

Organometallic Chemistry and Homogeneous Catalysis

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Lecture N5

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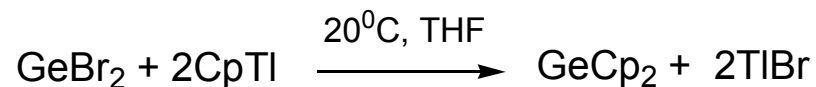
Main group organometallic chemistry

Group IV: Ge, Sn, Pb

Organogermanium compounds: GeR_4 , XGeR_3 , X_2GeR_2 , ... etc.

-Covalent character of M-C bond

-Oxidation state **+4** for most compounds
Exception – Cp_2Ge (oxidation state +2):



- Rare and expensive

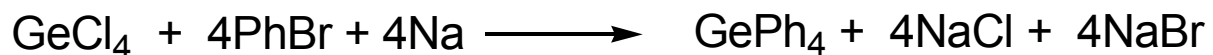
Synthesis:



1) Direct synthesis from copper-germanium alloy and organic halides:



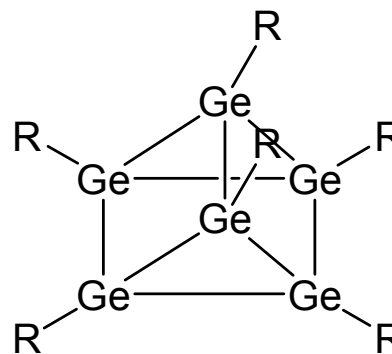
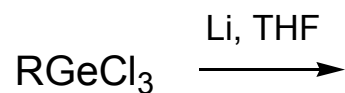
2) Coupling reactions of germanium halides and organic halides:



Structure:

In most cases monomeric, tetrahedral structures (like organic compounds).

In some cases oligomers also can be obtained:



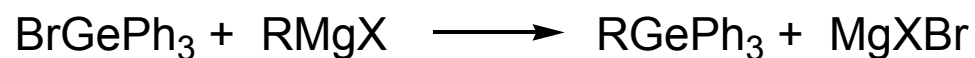
Reactivity:



Tetraorganogermanes are rather inert chemically. They react only with very strong oxidizing agents:

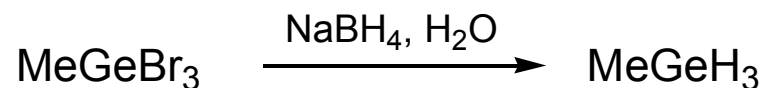
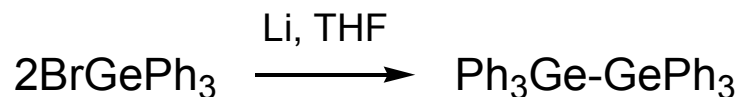


The product is employed in synthesis of other tetraorganogermanes:



Organohalogermanes are more reactive and more sensitive to water

They can react with different reducing agents:



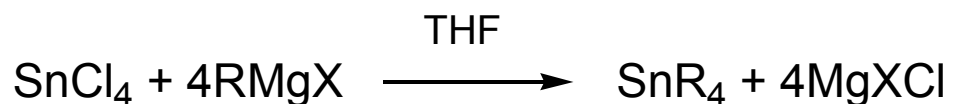
Organotin compounds: SnR_4 , XSnR_3 , X_2SnR_2 , ... etc.

- Covalent character of M-C bond
- Large variety of accessible coordination numbers and oxidation states
- Application of ^{119}Sn -NMR for the structure characterization

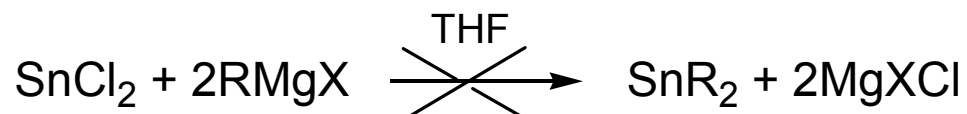
Synthesis:

1) Using of Mg-organic compounds:

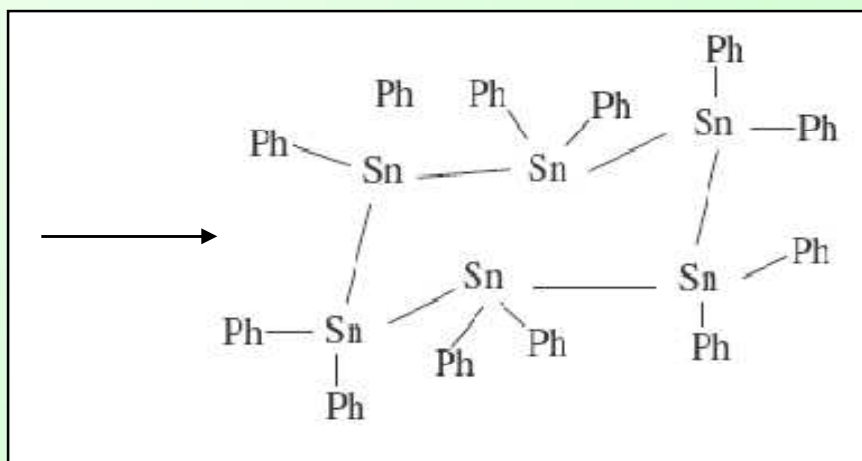
a) Sn(IV):



b) Sn(II): usually do not get positive result



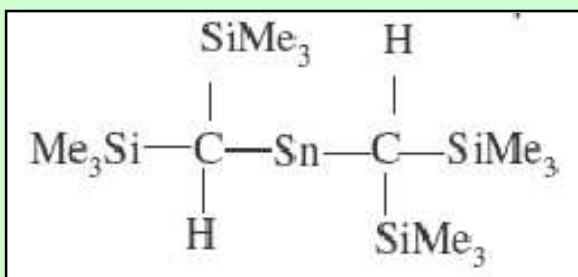
The problem is that Sn(II) organyls with not very bulky R tends to oligomerize:



← $d(\text{Sn-Sn}) = 277 \text{ pm}$
Compare to the
 $d(\text{Sn-Sn}) = 281 \text{ pm}$
in a grey α -tin

Formation of $\text{Ph}_{12}\text{Sn}_6$ was confirmed with X-ray diffraction

One strategy would be to increase the bulk of the SnR_2 groups so that their interaction prevents oligomerisation.



Even if bulky substituents are used oligomerisation (polymerisation) can occur e.g. $\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{Sn}$ is monomeric in solution and dimeric in the solid state

2) Using of Sn-H addition to the C=C double bond:



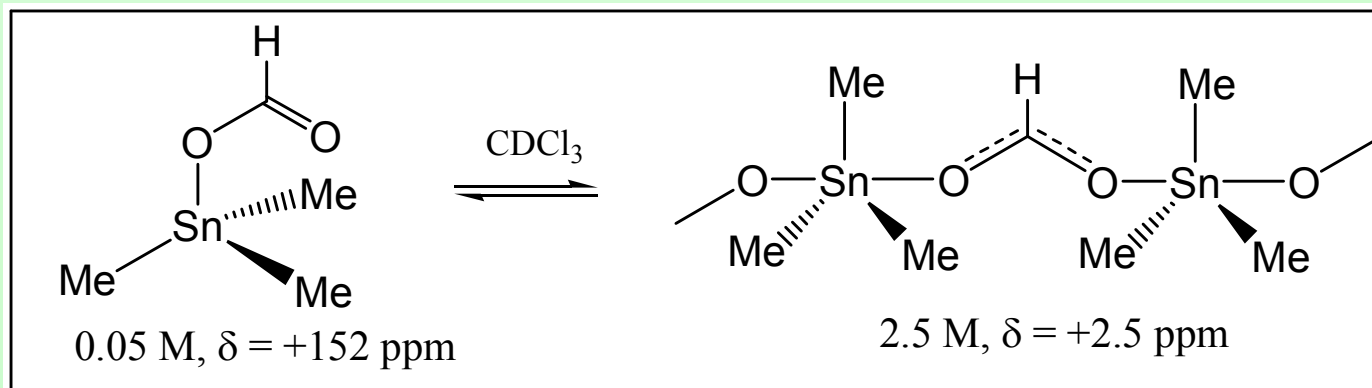
^{119}Sn -NMR:

Relative to the standard ($\text{Sn}(\text{CH}_3)_4$), chemical shifts are between +150 and -400 ppm.

