

Pyrophoric Materials

Chemical Class Standard Operating Procedure

Berkeley EH&S

Pyrophoric Materials (PYR)

H250



Examples: tert-ButylLithium, sec-ButylLithium, n-ButylLithium, DiethylZinc, Organoaluminum compounds (as Et₃Al, Et₂AlCl, EtAlCl₂, Me₃Al), Raney Nickel catalyst, Palladium catalyst

WORKING ALONE¹ is PROHIBITED while handling PYR materials

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

Areas with blue text indicate that information must be provided or modified by researcher prior to the SOP approval.

This SOP is not a substitute for hands-on training.

Print a copy and insert into your laboratory SOP binder.

Department:	Chemistry
Date SOP was written:	Monday, October 24, 2016
Date SOP was approved by PI/lab supervisor:	[]
Principal Investigator:	Name: R. Sarpong Signature:
Internal Lab Safety Coordinator or Lab Manager:	Name: Melissa Hardy/Justin Jurczyk Lab Phone: 406-696-1225/412-728-1952 Office Phone: 510-642-6312
Emergency Contact:	Name: Melissa Hardy/Justin Jurczyk Lab Phone: 406-696-1225/412-728-1952
Location(s) covered by this SOP:	Latimer Hall 831,832,834,836,837,838,839,842,844,847,849

1. Purpose

This SOP covers the precautions and safe handling procedures for the use of Pyrophoric Materials (PYR). For a list of PYR covered by this SOP and their use(s), see the "List of Chemicals". Procedures described in Section 12 apply to all materials covered in this SOP.

¹When included in a standard operating procedure, for any duration of time, a person is <u>working alone</u> when performing a task in a laboratory and they cannot be seen or heard by other workers, and when assistance is not readily available. In this context, a task is any portion or section of an operation or job, and does not refer to a job in its entirety.



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 <u>ucbcho@berkeley.edu</u>.

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} \leq Rate_{GAS}.

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

As most pyrophorics react violently with water, do not allow pyrophoric materials to come in contact with water (except during the quenching process). 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, must be considered together and procedures for safe handling must 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 are designated by the following H code:

H250 Catches fire spontaneously if expose to air

It is the Principal Investigator's responsibility to ensure activity-specific laboratory procedures and/or processes are taken into account when using this Chemical Class SOP.

Please, review the SDS of any chemical before use (see Section 11 – SDS Location)

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.
- 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.
- Remove any flammables (squirt bottles containing solvents, oil baths) and combustibles (Kimwipes, paper towels) from the work area.
- Laboratories and rooms where Pyrophorics are used must have general room ventilation that is negative pressure with respect to the corridors and external environment. The laboratory/room door must be kept closed at all times.



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 must be worn.

Skin Protection

- A. Wear non-synthetic clothing under lab coat.
- B. Flame-resistant lab coat (Nomex IIIA, NFPA 2112) must be worn when working with pyrophorics.
- C. A combination of fire resistant (FR) liners, covered with a pair of chemical-resistant disposable gloves (e.g. nitrile gloves or those specified in the specific SDS), must be worn AT ALL TIMES. The following products are Approved FR Liners: Ansell Kevlar[®] Goldknit[®] Lightweight 70-200 and Hanz Nomex[®] Flame Resistant Utility Liner Gloves.
- D. Long pants, closed-toe/closed-heel shoes, covered legs, and ankles.

6. First Aid Procedures and Medical Emergencies

In the event of an injury, notify your supervisor immediately and EH&S within 8 hours.

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 are not 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.



If inhaled Move into fresh air.

7. Special Handling, Storage, and Disposal 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.

Handling Pyrophoric Liquids

- There are two basic techniques to transfer pyrophoric liquids: the syringe and the cannula needle (over-pressure transfer). The syringe must only be used for small quantities (less than 20 mL). To conveniently transfer 20 mL or more of reagent at once, the cannula technique must be used.
- A glovebox or a Schlenk line in a fume hood with inert gas flow will be necessary. The sure-seal cap system provides a convenient method for storing and dispensing air-sensitive reagents.
- Pyrophoric solids must be transferred under an inert atmosphere in a glove box.
- Pyrophoric gases must be handled in compliance with the California Fire Code, Chapter 41.
- Eliminate or substitute for a less hazardous material when possible.
- Design your experiment to use the least amount of material possible to achieve the desired result.
- Do not exceed the scale of procedures specified in Protocol/Procedure section without approval of the PI.
- Verify your experimental set-up and procedure prior to use.
- Know the location of the nearest eyewash, safety shower and fire extinguisher before beginning work.
- Upon leaving the work area, remove any personal protective equipment worn and wash hands.
- At the end of each project, thoroughly decontaminate the work area according to the material being handled.

