe in such a way that an accidental spill will be directed away from you.

Never overfill the syringe; fill the syringe half full, even if you need to make multiple transfers.

The pressure in bottles of air sensitive chemicals must be tightly controlled. Draw out pyrophoric liquid only in the presence of a flow of inert gas to prevent air from entering the reagent container.

For extended storage of unused reagents, use the solid plastic cap, or equip the bottle with an Oxford Sure/Seal valve or equivalent.

Use a long flexible needle that is one to two feet long to transfer liquid via the cannula method.

Clamp the reagent bottle to prevent it from moving. Clamp/secure the receiving vessel too. |
**Appropriate hand protection. Consider the use of fire resistant (FR) gloves or liners.**

**Clothing:** Wear Nomex IIIA (NFPA 2112) lab coat; cotton based clothing; full length pants or equivalent; and close-toed and close-heeled shoes.

---

**- Reagent Transfer with Syringe -**

The syringe transfer of liquid reagents is readily accomplished by first pressurizing the Sure/Seal™ reagent bottle with inert gas followed by filling the syringe.

The inert gas pressure is used to slowly fill the syringe with the desired volume plus a slight excess (to compensate for gas bubbles) of the reagent.

Note the inert gas pressure pushes the plunger back as the reagent enters the syringe. The plunger should not be pulled back as this tends to cause leaks and creates gas bubbles.

The excess reagent along with any gas bubbles is forced back into the reagent bottle.

The accurately measured volume of reagent in the syringe is quickly transferred to the reaction apparatus by puncturing a rubber septum on the reaction flask or addition funnel.

Following its use, a syringe contains amount of residual reagent. It is advisable to rinse out the reactive reagent by first placing a few milliliters of the same solvent that was used for the reaction in a small Erlenmeyer flask in the hood.

Keeping the needle tip under the solvent at all times, no more than half the solvent is then drawn into the syringe.

The solvent plus dissolved residual reagent is ejected from the syringe back into the same Erlenmeyer flask. Repeat this rinse treatment at least three times. The wash solution can be safely combined with other waste solvents and the syringe may be further cleaned with water and acetone.
- Reagent Transfer with Cannula (Double-Tipped Needle) -

Use a long flexible needle that is one to two feet long to transfer liquid via the cannula method.

The double-tipped needle technique is recommended when transferring 20 mL or more.

Pressurize the Sure/Seal bottle with nitrogen and then insert the double-tipped needle through the septum into the headspace above the reagent. Nitrogen will pass through the needle.

Insert the other end through the septum at the calibrated addition funnel on the reaction apparatus.

Push the needle into the liquid in the Sure/Seal reagent bottle and transfer the desired volume.
Then withdraw the needle to above the liquid level. Allow nitrogen to flush the needle. Remove the needle first from the reaction apparatus and then from the reagent bottle.

For an exact measured transfer, convey from the Sure/Seal bottle to a dry nitrogen flushed graduated cylinder fitted with a double-inlet adapter.

Transfer the desired quantity and then remove the needle from the Sure/Seal bottle and insert it through the septum on the reaction apparatus.

Apply nitrogen pressure as before and the measured quantity of reagent is added to the reaction flask.

After use, the double-tipped needle is flushed free of reagent with nitrogen in the transfer system, and then immediately removed and placed in a clean sink.

With water running in the sink and in the complete absence of flammable solvents and vapors, the double-tipped needle can be rinsed with water.

When no activity in the rinse water is observed, acetone from a squeeze bottle can be flushed through the needle.
Notes

Any deviation from this SOP requires approval from PI.
13. **Documentation of Training (signature of all users is required)**

- Prior to conducting any work with pyrophoric materials, designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
- The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the pyrophoric material MSDS provided by the manufacturer.

I have read and understand the content of this SOP:

<table>
<thead>
<tr>
<th>Name</th>
<th>Signature</th>
<th>Identifier</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Rev. Date: 23March2015
Appendix. Comprehensive List of Pyrophoric Chemicals.