Examples:

Compound	Chemical shift, ppm
$\text{Me}_3\text{SnCCl}_3$	+85
Me_4Sn	0
Me_3SnH	-104
Ph_4Sn	-137

The transition from coordination number 4 to higher (5, 6) gives shift of the ^{119}Sn signal to the higher field (to less positive numbers):

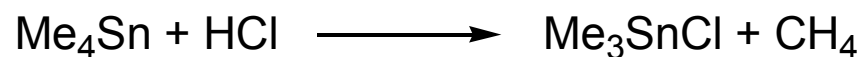
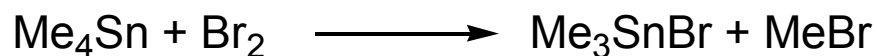


Reactivity:

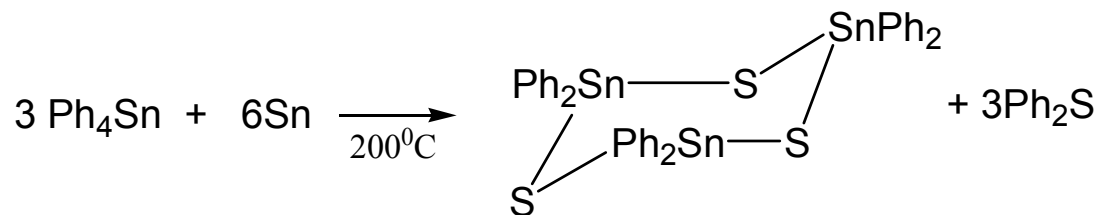


Tetraorganostannates are inert towards O_2 , H_2O , usually they are also thermally stable (Me_4Sn decomposes above $400^\circ C$).

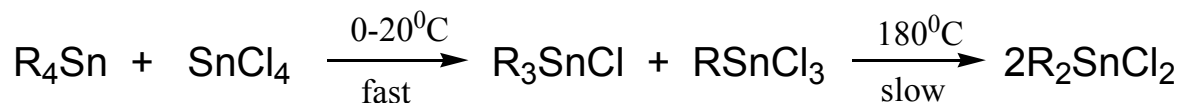
They react with halogens and hydrogen halides:



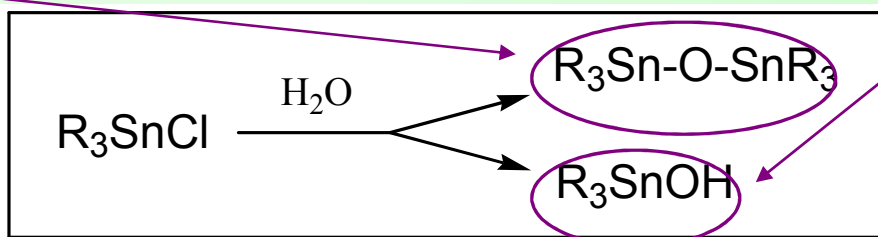
Thiophilic nature of tin express in the reaction of Ph_4Sn with sulfur:



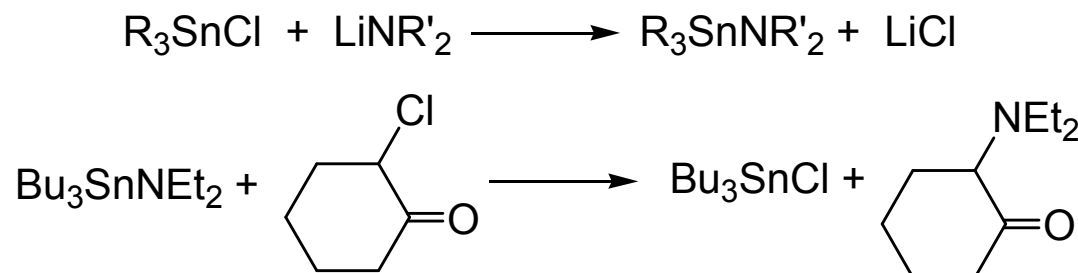
Organohalostannates can be obtained from the corresponding tetraorgano-stannates:



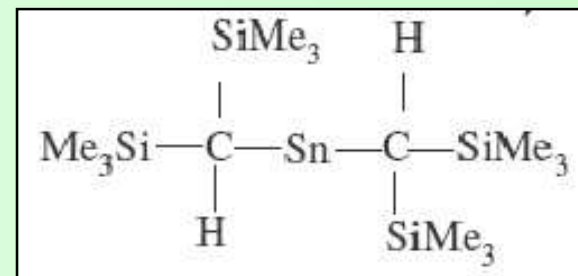
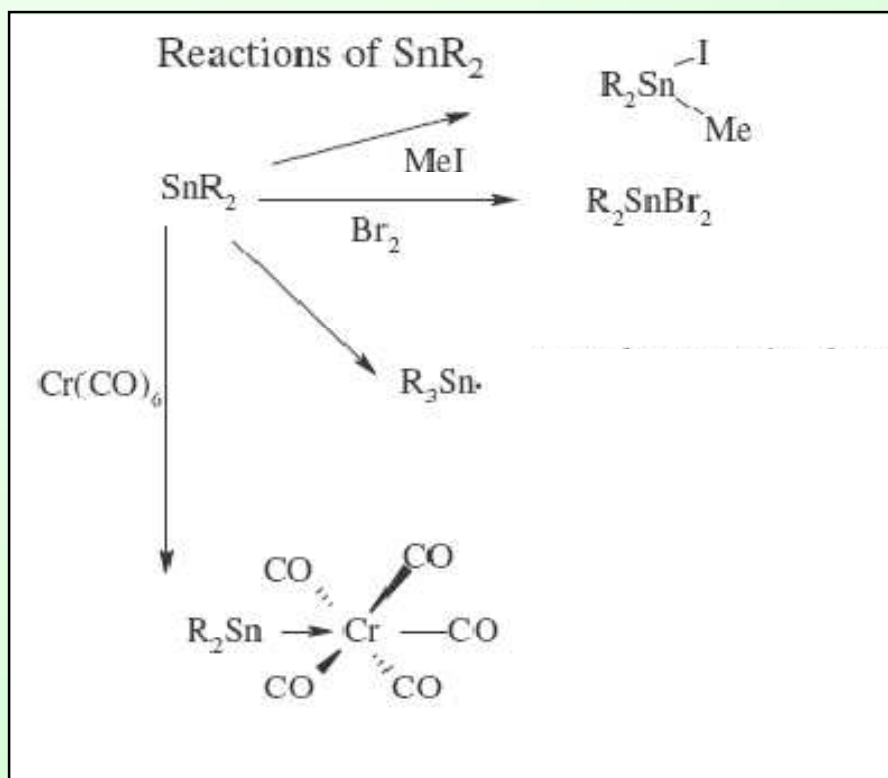
R_3SnX (in contrast to R_4Sn) can undergo hydrolysis to form stannanols and distannoxanes:



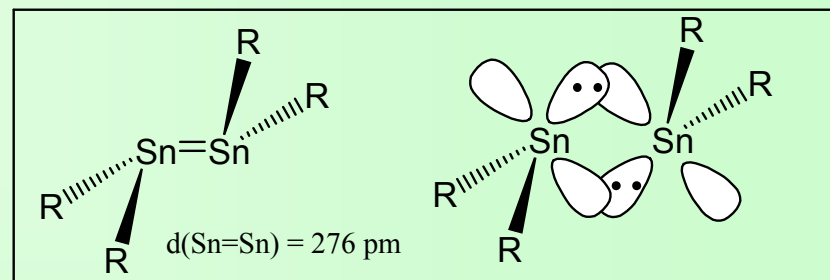
R_3SnX are good precursors for the synthesis of organotin amides which have found application in organic synthesis:



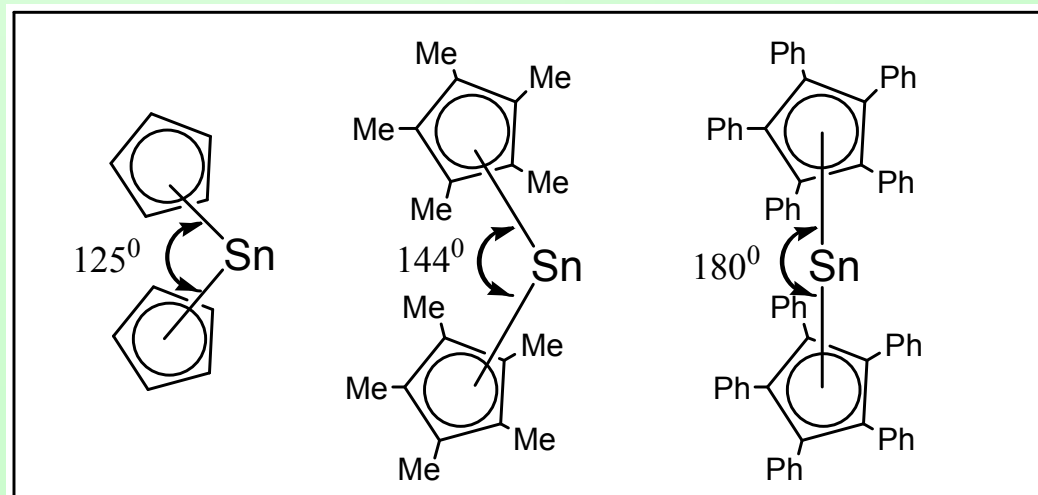
Stannylenes R_2Sn mostly exist as a reactive intermediates:



As it was said this compound exists as a monomer in solution, but as a dimer in a solid state:



Stannocenes (Cp_2Sn) are thermally stable but air and moisture sensitive



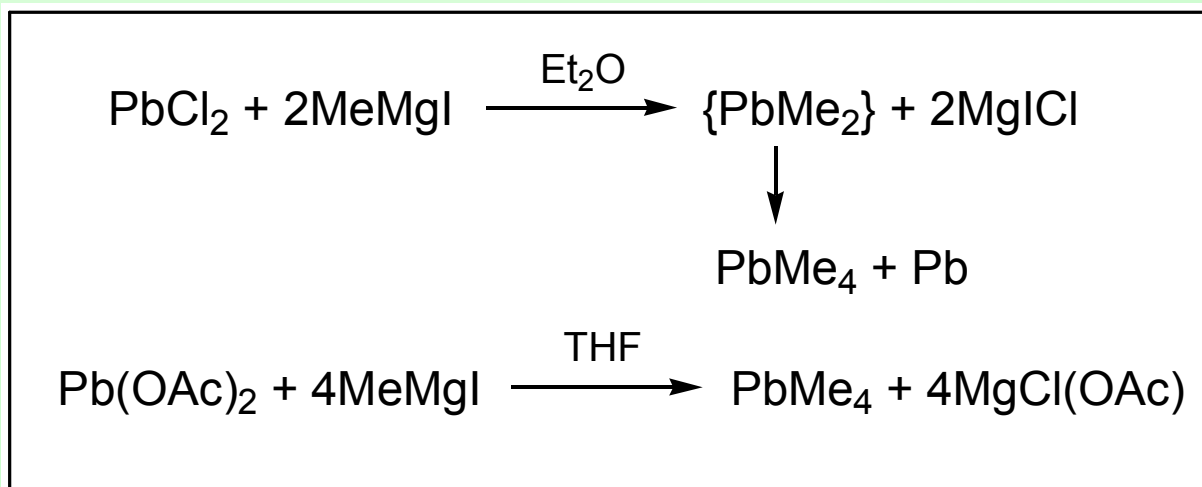


Organolead compounds: PbR_4 , XPbR_3 , ... etc.

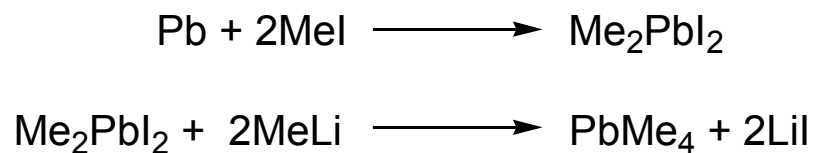
- Reactive and relatively weak M-C bond
- Absence of tendency to form M-M bond (in contrast to Ge, Sn)
- Large variety of accessible coordination numbers and oxidation states
- Application of ^{207}Pb -NMR for the structure characterization

Synthesis:

1) Using of Li or Mg-organic compounds:



2) Direct synthesis from Pb and organyl halides is possible in some cases:



Reactivity:

Tetraorganoplumbanes PbR_4 are colorless liquids (R = alkyls) or white solid (R = Ph)

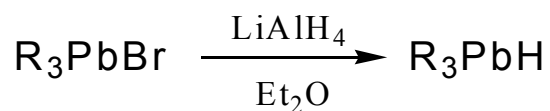
At ambient conditions PbR_4 are stable towards air, oxygen, light.

Thermal stability of PbR_4 decreases in the order:

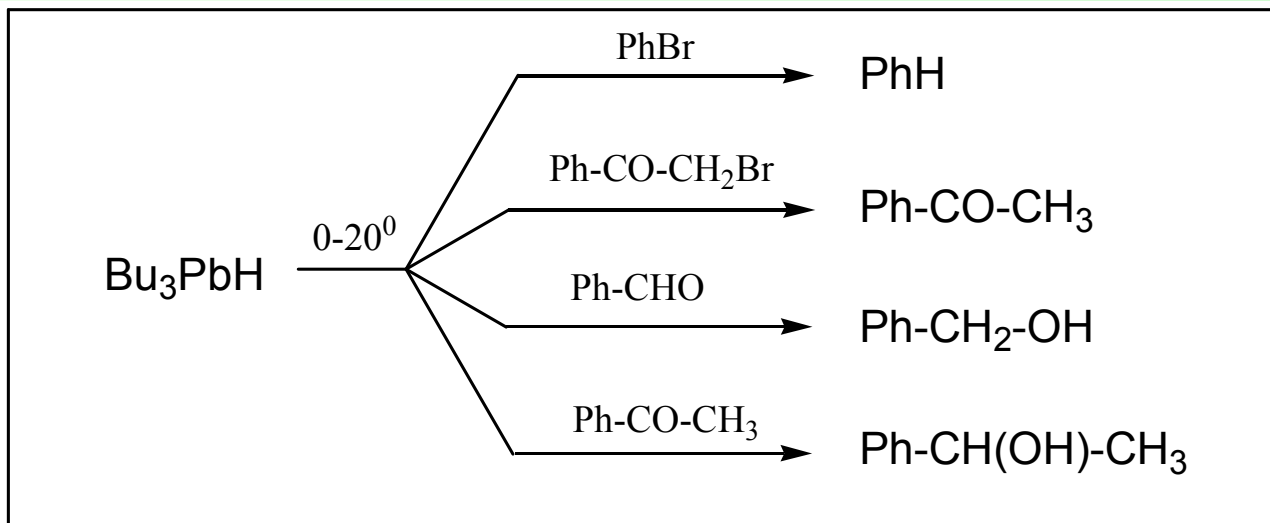


TEL (PbEt_4) is added to gasoline in a concentration of about 0.1% to serve as an antiknock compound

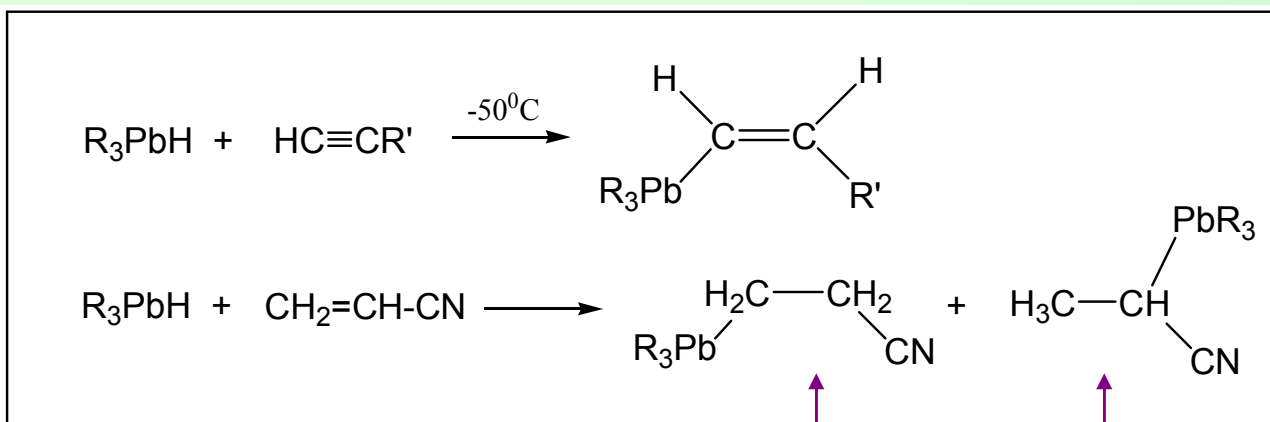
Among organolead compounds the most reactive are organyl hydrides. They can be synthesized by the reaction of LiAlH_4 with organolead halides:



Organolead hydrides are good reducing agent at mild conditions:



Organolead hydrides readily reacts with C=C double and triple bonds at mild conditions:



In Et₂O, at 0°C, radical mechanism, 92%

In BuCN, at 20°C, polar mechanism, 24%

8%

76%

Group IB: **Cu**, Ag, Au

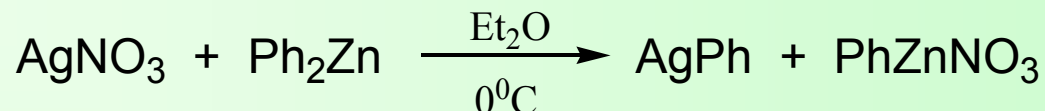
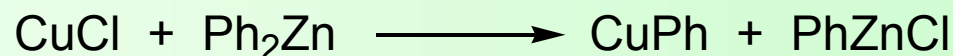


- Covalent character of M-C bond
- Oxidation state **+1** for most organometallic compounds of **copper** and **silver** (for copper +2 is possible sometimes)
- Oxidation states **+1** and **+3** for organo**gold** compounds
- Polymers and oligomers are possible
- Non-stoichiometric adducts are also possible: $[(\text{CuR})_x^*(\text{CuBr})_y]$

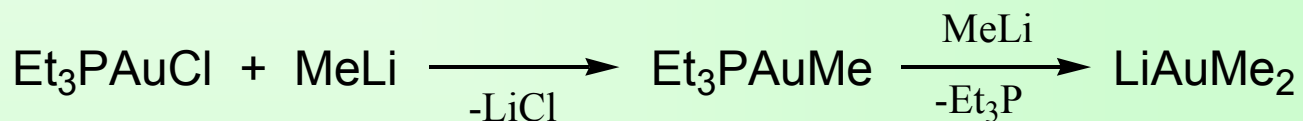
Synthesis:



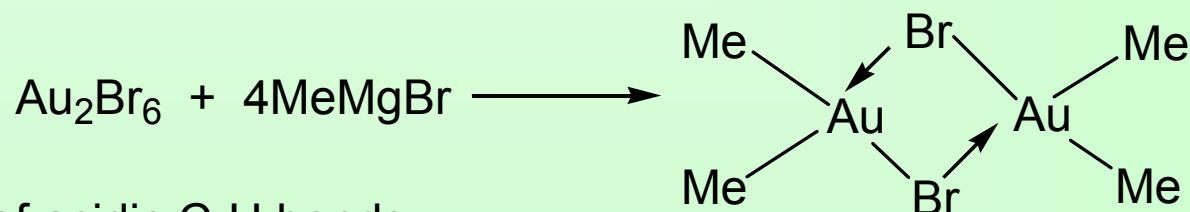
1) Using Li, Mg, Zn, Pb – organic compounds



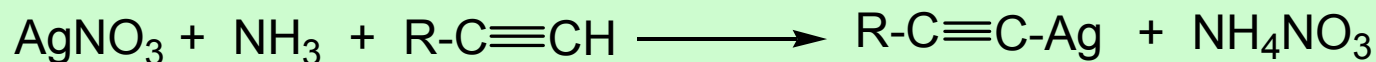
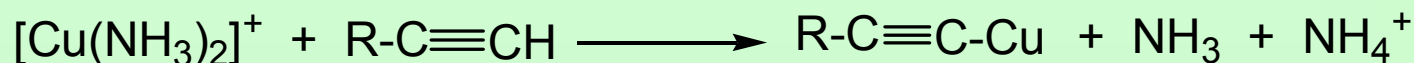
Simple binary compounds of gold are yet unknown. But Au(I) organyls are known as adducts LAuR or organoaurates MAuR_2



Au(III) organyls are also known:

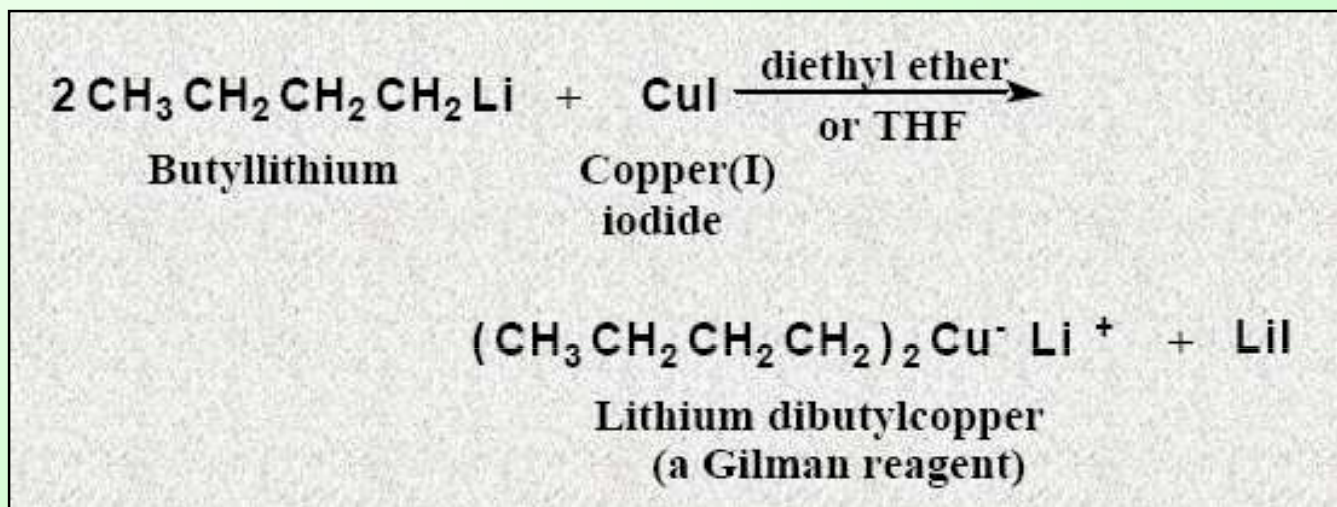


2) Metallation of acidic C-H bonds

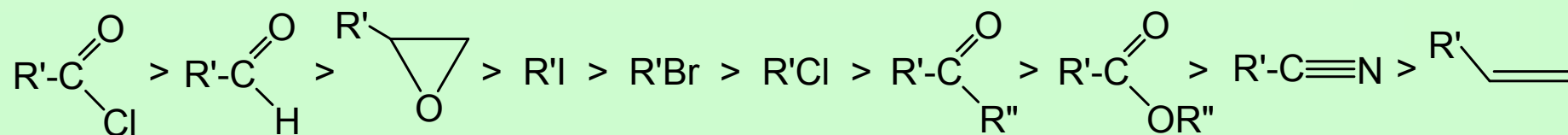


Application of Cu(I) compounds (Gilman reagents):

Lithium diorganocopper reagents, known more commonly as Gilman reagents
 - prepared by treating an alkyl, aryl, or alkenyl lithium compound with Cu(I) iodide:

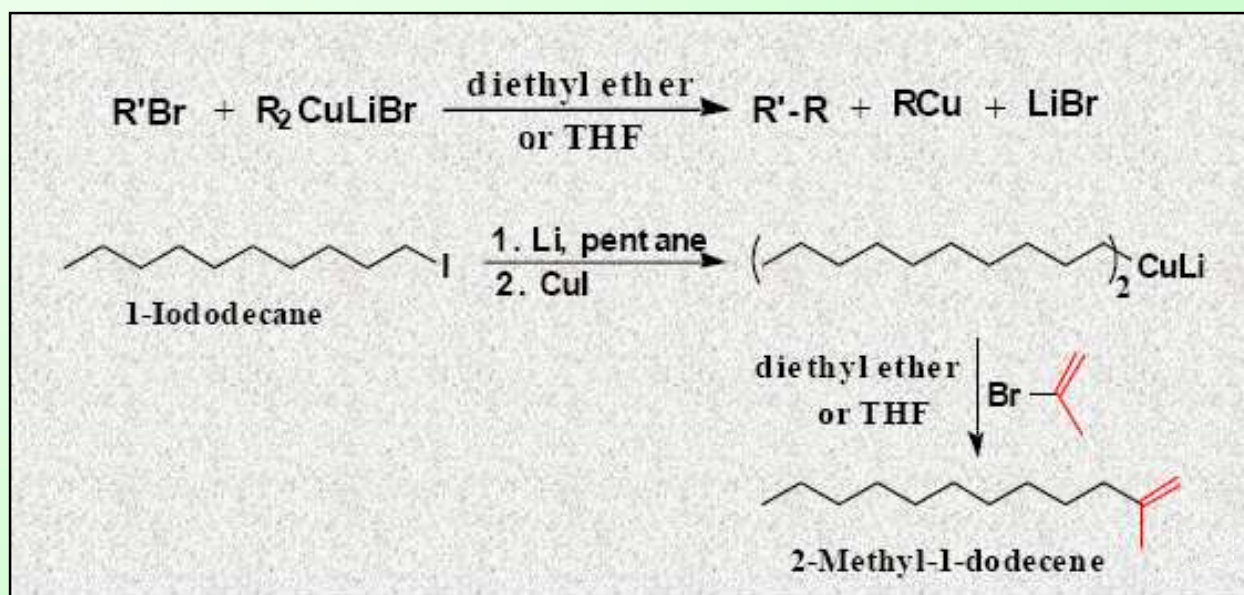


Lithium diorganocopper compounds (Gilman reagents) are less nucleophilic than LiR compounds, therefore, they react more selectively with organic substrates. In general, the following order of decreasing reactivity towards LiCuR₂ is observed:

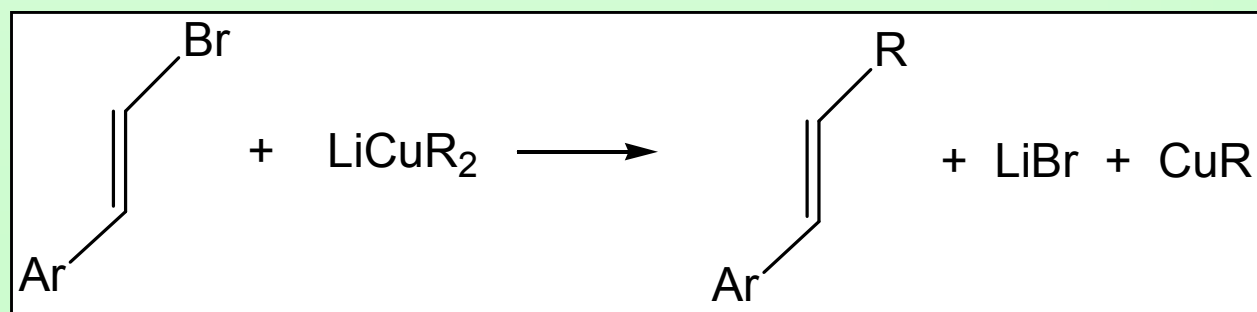


Coupling within organohalogen compounds:

form new carbon-carbon bonds by coupling with alkyl and alkenyl chlorides, bromides, and iodides