Storage of Pyrophoric Materials

- Keep the material under inert atmosphere when not in use.
- Store minimal amounts of pyrophoric chemicals. 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.
- If pyrophoric materials are received in specially designed shipping, storage or dispensing container (such as the sure-seal cap 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. Use corrosion and shatter-resistant containers.
- Pyrophoric chemicals that require refrigeration must be stored in a flammable rated refrigerator. Materials should be in a clearly labeled secondary container on the top shelf of the refrigerator. **Do not stored materials in the fridge door.**



- 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.

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 of Pyrophoric Materials". As an alternative to quenching, remember that pyrophoric chemicals can be disposed of as hazardous waste (contact EH&S for guidance on disposal).
- Waste materials generated must be treated as a hazardous waste.
- The empty container must be rinsed three times with a COMPATIBLE solvent; leave it open in the back of the hood overnight. The rinse solvent must be transferred in and out of the container under an inert atmosphere using the syringe or cannula technique. Solvent rinses and water rinse must be disposed of as hazardous waste.
- As an alternative, unrinsed empty containers can be disposed of through EH&S as hazardous waste. The unrinsed empty containers must be capped.
- Do not mix with incompatible waste streams.
- Decontamination of containers in order to use them for other purposes is not permitted.

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, extinguish the fire with an appropriate fire extinguisher. Use only dry chemical fire extinguishers (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.

<u>Be AWARE</u>: Small flames at the tip of the needles can be produced – 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 Section 12 - Protocol/Procedure.

- Wearing proper PPE, laboratory work surfaces must be cleaned at the conclusion of each procedure and at the end of each work day.
- Decontaminate 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.

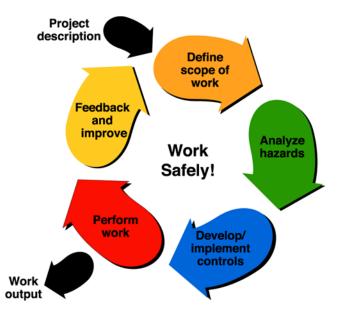
Dispose of Waste

- Dispose of regularly generated chemical waste within 6 months.
- Contact EH&S at 642-3073 if you need assistance.

11. Safety Data Sheet (SDS) Location

SDS can be accessed online at http://ucsds.com





Before starting any work, ask yourself:

- 1- What will I be doing?
- 2- Do I know what the hazards are?
- 3- Do I have everything I need to do the job safely?
- 4- Am I doing the job safely?
- 5- What can we do better?





12. Protocol/Procedure for: Pyrophoric Chemicals

Section 12 must be customized to your specific needs. Delete any procedure that does not apply to your laboratory.

Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Special Precautions for this Procedure
1. Transferring of liquid pyrophoric chemicals.	Up to 150 mL or less of liquid pyrophor material as supplied in the reagent bottle. The reaction vessel can hold more than 150ml of total solution but no more than 150ml of liquid pyrophor. Obtain PI approval if higher scale is necessary.	Conduct in a clean and properly operating fume hood with the sash as low as possible using the Schlenck techniques, or an inert atmosphere glove box.	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. Hand Protection: Confirm compatibility of glove material with chemical being used. Gloves must be inspected prior to use. Wash and dry hands after use. <u>General guidance :</u> For <u>indirect contact</u> (closed- system procedures such as transfers via syringe or cannula) AND <u>direct contact</u> (open system procedures such as spill handling, wiping of residual pyrophorics) <u>with pyrophoric</u> <u>material</u> - a combination of fire resistant (FR) liners, covered with a pair of chemical-resistant disposable gloves (e.g. nitrile gloves or those specified in the specific SDS)), must be worn AT ALL TIMES. The following	General Considerations²:The reagent can be dispensed using a syringe for smallquantities (<20 mL) or double-tipped needle - cannula

