Water Reactive Materials (WR)

H260 H261

Examples: lithium, sodium, cesium, lithium aluminum hydride, calcium hydride, potassium hydride, Grignard reagents

Note: Before handling any water reactive material, researchers must also read and sign the "Quenching of Water Reactive 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 Water Reactive Materials (WR).

For a list of WR 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.

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. Water Reactive Materials Information

Water reactive materials are chemicals that can react violently with water to produce a flammable and/or toxic gas and heat. This classification for "Water Reactive" follows the definitions of Global Harmonization System (GHS) of Classification and Labeling of Chemicals. The risks associated with a specific water reactive chemical depend on its reactivity and the nature of the gaseous product (flammable, toxic, or both). Prior to working with a water reactive chemical, identify the gas to be formed when exposed to water, learn the risks associated with this gas, and develop plans to minimize the risks of handling that material. "Water" can include moisture in the atmosphere, therefore water reactive are usually used under air-free conditions.

3. Potential Hazards/Toxicity

Water reactive substances are **dangerous when wet** because they can undergo a chemical reaction with water. This reaction may release a gas that can be flammable and/or toxic. In addition, the heat generated when water contacts such materials is often enough to spontaneously combust or explode.
When quenching WR materials, the hazards of the mixture, the WR chemical and the solvent, must be considered together and procedures for safe quenching must reflect the hazard properties of both solvent and solute.
As defined by the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), WR materials are defined as "**substances and mixtures which, in contact with water, emit flammable gases**" and are designated by one or more of the following H codes:

H260 In contact with water releases flammable gases which may ignite spontaneously
H261 In contact with water releases flammable gases

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 that are required when quenching WR chemicals:

- When using liquid WR, 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.
- 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.
- Keep liquid WR under inert atmosphere when not in use.
- Remove any flammables (squirt bottles, solvents, oil bath) 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 must be worn.

Skin Protection

A. Flame-resistant lab coat (Nomex IIIA, NFPA 2112) must be worn when working with WR
B. Gloves are required when handling hazardous chemicals.
    - Refer to specific chemical SDS for information on glove selection.
    - For additional information on glove selection, go to: http://ehs.berkeley.edu/hs/63-laboratory-safety/94-glove-selection-and-usage.html
C. 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.

If inhaled

Move into fresh air.

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.

7. Special Handling, Storage, and Disposal Requirements

WR chemicals can be handled and stored safely as long as all exposure to moisture or other incompatible chemicals is minimized. Never leave a container with a residue of a WR material open to the atmosphere.

Lab-specific information on handling and storage may be included in Section 12 - Protocol/Procedure section.

Precautions for safe handling

- There are two basic techniques to transfer liquid WR: 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, the cannula technique must be used.
- Only use if the area is properly equipped with a properly operating eye wash/safety shower within ten seconds of travel.
- Work away from any water sources or where there is the potential of water splash.
- 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.

Conditions for safe storage

- Store liquid WR under dry inert gas (Nitrogen or Argon).
- Store in a location separated from bases, oxidizing and other incompatible materials.
- Never allow product to get in contact with water or water-based compounds during storage. Keep in a dry place (such as a desiccator or a dry box or glove box) free of moisture/humidity and away from sources of heat.
- Do not leave the container near a lab sink, emergency eyewash, or safety shower or on the bench top - even momentarily.
- Ensure that a sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.

Disposal

- Any unused or unwanted water reactive materials must be destroyed by following the Quenching of Water Reactive Chemicals SOP. If you have large quantities of unreacted water reactive reagent material contact EH&S for guidance on disposal options.
- 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. 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

Water-Reactive 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.
- 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.

Water-Reactive Fire Response

- Call **911** (from a cell phone: **510-642-3333**) 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. Use only dry chemical fire extinguishers (classes ABC or D).
- 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 WR 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.