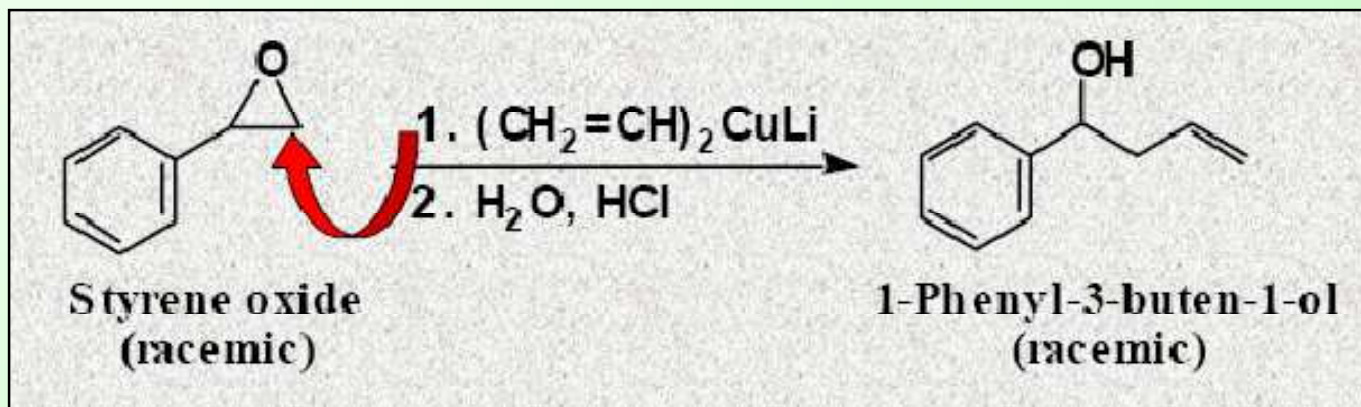


The configuration of alkyl halide is preserved during the substitution:

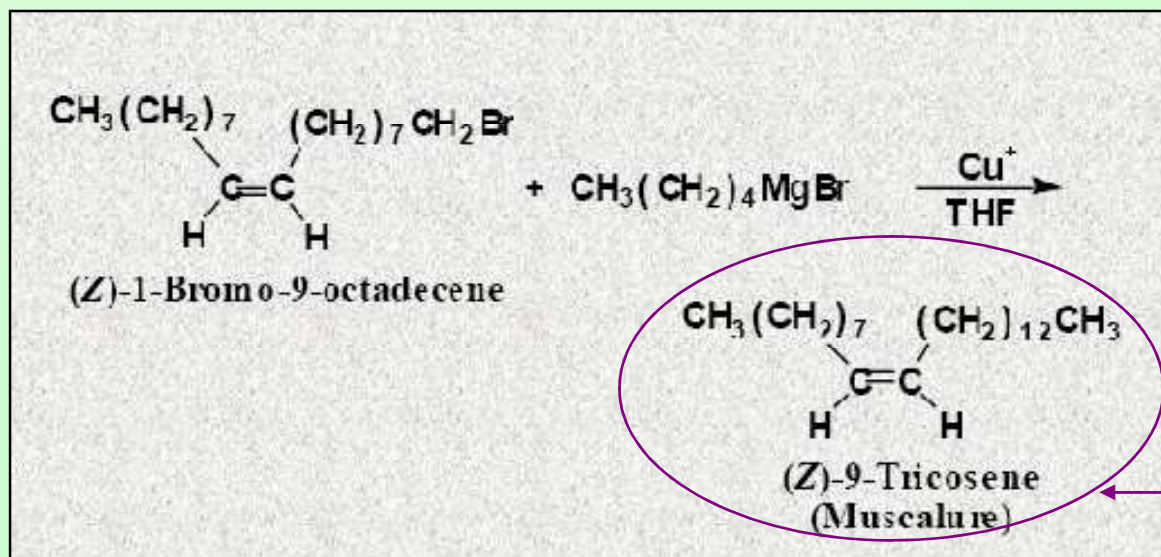


Reaction with epoxides:

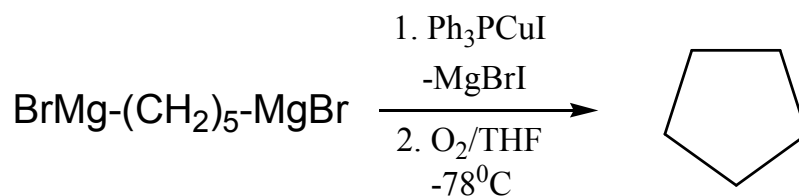
- regioselective ring opening
- approaches from the least hindered side



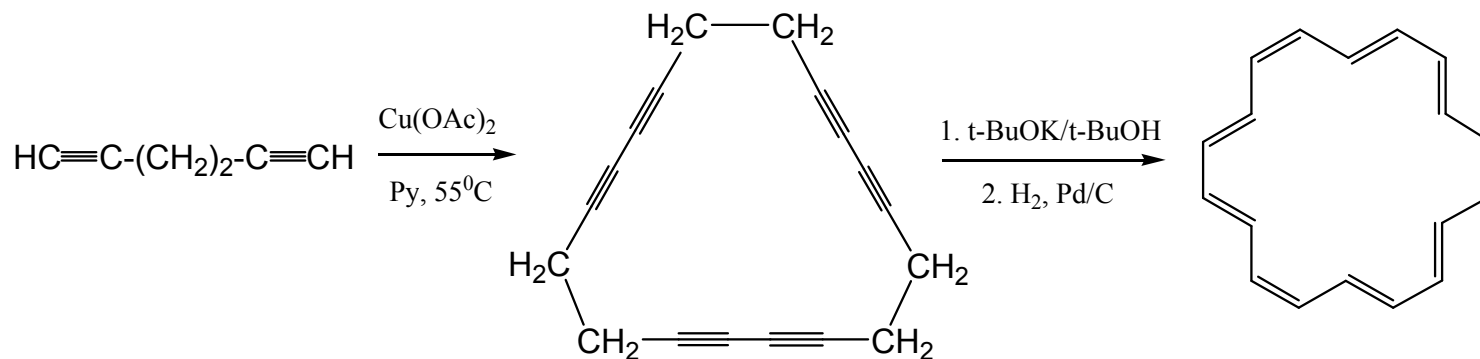
A variation on the preparation of a Gilman reagent is to use a Grignard reagent with a catalytic amount of a copper(I) salt:



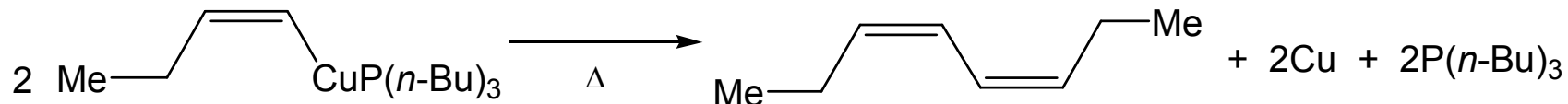
Oxidative coupling:



Synthesis of annulene:



Homolytic thermal coupling:



cis-cis adduct

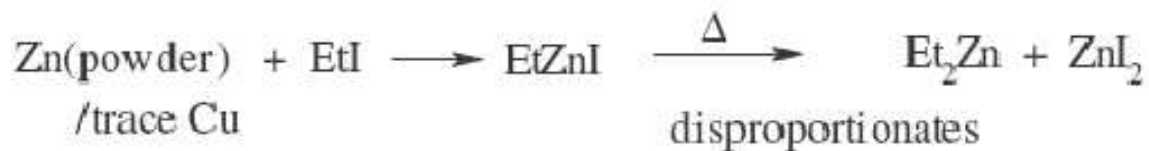
Group IIB: Zn, Cd, Hg



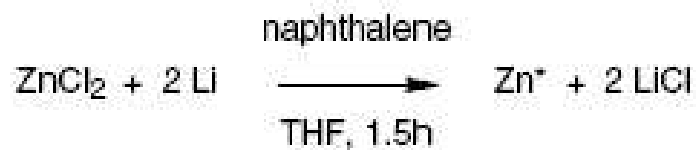
- Elements of IIB group possess completely filled d-shells of low energy, void of donor or acceptor properties
- Covalent character of M-C bond
- Oxidation state **+2** for most organometallic compounds of **Zn, Cd and Hg**
- Compounds of both types – **MR₂** and **X-M-R** are possible

Synthesis:

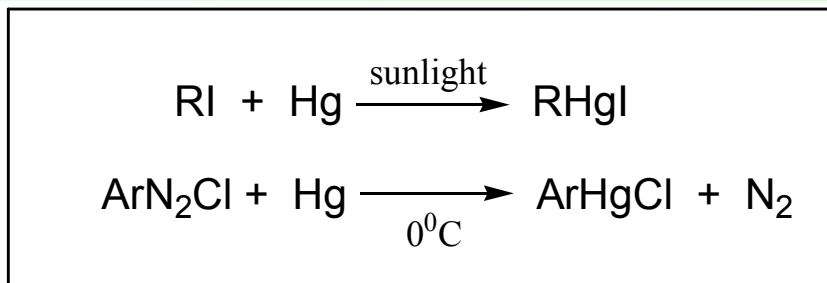
1) Direct synthesis from Zn powder and organyl halides:



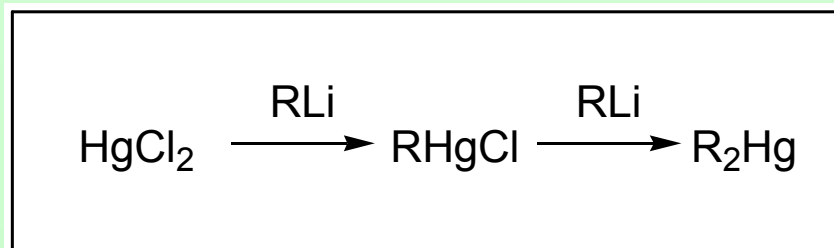
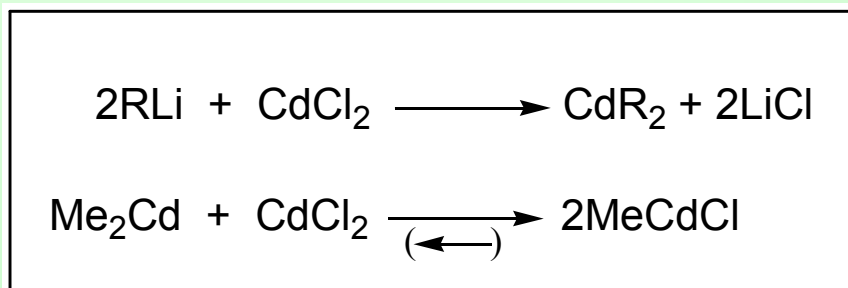
Zinc powder can be made more reactive via reduction of ZnCl₂ using lithium and naphthalene as electron-transfer mediator in THF (Riecke Zn*)



For Cd-organic compound other methods (Li, Mg-organyls) can be applied.
For Hg-organic compounds direct synthesis is also possible:



2) Using Li, Mg – organic compounds

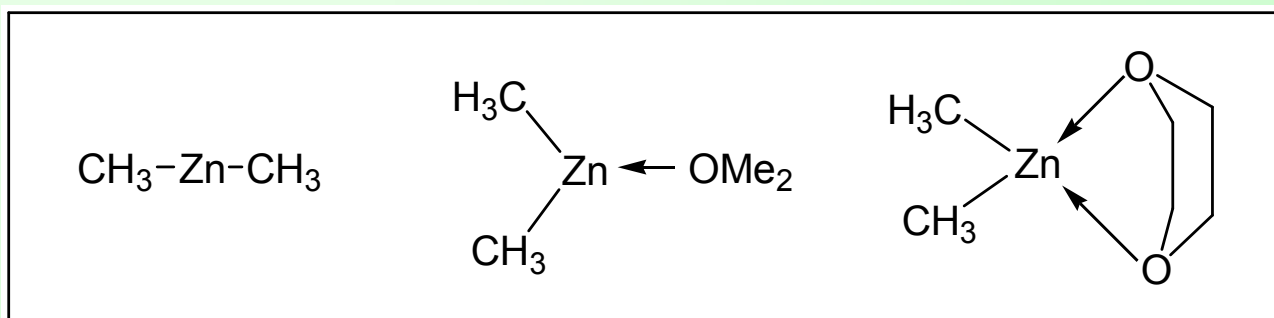


Structure:

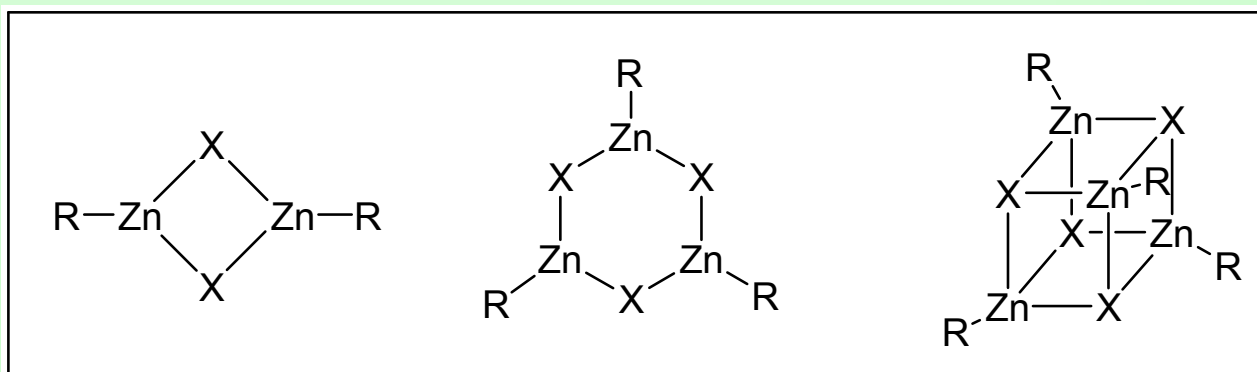
ZnR_2 compounds are monomeric (in contrast to BeR_2 and MgR_2)

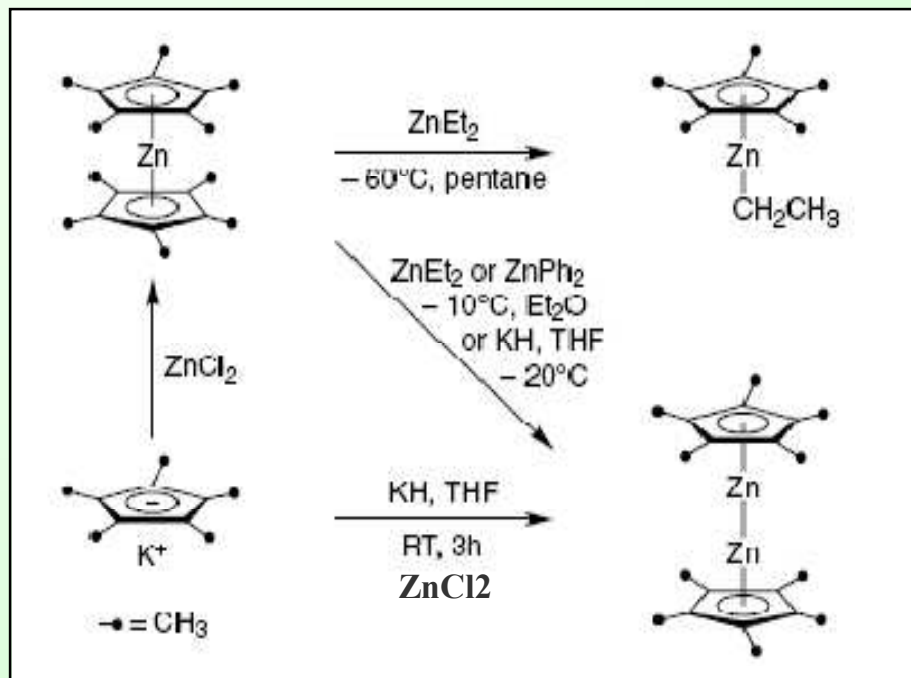
The molecules are linear. ZnR_2 compounds have low melting and boiling points:
 ZnEt_2 : mp = -28°C , bp = 118°C .

When coordinated to some ligand, angle C-Zn-C decreases:



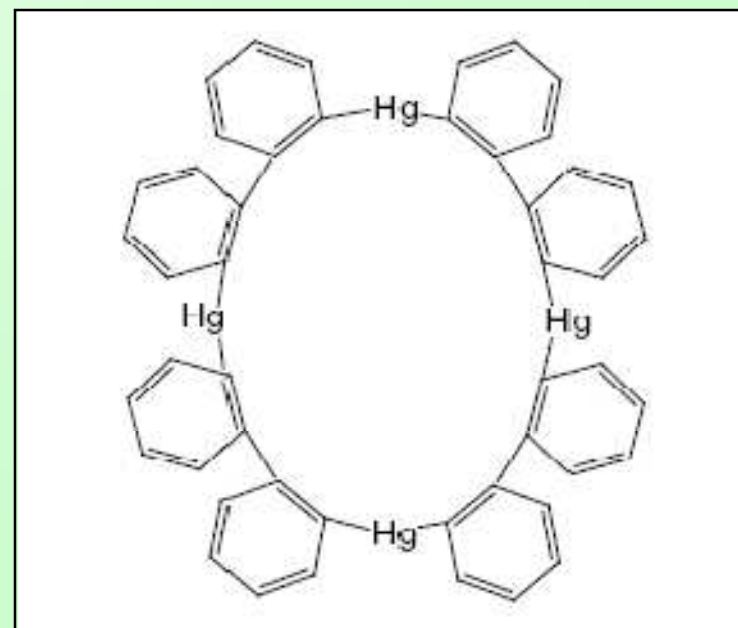
RZnX (X = halide or OR) are mostly oligomers:





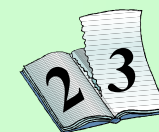
Metalloenes (MCp_2 and MCp^*_2 complexes) are known with Zn as with the other main-group metals.

More unexpected was the finding by the Carmona group in 2004 of sandwich complexes in which a relatively strong Zn-Zn bond was found.