<table>
<thead>
<tr>
<th>Pyrophoric Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-)-1,2-bis-(2S,5S)-2,5-diethylphospholano)ethane</td>
</tr>
<tr>
<td>(+)-1,2-bis-(2R,5R)-2,5-dimethylphospholano)ethane</td>
</tr>
<tr>
<td>(3-Lithio-propoxy)-iso-propyl-dimethyl-silane</td>
</tr>
<tr>
<td>1,1,1,3,3,3-hexamethyldisilazane</td>
</tr>
<tr>
<td>1,1,1-Tris(diethylphosphino-methyl)ethane</td>
</tr>
<tr>
<td>1,2-bis-diethylphosphino)ethane</td>
</tr>
<tr>
<td>1,2-Phenylenedisphosphine</td>
</tr>
<tr>
<td>2,2-Disilyltri-silane</td>
</tr>
<tr>
<td>2-thienyllithium</td>
</tr>
<tr>
<td>3-butoxypropan-2-ol; propylene glycol monobutyl ether</td>
</tr>
<tr>
<td>9-borabicyclo[3.3.1]nonane</td>
</tr>
<tr>
<td>alane N,N-dimethyl ethylamine complex</td>
</tr>
<tr>
<td>alane-N-methyl pyrrolidine</td>
</tr>
<tr>
<td>allyl(cyclopentadienyl)nickel(ii)</td>
</tr>
<tr>
<td>allylmagnesium bromide</td>
</tr>
<tr>
<td>allylmagnesium chloride</td>
</tr>
<tr>
<td>aluminium alkyls</td>
</tr>
<tr>
<td>aluminium powder (pyrophoric)</td>
</tr>
<tr>
<td>aluminium powder (stabilised)</td>
</tr>
<tr>
<td>aluminium tri-titanium dodecachloride</td>
</tr>
<tr>
<td>aluminoxanes, iso-bu, branched, cyclic and linear</td>
</tr>
<tr>
<td>bis-cyclopentadienyl)magnesium</td>
</tr>
<tr>
<td>bis-dimethylphosphino)methane</td>
</tr>
<tr>
<td>bis-ethylcyclopentadienyl)chromium(ii)</td>
</tr>
<tr>
<td>bis-ethylcyclopentadienyl)magnesium</td>
</tr>
<tr>
<td>bis-ethylcyclopentadienyl)manganese(ii)</td>
</tr>
<tr>
<td>bis-ethylcyclopentadienyl)vanadium(ii)</td>
</tr>
<tr>
<td>bis-methylcyclopentadienyl)magnesium</td>
</tr>
<tr>
<td>bis-pentamethylcyclopentadienyl)-magnesium</td>
</tr>
<tr>
<td>bis-propylcyclopentadienyl)magnesium</td>
</tr>
<tr>
<td>boron</td>
</tr>
<tr>
<td>bromo(1-methylethyl)magnesium</td>
</tr>
<tr>
<td>bromo(p-chlorophenyl)magnesium</td>
</tr>
<tr>
<td>bromo(tri--tert-butylphosphine)palladium(i) dimer</td>
</tr>
<tr>
<td>bromocyclopentylmagnesium</td>
</tr>
<tr>
<td>bromodimethylborane</td>
</tr>
<tr>
<td>bromoethylmagnesium</td>
</tr>
<tr>
<td>bromohexylmagnesium</td>
</tr>
<tr>
<td>bromopentylmagnesium</td>
</tr>
<tr>
<td>bromopropylmagnesium</td>
</tr>
<tr>
<td>Pyrophoric Chemical</td>
</tr>
<tr>
<td>---------------------------------------------------------</td>
</tr>
<tr>
<td>butyl(1-methylpropyl)magnesium</td>
</tr>
<tr>
<td>butylethylmagnesium</td>
</tr>
<tr>
<td>butyllithium</td>
</tr>
<tr>
<td>butylmagnesium chloride</td>
</tr>
<tr>