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

-Take Ownership of Your Safety-

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 - Water Reactive Materials

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. Removal of oil from Li/Na/K prior to use in reactions.	Up to 40 g as supplied in the reagent bottle. Remember to obtain PI approval if higher scale is necessary.	All reactions using these materials must be performed in a properly operating fume hood with the sash as low as possible. Or in an inert atmosphere glovebox.	**Eye Protection:** Wear tight-fitting 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. General guidance (unless otherwise specified in the specific SDS): Nitrile gloves must be used to prevent incidental contact. For spill handling or for potential contact with larger quantities, use double nitrile or heavier gauge nitrile or neoprene gloves. Gloves must be inspected prior to use. Wash and dry hands after use. **Clothing:** Wear Nomex IIIA (NFPA 2112) lab coat; full length pants or equivalent; and close-toed and close-heeled shoes.	General Procedure: Pieces (~5 g) are transferred to a beaker containing hexanes that covers the metal fully. Pieces are then washed with more hexanes to remove the oil and transferred to a second beaker containing more hexanes. The pieces are flattened in the beaker containing hexanes then removed, washed with hexanes and transferred to the reaction vessel containing solvent. For quenching procedure, see "Quenching of Water Reactive Materials" SOP.
Notes	Any deviation from this SOP requires approval from PI.			

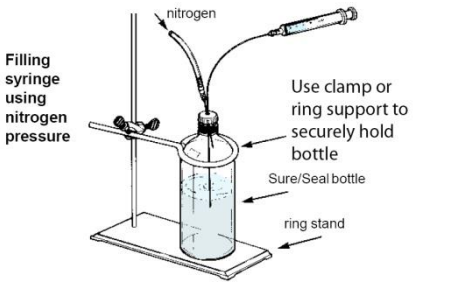
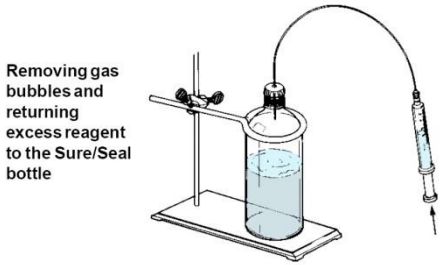
Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Special Precautions for this Procedure
2. Sodium Hydride, Calcium Hydride, and Lithium Hydride are used as bases/ reducers in organic chemical reactions.	Up to 10 g as supplied in the reagent bottle. Remember to obtain PI approval if higher scale is necessary.	All reactions using these materials must be performed in a properly operating fume hood with the sash as low as possible. Or in an inert atmosphere glovebox. The hydrogen gas evolved here is very flammable, if an ignition source is found, but is not spontaneously flammable.	**Eye Protection:** Wear tight-fitting 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. General guidance (unless otherwise specified in the specific SDS): Nitrile gloves must be used to prevent incidental contact. For spill handling or for potential contact with larger quantities, use double nitrile or heavier gauge nitrile or neoprene gloves. Gloves must be inspected prior to use. Wash and dry hands after use. **Clothing:** Wear Nomex IIIA (NFPA 2112) lab coat; full length pants or equivalent; and close-toed and close-heeled shoes.	General Procedure: Add hydride reagents to reactions in a slow and controlled manner. Monitor reactions for the formation of H_2 gas. Avoid vigorous or exothermic reactions and the buildup of pressure within a reaction vessel. Cool if necessary. Adequate ventilation (pressure bubbler on Schlenk manifold or an equilibrating balloon) has to be used to prevent dangerous over pressurization. For quenching procedure, see “Quenching of Water Reactive Materials” SOP.
Notes	Any deviation from this SOP requires approval from PI.			

Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Special Precautions for this Procedure
3. Using Water Reactive (WR) as reactant. Procedure includes WR that liberate toxic but not flammable product(s) when in contact with water. These are mostly halides and acid halides of organics, metals, and non-metals.	Up to 10 g as supplied in the reagent bottle. Remember to obtain PI approval if higher scale is necessary.	All reactions using these materials must be performed in a properly operating fume hood with the sash as low as possible. Or in an inert atmosphere glovebox. For halide-based WR is a good practice to have a scrubber at the exit point of the vessel to absorb any toxic gases, such as HCl, that could formed. For hydrides and complex hydrides, the hydrogen gas evolved during the reaction is very flammable, if an ignition source is found, but is not spontaneously flammable.	**Eye Protection:** Wear tight-fitting 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. General guidance (unless otherwise specified in the specific SDS): Nitrile gloves must be used to prevent incidental contact. For spill handling or for potential contact with larger quantities, use double nitrile or heavier gauge nitrile or neoprene gloves. Gloves must be inspected prior to use. Wash and dry hands after use. **Clothing:** Wear Nomex IIIA (NFPA 2112) lab coat; full length pants or equivalent; and close-toed and close-heeled shoes.	General Procedure: Add these WRC reagents to reactions in a slow and controlled manner. Monitor reactions for the formation of gas (such as HCl), which could be indicative of water intrusion. Avoid vigorous or exothermic reactions and the buildup of pressure within a reaction vessel. Cool if necessary. Adequate ventilation (pressure bubbler on Schlenk manifold or an equilibrating balloon) has to be used to prevent dangerous over pressurization. For quenching procedure, see “Quenching of Water reactive Materials” SOP.
Notes	Any deviation from this SOP requires approval from PI.			

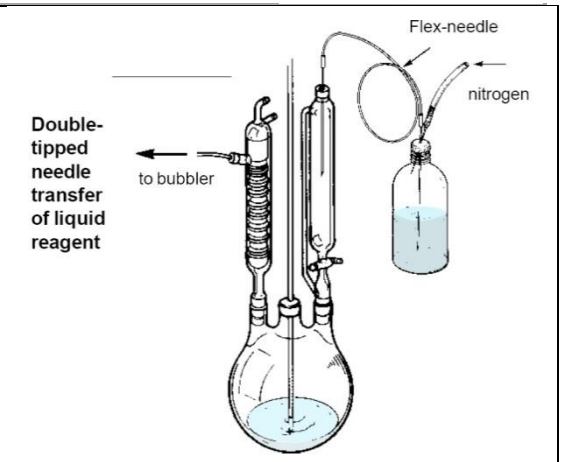
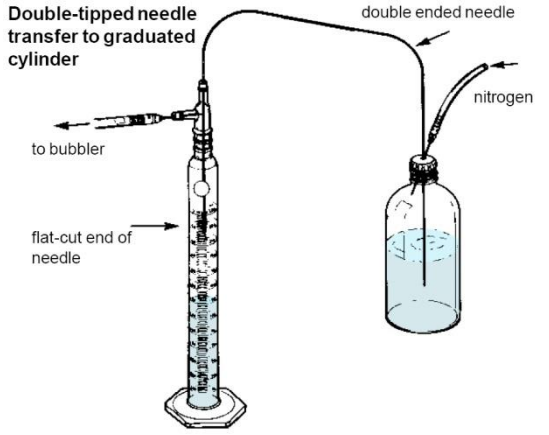
Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Special Precautions for this Procedure
4. Transferring of liquid Water Reactive (WR).	Up to 1 L as supplied in the reagent bottle. The reaction vessel can hold more than 1 L of total solution but no more than 1 L of liquid WR. Remember to obtain PI approval if higher scale is necessary.	Conduct in a clean fume hood with the sash as low as possible using the Schlenk techniques, or an inert atmosphere glove box.	**Eye Protection:** Wear tight-fitting 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. General guidance (unless otherwise specified in the specific SDS): Nitrile gloves must be used to prevent incidental contact. For spill handling or for potential contact with larger quantities, use double nitrile or heavier gauge nitrile or neoprene gloves. Gloves must be inspected prior to use. Wash and dry hands after use. **Clothing:** Wear Nomex IIIA (NFPA 2112) lab coat; full length pants or equivalent; and close-toed and close-heeled shoes.	General Considerations[1]: The reagent can be dispensed using a syringe for small quantities (<20 mL) or double-tipped needle - cannula method for larger quantities (≥20 mL). Insert the needle (no larger than 16 gauge) through the hole in the metal cap. Use plastic syringes and needles only once. If used more than 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 water-reactive 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 moisture sensitive chemicals must be tightly controlled. Draw out water reactive 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 a sure-seal cap or equivalent. Use a long flexible needle that is one to two feet