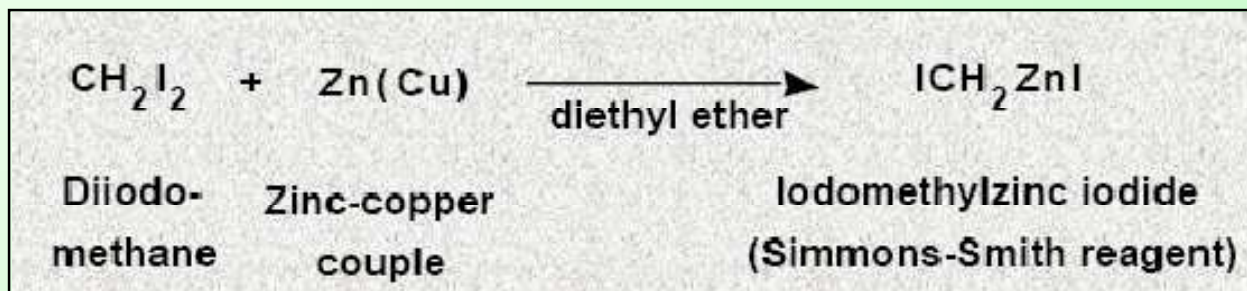
The derivatives HgR_2 , prepared by alkylation of HgCl_2 using a Grignard reagent or an aluminum reagent, are very toxic volatile liquids of reduced thermal stability. They most of the time have a linear structure in agreement with their sp hybridization. Some cyclic structures are known in aromatic series:

Application of Zn(II) organyls (Simmons-Smith reagent):

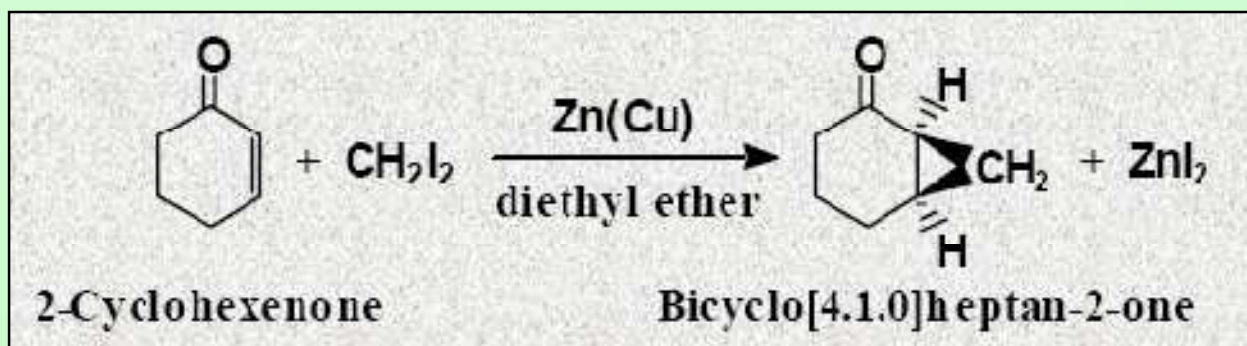
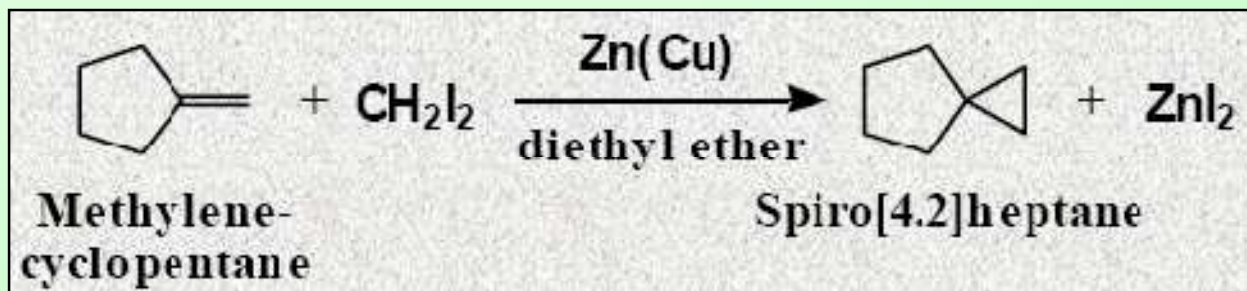


Simmons-Smith reaction – a way to add methylene to an alkene to form a cyclopropane

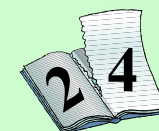
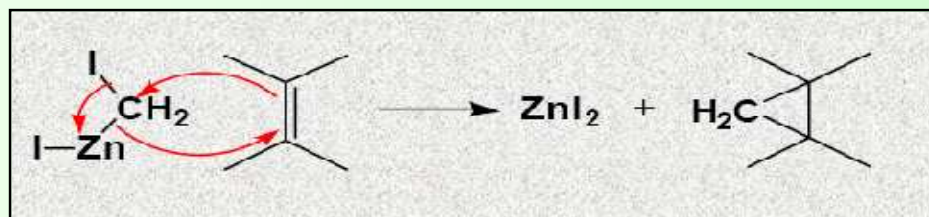
Generation of the Simmons-Smith reagent:



this organozinc compound reacts with a wide variety of alkenes to give cyclopropanes:



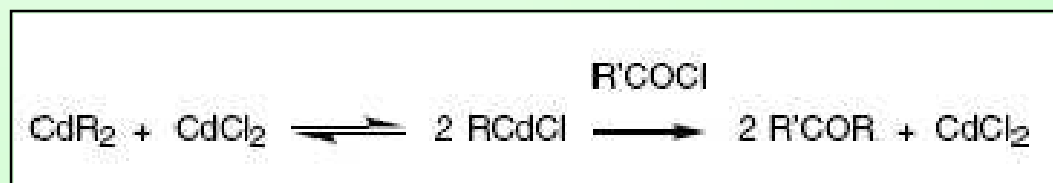
Mechanism:



The organozinc compound reacts with an alkene by a concerted mechanism.

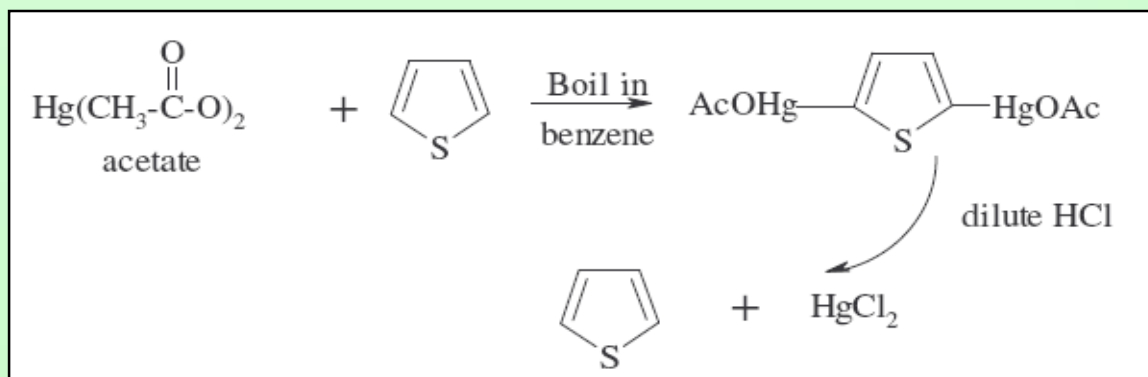
Application of Cd-organyls:

The organocadmiums allow to selectively alkylate acyl chlorides without reacting with ketone, ester or nitrile groups that may eventually be present in the molecule and that would be attacked by the Grignard reagents which are more reactive:



Application of Hg-organyls:

Ability of Hg-compounds to attack aromatic C-H bonds is applied in desulfurization of coal tar:



Group IIIB: Sc, Y, Lanthanides, Actinides



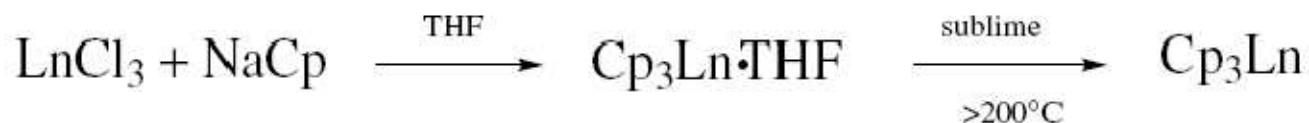
- Sc, Y, La, Ac have an incomplete d -subshell
- lanthanides and actinides have an incomplete f -subshell
- the $4f$ -orbitals of lanthanides are contracted and of lower energy than the $5d^1$ and $6s^2$ valence orbitals. Thus, the lanthanide complexes are **ionic**, with domination of the oxidation state +3
- the actinide's f orbitals have sufficient radial extension to cover the ligand orbital up to a certain extent. As a consequence, various oxidation states and **partially covalent** metal-ligand bonds are found for the first actinides. This covalent character remains minor, however, and the ionic character dominates. The accumulation of nuclear charges provokes the contraction of the $5f$ orbitals as one moves forward in the actinide series. The oxidation state +3 dominates and the complexes are completely **ionic** for the later actinides as for the lanthanides.

