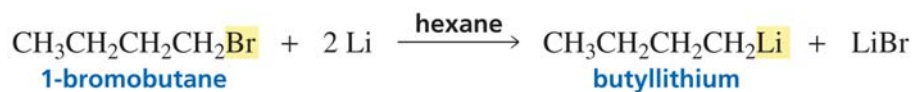


# Organolithium reagents



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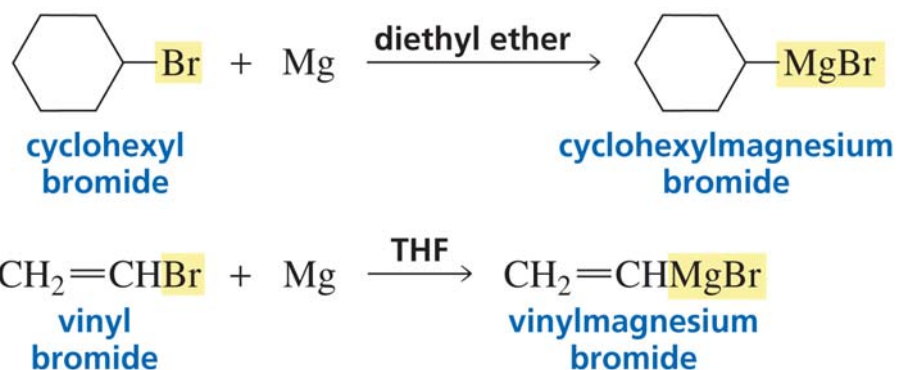
Organolithium compounds are very strong bases; they are NOT compatible with proton acids or carbonyl groups or good leaving groups!

But they DO add to epoxides and carbonyls, just like Grignards.  
Furthermore, they function in totally nonpolar solvents.

Organolithium compounds are used to make Gilman (diorganocopper) reagents.

Organolithium compounds are prepared by adding lithium to an alkyl halide in a nonpolar solvent such as hexane.

## Grignard reagents



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Grignard reagents are strong bases, and are not compatible with good leaving groups or proton acids. However, they add to epoxides and carbonyl groups, and can be used to make other organometallic reagents by reacting with metal-halogen bonds.

Organomagnesium compounds are prepared by adding an alkyl halide to magnesium shavings in diethyl ether or tetrahydrofuran.

## Other organometallics



$\text{CH}_3\text{CH}_2\text{MgBr}$   
ethylmagnesium  
bromide

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$   
butyllithium

$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Cd}$   
dipropylcadmium

$(\text{CH}_3\text{CH}_2)_4\text{Pb}$   
tetraethyllead

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Organometallic compounds are named by naming the alkyl group, followed by the name of the metal.

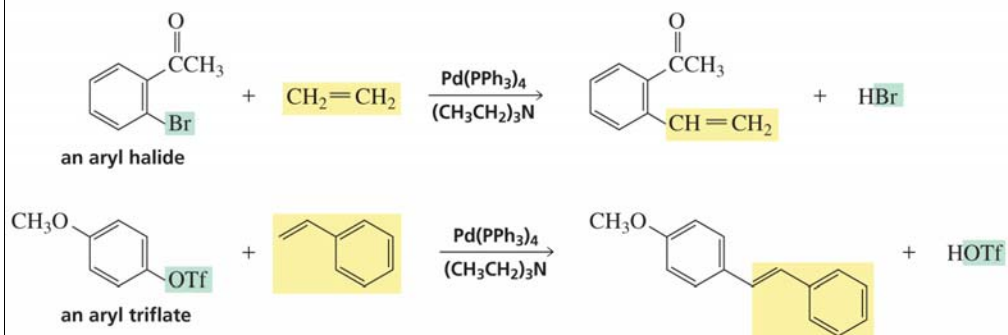
Organometallic compounds are often prepared by adding a Grignard or organolithium compound to a metal halide.

Gilman reagents are prepared from organolithium compounds, and thus have all the limitations of organolithium compounds (e.g. no proton acids, no carbonyls). However, they are very mild reagents. While they are sensitive to proton acids, they will couple to ANY carbon-halogen bond – including carbonyl halides – so long as the halogen is not fluorine.