<td>butyloctylmagnesium</td>
</tr>
<tr>
<td>cadmium (pyrophoric)</td>
</tr>
<tr>
<td>cerium</td>
</tr>
<tr>
<td>chloro(1-methylethyl)magnesium</td>
</tr>
<tr>
<td>chlorodicyclohexylborane</td>
</tr>
<tr>
<td>chlorodi-iso-butylaluminium</td>
</tr>
<tr>
<td>chlorodiocetylaluminium</td>
</tr>
<tr>
<td>chloroethylmagnesium</td>
</tr>
<tr>
<td>chloropropylmagnesium</td>
</tr>
<tr>
<td>chromium oxide</td>
</tr>
<tr>
<td>cobalt</td>
</tr>
<tr>
<td>cyclohexylzinc bromide</td>
</tr>
<tr>
<td>diallylphenylphosphine</td>
</tr>
<tr>
<td>dibutylchlorophosphine</td>
</tr>
<tr>
<td>dibutylmagnesium</td>
</tr>
<tr>
<td>dibutylzinc</td>
</tr>
<tr>
<td>dichloro(di-iso-propylamino)borane</td>
</tr>
<tr>
<td>dichloro(phenyl)phosphine</td>
</tr>
<tr>
<td>dichlorodisilane</td>
</tr>
<tr>
<td>dichloroethylphosphine</td>
</tr>
<tr>
<td>dichloroiso-butylaluminium</td>
</tr>
<tr>
<td>dicyclohexyl(ethyl)phosphine</td>
</tr>
<tr>
<td>dicyclohexylphosphine</td>
</tr>
<tr>
<td>dicyclopentylphosphine</td>
</tr>
<tr>
<td>diethyl(ethyldimethylsilanolato)aluminium</td>
</tr>
<tr>
<td>diethylaluminium chloride</td>
</tr>
<tr>
<td>diethylaluminium iodide</td>
</tr>
<tr>
<td>diethylamidosilane</td>
</tr>
<tr>
<td>diethylgallium chloride</td>
</tr>
<tr>
<td>diethylhydridoaluminium</td>
</tr>
<tr>
<td>diethylmethoxyborane</td>
</tr>
<tr>
<td>diethylphosphine</td>
</tr>
<tr>
<td>diethylzinc</td>
</tr>
<tr>
<td>dihydridoaluminium borohydride tri-methylamine complex</td>
</tr>
<tr>
<td>di-iso-butylaluminium hydride</td>
</tr>
<tr>
<td>di-iso-propylphosphoramidous dichloride</td>
</tr>
<tr>
<td>dimethylaluminium chloride</td>
</tr>
<tr>
<td>dimethylaluminiumhydride</td>
</tr>
<tr>
<td>Pyrophoric Chemical</td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
</tr>
<tr>
<td>dimethylaluminum hydride</td>
</tr>
<tr>
<td>dimethylaluminum methoxide</td>
</tr>
<tr>
<td>dimethylzinc</td>
</tr>
<tr>
<td>di-n-butylzinc</td>
</tr>
<tr>
<td>di-n-octylaluminium iodide</td>
</tr>
<tr>
<td>diphenylphosphine</td>
</tr>
<tr>
<td>d-iso-dium tetracarbonylferrate(2-), compound with 1,4-dioxane (2:3)</td>
</tr>
<tr>
<td>di-t-butylphosphine</td>
</tr>
<tr>
<td>di-tert-butylmethylphosphine</td>
</tr>
<tr>
<td>di-tert-butylphenylphosphine</td>
</tr>
<tr>
<td>di-tert-butylphosphine</td>
</tr>
<tr>
<td>dysprosium</td>
</tr>
<tr>
<td>ethoxydiethylaluminium</td>
</tr>
<tr>
<td>ethylaluminium dichloride</td>
</tr>
<tr>
<td>ethylenebis[phenylphosphine]</td>
</tr>
<tr>