² Aldrich Technical Bulletin, AL-134 Handling Air-Sensitive Reagents

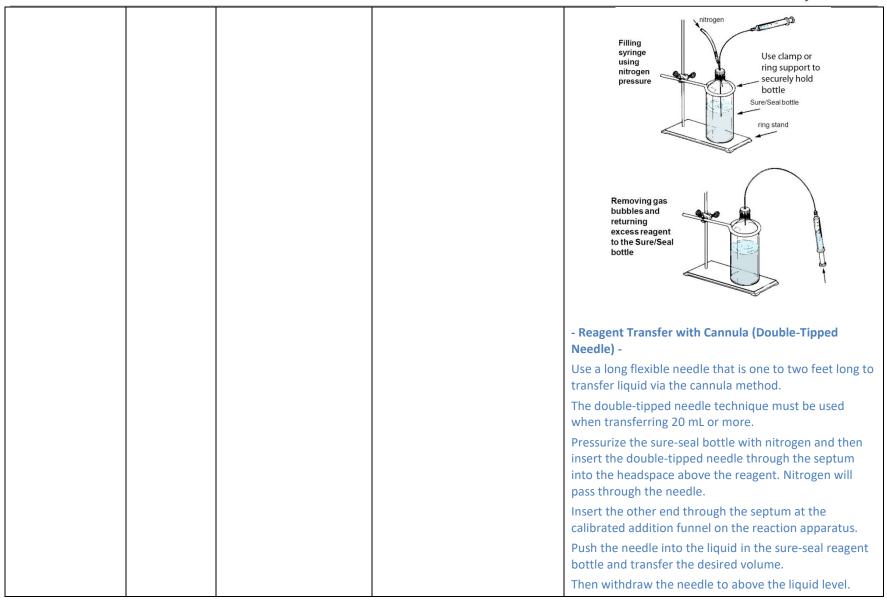


products are Approved FR Liners: Ansell Kevlar® Goldknit Lightweight 70-200 and Hanz Nomex® Flame Resistant Utility Liner Gloves. Clothing: Wear Nomex IIIA (NFPA 2112) lab coat; wear non synthetic clothing under lab coat; full length pants or equivalent; and close-toed and close-heeled shoes.	Clamp/secure the receiving vessel too.
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Pyrophoric Materials

Chemical Class Standard Operating Procedure





	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.
	Double- tipped needle transfer of liquid reagent

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		Double-tipped needle cylinder to bubbler flat-cut end of needle
Notes	Any deviation from this SOP requires app	roval from PI.



Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Precautions
2. Use of H ₂ for a hydrogenation reaction with a catalyst (Pd, Ni, Rh, Pt, Ir, Ru)	Up to 10g or less of catalyst as supplied in the reagent bottle. The reaction vessel can hold more than 10g of total solution but no more than 10g of catalyst. Obtain PI approval if higher scale is necessary.	Conduct all operations in clean and properly operating designated fume hood with sash as low as possible. Or in an inert atmosphere glovebox. Blast shields must be used if the reaction has the potential to generate large quantities of gases or is strongly exothermic. Open flames and possible sparking and static electricity must be avoided	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. Hand Protection: Confirm compatibility of glove material with chemical being used. Gloves must be inspected prior to use. Wash and dry hands after use. <u>General guidance :</u> For <u>indirect contact</u> (closed- system procedures such as transfers via syringe or cannula) AND <u>direct contact</u> (open system procedures such as spill handling, wiping of residual pyrophorics) <u>with</u> <u>pyrophoric material - a</u> combination of fire resistant (FR) liners, covered with a pair of chemical-resistant disposable gloves (e.g. nitrile gloves or those specified in the specific SDS)), must be worn AT ALL TIMES. The following products are Approved FR	 1) For use at 1 atm pressure (i.e H₂ balloon): -First, Flush out air from the reaction vessel using a stream of inert gas. Attach the balloon of gas and bubble until saturated. When reaction is judged complete, or if more catalyst is needed, removed the balloon and reflush the system with inert gas before opening to the atmosphere. Deactivate the catalyst by flushing inert gas for several minutes. Filter out the catalyst through Celite. BE CAREFUL – DO NOT DRY OUT THE CATALYST!! Have plenty of solvent on hand so that you can add more to wash the filter cake before it starts to dry out. Have also plenty of <u>water</u> on hand. When you have finished washing your filter cake (leaving some solvent so it doesn't dry out), turn off the vacuum, and place the residue in the back of the fume hood for several hours before removing as solid waste. OR BE CAREFUL – DO NOT DRY OUT THE CATALYST!! Have also plenty of <u>water</u> on hand. When you have finished wash the filter cake before it starts to dry out. Have also plenty of solvent on hand so that you can add more to wash the filter cake (leaving some solvent so it doesn't dry out), turn off the vacuum, and place the residue in the back of the fume hood for several hours before removing as solid waste. OR



		Liners: Ansell Kevlar [®] Goldknit [®] Lightweight 70-200 and Hanz Nomex [®] Flame Resistant Utility Liner Gloves. Clothing: Wear Nomex IIIA (NFPA 2112) lab coat; wear non-synthetic clothing under lab coat; full length pants or equivalent; and close-toed and close-heeled shoes.	2) For pressurized reactions: Be sure that the delivery pressure of the FG is compatible with the reaction apparatus. Use a compatible gas regulator. Insure that the gas being passed through the reactor is properly vented into the fume hood and that any vented gases do not constitute a potential fire or explosion threat to coworkers or nearby populations. Take extreme care not to over pressurize glass reactors.
Notes	Any deviation from this SOP requires appr	roval from PI.	



Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Precautions
3. A solid PYR material is used in the lab as a reagent in a reaction. Examples are metal carbonyls, metal powders, non-metal hydrides; metal alloys, non-metal sulfides.	Up to 10g or less of solid PYR as supplied in the reagent bottle. The reaction vessel can hold more than 10g of total solution but no more than 10g of PYR solid. Obtain PI approval if higher scale is necessary.	Conduct in a clean and properly operating fume hood with the sash as low as possible using the Schlenck 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.	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. Hand Protection: Confirm compatibility of glove material with chemical being used. Gloves must be inspected prior to use. Wash and dry hands after use. General guidance : For indirect contact (closed- system procedures such as transfers via syringe or cannula) AND direct contact (open system procedures such as spill handling, wiping of residual pyrophorics) with pyrophoric material - a combination of fire resistant (FR) liners, covered with a pair of chemical-resistant disposable gloves (e.g. nitrile gloves or those specified in the specific SDS)), must be worn AT ALL TIMES. The following products are Approved FR	General Considerations:Keep the material under inert atmosphere when not in use. Ideally, store the PYR solid in a glovebox. If not possible, make sure to keep the PYR in a sealed vial under a cloud of inert gas.Care must be taken to prevent a dangerous exothermic reaction upon addition to the reaction vessel. Portionwise addition is necessary to prevent uncontrollable reaction.Pressure can be built up in reactions utilizing PYR solids. Never use in a closed system.Ideally, weigh out the PYR material directly into your reaction vessel.If not possible, follow one of the two following options: - Addition to the reaction vessel as a SOLID - Weigh out the appropriate mass into a clean and dry vessel, and directly transfer the content to the reaction vessel.Be careful - Add the PYR in small portions as it can lead to an exothermic reaction.Be careful - Keep the reaction vessel under a low inert gas flow as it can push out some of your PYR solid.Be careful to minimize dust accumulation. Wearing proper PPE, clean balance area after weighting the material. Dust residue on a vial or weighing paper should be appropriately quenched prior to disposal into waste Addition to the reaction vessel as a SOLUTION -



		Liners: Ansell Kevlar [®] Goldknit [®] Lightweight 70-200 and Hanz Nomex [®] Flame Resistant Utility Liner Gloves. Clothing: Wear Nomex IIIA (NFPA 2112) lab coat; wear non-synthetic clothing under lab coat; full length pants or equivalent; and close-toed and close-heeled shoes.	 Weigh out the appropriate mass into a clean and dry vessel. Add <u>slowly</u> the desired amount of dry solvent under inert atmosphere via syringe (<20 mL) or double-tipped needle - cannula (≥20 mL). Under inert atmosphere, transfer slowly the PYR solution into the reaction vessel via syringe (<20 mL) or double-tipped needle - cannula (≥20 mL). For details on how to transfer the solution with syringe or cannula, see Procedure 1 See Quenching of Pyrophoric Materials SOP for disposal of pyrophoric material.
Notes	Any deviation from this SOP requires app	roval from PI.	





Chemical Class Standard Operating Procedure

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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 SDS provided by the manufacturer.

I have read and understand the content of this SOP:

Name	Signature	Identifier	Date



Berkeley EH&S

List of Chemicals

Chemical(s)	Chemical(s)	Chemical(s)
alane n,n-dimethylethylamine complex	chlorodicyclohexylborane	DIBAL-H
DIBAL-H, 25% in toluene	diethylaluminum chloride	diethylmethoxyborane
diisobutylaluminium hydride, 0.1 mol/l in Toluene	diisobutylaluminum chloride	diisopropylphosphoramidous dichloride
dimethylaluminum chloride	dimethylboron bromide	dimethylzinc
diphenylphosphine	ethylaluminum dichloride	l-selectride
l-selectride, 1M in THF	methyllithium	n-butyllithium
palladium (i) tri-tert-butylphosphine bromide	r-alpine-borane	s-alpine-borane
sec-butyllithium	sec-butyllithium, 1.3 M in hexanes	tert-butyllithium
tert-butyllithium, 0.155 mol/l in pentane	titanium trichloride	tributylborane
tributylphosphine	trichlorosilane	triethylaluminum
triethylborane	trimethylaluminum	trimethylaluminum, 0.2 mol/l in toluene