[1] Aldrich Technical Bulletin, AL-134 Handling Air-Sensitive Reagents

				long to transfer liquid via the cannula method. Clamp the reagent bottle to prevent it from moving. Clamp/secure the receiving vessel too. **- 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. Gently pull back on the syringe to slowly fill the syringe with the desired amount of reagent. 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 must be used when transferring 20 mL or more at once. 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 WR designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with the substance(s), 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 SDS provided by the manufacturer.

I have read and understand the content of this SOP:

Name	Signature	Identification	Date

List of Chemicals

Chemical(s)	Chemical(s)	Chemical(s) – Use(s) :
1-methyl-2-propenylmagnesium chloride	1-propenylmagnesium bromide, 0.05 mol/l in THF	1-propynylmagnesium bromide, 0.05 mol/l in THF
4,4,5,5-tetramethyl-1,3,2-dioxaborolane	alane n,n-dimethylethylamine complex	allylmagnesium bromide
bis(cyclopentadienyl)zirconium(iv) chloride hydride	borane dimethylsulfide complex	borane tetrahydrofuran complex
calcium hydride	chloro(pentamethylcyclopentadienyl)(cyclooctadiene)ruthenium(ii)	chlorodiethylisopropylsilane
chlorodimethylsilane	DIBAL-H	DIBAL-H, 25% in toluene
diethylaluminum chloride	diethylzinc	diisobutylaluminium hydride, 0.1 mol/l in Toluene
diisobutylaluminum chloride	dimethylaluminum chloride	dimethylzinc
ethylaluminum dichloride	ethylmagnesium bromide	ethylmagnesium bromide, 0 in THF
ethynylmagnesium bromide	isobutylmagnesium chloride	isopropylmagnesium chloride
lawesson reagent	lithium	lithium acetylide ethylenediamine complex
lithium aluminum deuteride	lithium aluminum hydride	lithium amide
lithium diisobutyl-tert-butoxyaluminum hydride	lithium hydride	lithium tetrahydroborate
lithium triethylborohydride	lithium tri-tert-butoxyaluminum hydride	lithium, 98% in mineral oil
l-selectride	l-selectride, 1M in THF	magnesium
manganese	methylaluminum dichloride	methyllithium
methylmagnesium bromide	methylmagnesium chloride, 0.3 mol/l in THF	n,n-diethylaniline borane complex
NaK Silica Gel (K2Na) Stage 1	n-butyllithium	n-butylmagnesium chloride
palladium (i) tri-tert-butylphosphine bromide	pentylmagnesium bromide, 0.2 mol/l in Et2O	phenylsilane
phosphorus pentasulfide	potassium	potassium hydride
potassium tert-butoxide	sec-butyllithium	sec-butyllithium, 1.3 M in hexanes
sodium	sodium amide	sodium bis(2-methoxyethoxy)aluminiumhydride
sodium borodeuteride	sodium borohydride	sodium cyclopentadienide
sodium hydride	sodium mercury amalgam	sodium triacetoxyborohydride
tert-butyllithium	tert-butyllithium, 0.155 mol/l in pentane	tetrafluoroboric acid diethyl ether complex
tetramethylammonium triacetoxyborohydride	titanium tetrakis(dimethylammonium)	triethylaluminum
trimethylaluminum	trimethylaluminum, 0.2 mol/l in toluene	vinylmagnesium bromide