<td>ethyllithium</td>
</tr>
<tr>
<td>europium</td>
</tr>
<tr>
<td>hafnium</td>
</tr>
<tr>
<td>iso-butyllithium</td>
</tr>
<tr>
<td>iso-butyllithium; (2-methylpropyl)lithium</td>
</tr>
<tr>
<td>iso-propyllithium</td>
</tr>
<tr>
<td>linseed oil</td>
</tr>
<tr>
<td>lithium dicyclohexylamide</td>
</tr>
<tr>
<td>lithium diethylamide</td>
</tr>
<tr>
<td>lithium di-iso-propylamide</td>
</tr>
<tr>
<td>lithium dimethylamide</td>
</tr>
<tr>
<td>lithium pentamethylcyclopentadienide</td>
</tr>
<tr>
<td>lithium tetramethylcyclopentadienide</td>
</tr>
<tr>
<td>lithium tri-ethylhydroborate</td>
</tr>
<tr>
<td>lithium tri-sec-butylhydroborate</td>
</tr>
<tr>
<td>magnesium alkyls</td>
</tr>
<tr>
<td>magnesium distearate</td>
</tr>
<tr>
<td>magnesium powder (pyrophoric)</td>
</tr>
<tr>
<td>magnesium, powder or turnings</td>
</tr>
<tr>
<td>magnesiumanthracene tetrahydrofuran complex</td>
</tr>
<tr>
<td>methylaluminiumoxane</td>
</tr>
<tr>
<td>methylithium</td>
</tr>
<tr>
<td>methylmagnesium bromide</td>
</tr>
<tr>
<td>methylmagnesium chloride</td>
</tr>
<tr>
<td>methylphenylphosphine</td>
</tr>
<tr>
<td>methylphosphonous dichloride</td>
</tr>
<tr>
<td>n-hexyllithium</td>
</tr>
<tr>
<td>Pyrophoric Chemical</td>
</tr>
<tr>
<td>---------------------------------------------------------</td>
</tr>
<tr>
<td>n-hexyllithium</td>
</tr>
<tr>
<td>niobium</td>
</tr>
<tr>
<td>n-pentyl lithium</td>
</tr>
<tr>
<td>octylmagnesium bromide</td>
</tr>
<tr>
<td>palladium</td>
</tr>
<tr>
<td>phenyllithium</td>
</tr>
<tr>
<td>phenylphosphine</td>
</tr>
<tr>
<td>potassium o-pentyl dithiocarbonate</td>
</tr>
<tr>
<td>potassium tetramethylocyclopentadienide</td>
</tr>
<tr>
<td>praseodymium</td>
</tr>
<tr>
<td>r-alpine-borane₆⁺ alpine-borane</td>
</tr>
<tr>
<td>raney nickel</td>
</tr>
<tr>
<td>red phosphorus</td>
</tr>
<tr>
<td>rhodium</td>
</tr>
<tr>
<td>s-alpine-borane₆⁺ alpine-borane</td>
</tr>
<tr>
<td>sec-butyllithium</td>
</tr>
<tr>
<td>sec-butylmagnesium chloride</td>
</tr>
<tr>
<td>sodium dipropylamide</td>
</tr>
<tr>
<td>sodium methoxide</td>
</tr>
<tr>
<td>sodium tetraethylborate</td>
</tr>
<tr>
<td>sodium tetraethylborate-d₂₀</td>
</tr>
<tr>
<td>tert-butyl hypochlorite</td>
</tr>
<tr>
<td>tert-butylarsine</td>
</tr>
<tr>
<td>tert-butylidicyclohexylphosphine</td>
</tr>
<tr>
<td>tert-butylidiso-propylphosphine</td>
</tr>
<tr>
<td>tert-butyllithium</td>
</tr>
<tr>
<td>tert-butylmagnesium chloride</td>
</tr>
<tr>
<td>tert-butylphosphine</td>
</tr>
<tr>