# Palladium coupling reactions



## Heck reaction

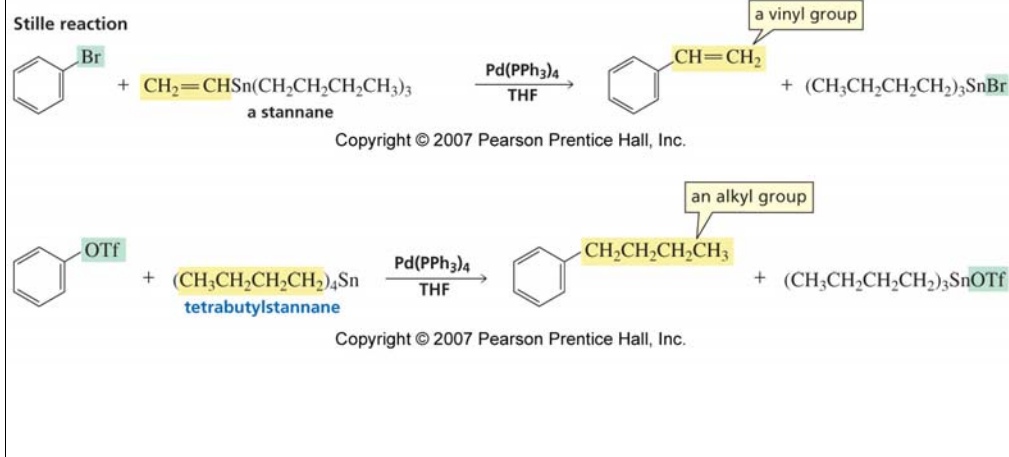


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The Heck reaction couples an aryl, benzyl, or vinyl halide or triflate with an alkene in a basic solution, in the presence of organometallic reagent consisting of a transition metal.

Notice that the vinyl C-H bond is replaced with the aryl, benzyl or vinyl group from the halide or triflate.

# Palladium coupling reactions



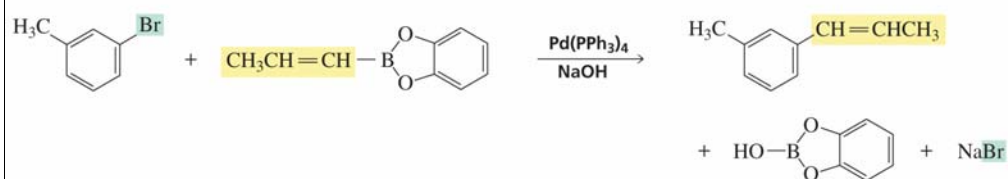
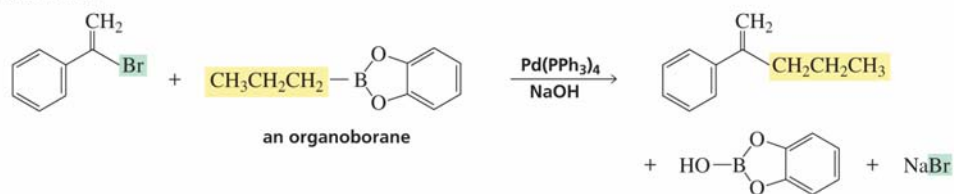
Stille reaction.

The Stille reaction couples an aryl, benzyl, or vinyl halide or triflate with a stannane, in the presence of organometallic reagent consisting of a transition metal. The stannane is made from a tin chloride and the corresponding organolithium compound or organomagnesium halide. This reaction is quite versatile.

# Palladium coupling reactions



## Suzuki reaction



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Suzuki reaction.

The Suzuki reaction couples an aryl, benzyl, or vinyl halide with an organoborane in a basic solution, in the presence of organometallic reagent consisting of a transition metal.

The organoborane is made from the corresponding B-H compound and either an alkene or an alkyne. The B-H bond adds syn to the alkene or alkyne, so that stereochemistry of the alkyl or vinyl group is controlled.