<td>tertiarybutylphosphine</td>
</tr>
<tr>
<td>tetraethylammonium hydridotetraacarbonylferrate</td>
</tr>
<tr>
<td>tetraphenyldiphosphine</td>
</tr>
<tr>
<td>titanium</td>
</tr>
<tr>
<td>titanium dichloride</td>
</tr>
<tr>
<td>titanium tri-chloride</td>
</tr>
<tr>
<td>tri-alkylboranes</td>
</tr>
<tr>
<td>tri-butylaluminium</td>
</tr>
<tr>
<td>tri-butylborane</td>
</tr>
<tr>
<td>tri-butylphosphine</td>
</tr>
<tr>
<td>tri-chlorosilane</td>
</tr>
<tr>
<td>tri-chloro tri-methyldialuminium</td>
</tr>
<tr>
<td>tri-cyclopentylphosphine</td>
</tr>
<tr>
<td>tri-ethylaluminium</td>
</tr>
<tr>
<td>Pyrophoric Chemical</td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
</tr>
<tr>
<td>tri-ethylborane</td>
</tr>
<tr>
<td>tri-ethylaluminium tri-chloride</td>
</tr>
<tr>
<td>tri-ethylgallium</td>
</tr>
<tr>
<td>tri-ethylindium</td>
</tr>
<tr>
<td>tri-ethylphosphine</td>
</tr>
<tr>
<td>tri-ethylstibine</td>
</tr>
<tr>
<td>tri-hexylaluminium</td>
</tr>
<tr>
<td>tri-hydro(tri-ethylamine)aluminium</td>
</tr>
<tr>
<td>tri-hydro(tri-methylamine)aluminium</td>
</tr>
<tr>
<td>tri-iso-butylaluminium</td>
</tr>
<tr>
<td>tri-iso-propylgallium</td>
</tr>
<tr>
<td>tri-iso-propylphosphine</td>
</tr>
<tr>
<td>tri-methylaluminium</td>
</tr>
<tr>
<td>tri-methylbismuthine</td>
</tr>
<tr>
<td>tri-methylborane</td>
</tr>
<tr>
<td>tri-methylgallium</td>
</tr>
<tr>
<td>tri-methylindium</td>
</tr>
<tr>
<td>tri-methylstibine</td>
</tr>
<tr>
<td>tri-octylaluminium</td>
</tr>
<tr>
<td>tri-phenylaluminium</td>
</tr>
<tr>
<td>tri-propylaluminium</td>
</tr>
<tr>
<td>tris-(1,1-dimethylethyl)phosphine</td>
</tr>
<tr>
<td>tris-(2,4,4-trimethylpentyl)aluminium</td>
</tr>
<tr>
<td>tris-(2-methylpropyl)phosphine</td>
</tr>
<tr>
<td>tris-(acetonitrile)tricarbonylchromium</td>
</tr>
<tr>
<td>tris-(butylcyclopentadienyl)erbium(iii)</td>
</tr>
<tr>
<td>tris-(trimethylsily)silane</td>
</tr>
<tr>
<td>tris-(trimethylsilyl)phosphine</td>
</tr>
<tr>
<td>tris-(trimethylsilylmethyl)borane</td>
</tr>
<tr>
<td>tri-sec-butylborane</td>
</tr>
<tr>
<td>tri-silane</td>
</tr>
<tr>
<td>tri-tertiarybutylaluminium</td>
</tr>
<tr>
<td>tri-μ-carbonylhexacarbonyldiiron</td>
</tr>
<tr>
<td>white phosphorus</td>
</tr>
<tr>
<td>yellow phosphorus</td>
</tr>
<tr>
<td>ytterbium</td>
</tr>
<tr>
<td>yttrium</td>
</tr>
<tr>
<td>zinc powder - zinc dust (pyrophoric)</td>
</tr>
<tr>
<td>zinc powder - zinc dust (stabilised)</td>
</tr>
<tr>
<td>zirconium powder (pyrophoric)</td>
</tr>
</tbody>
</table>