Synthesis:

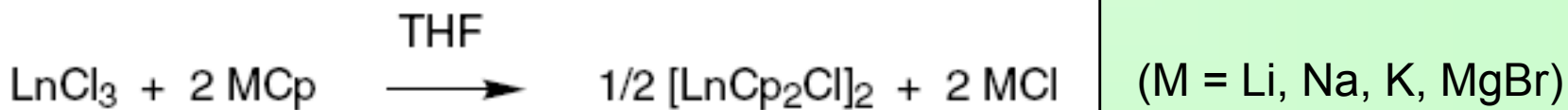


As hard Lewis acids, Ln^{3+} tend to prefer hard ligands, typically O donors, hence the term *oxophilic* often applied to these ions.

1) Using Li, Na, K, Mg - organic compounds

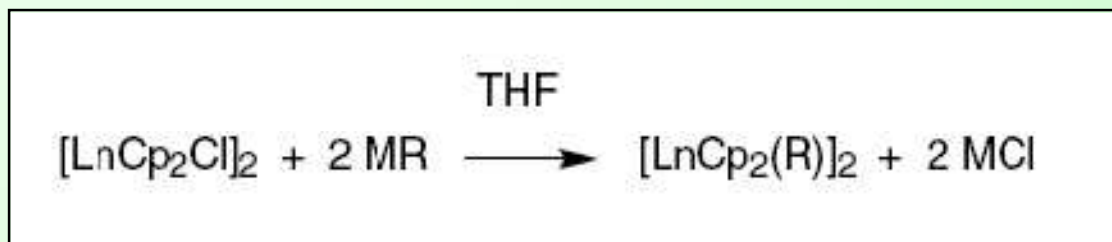


The binary compounds $[\text{LnCp}_3]$ are not monomeric, except $[\text{YbCp}_3]$, but oligomers or polymers, one of the Cp ligands bridging two metals with a pentahapto- or monohapto-coordination. Bulky alkyls are necessary if bridging is to be avoided: $[\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}_3]$



Likewise, the compounds $[\text{LnCp}_2\text{Cl}]_2$ are bridged by the two common chloride ligands, each monomer unit bringing one Cl.

$[\text{LnCp}_2\text{Cl}]_2$ compounds are extremely useful to reach the complexes $[\text{MCp}_2\text{R}]$ with various R groups that are X ligands: OR' , $\text{O}_2\text{CR}'$, NH_2 , PR_2 , BH_4 , acac, alkyl, allyl.

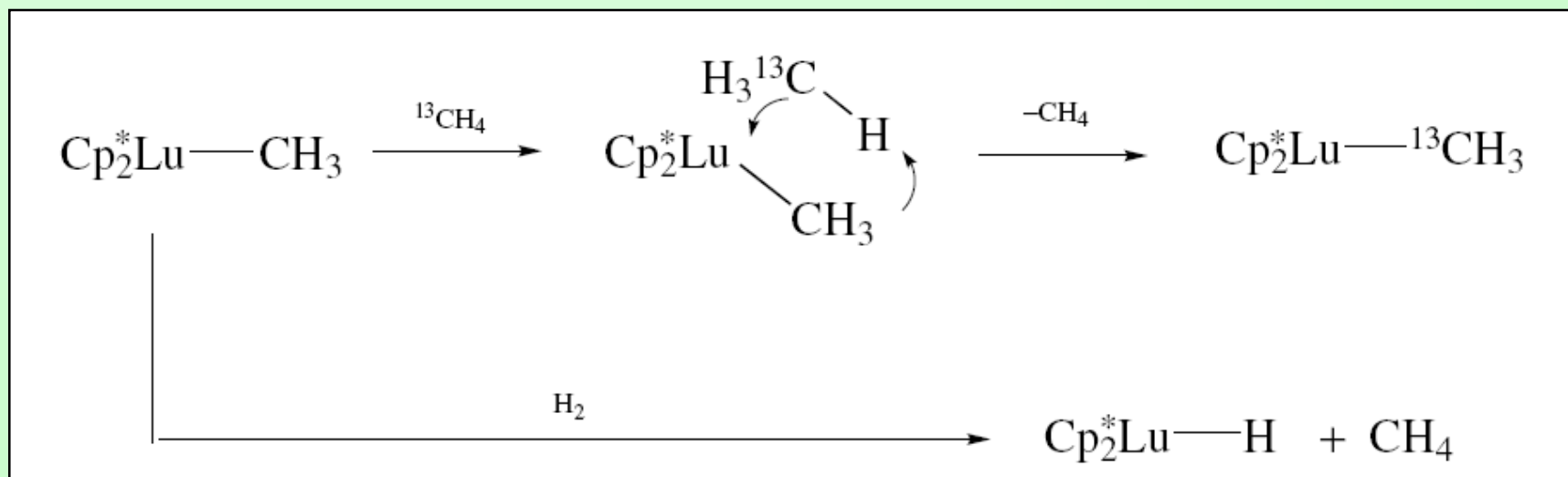


(M = Li, Na, K, MgBr)

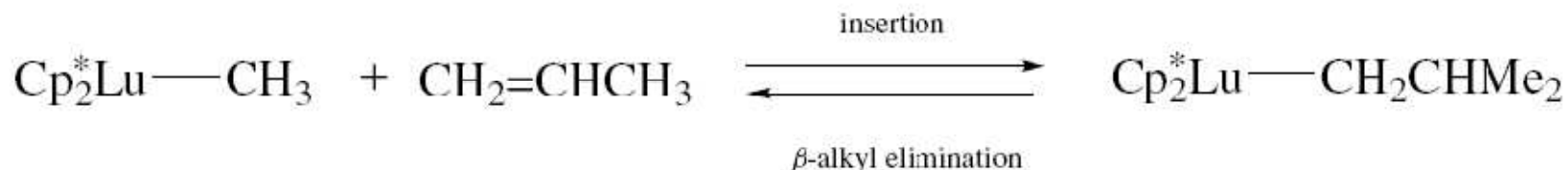
(R = alkyl)

Reactivity of the Ln-C bond

Watson's exchange reaction between a coordinated methyl group and free methane, via σ bond metathesis, discovered by ^{13}C isotope labeling of the methane carbon.

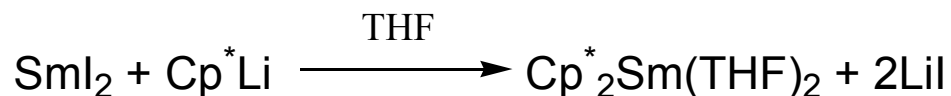


The same alkyl also undergoes insertion with alkenes, with β -alkyl elimination also being possible:

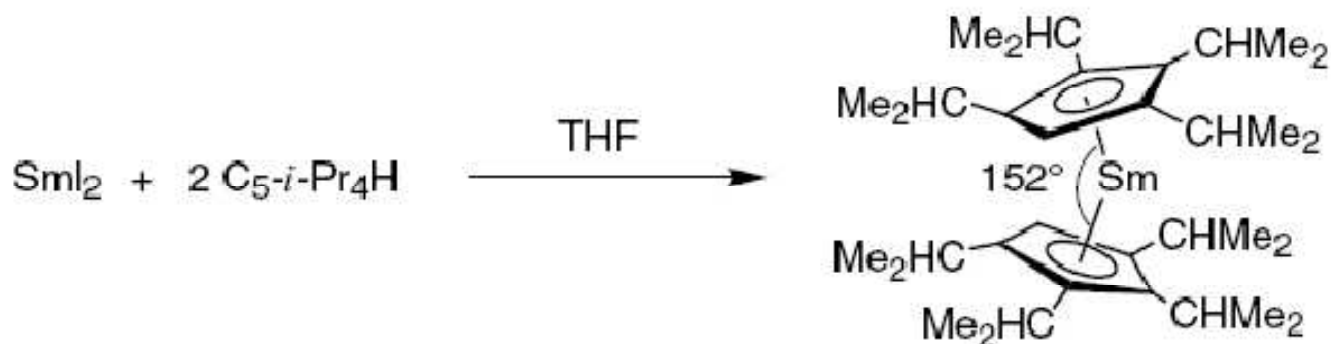


Structure and Reactivity of the Sm(II) compounds

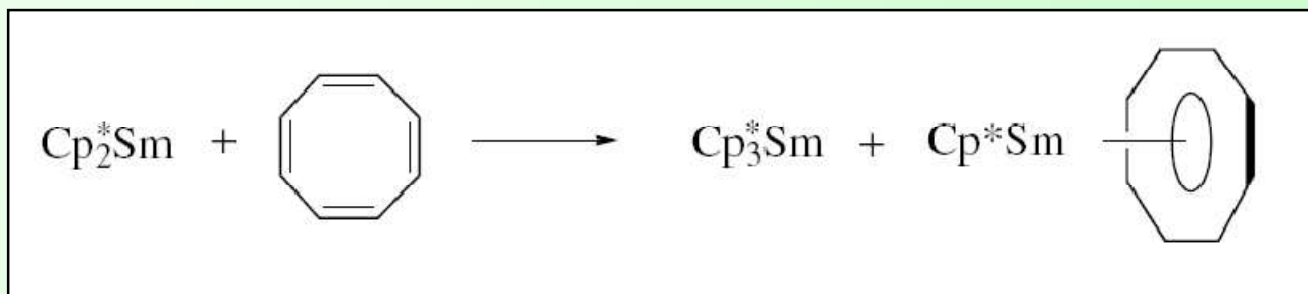
[SmCp^{*}₂(THF)₂] can be obtained by the reaction:



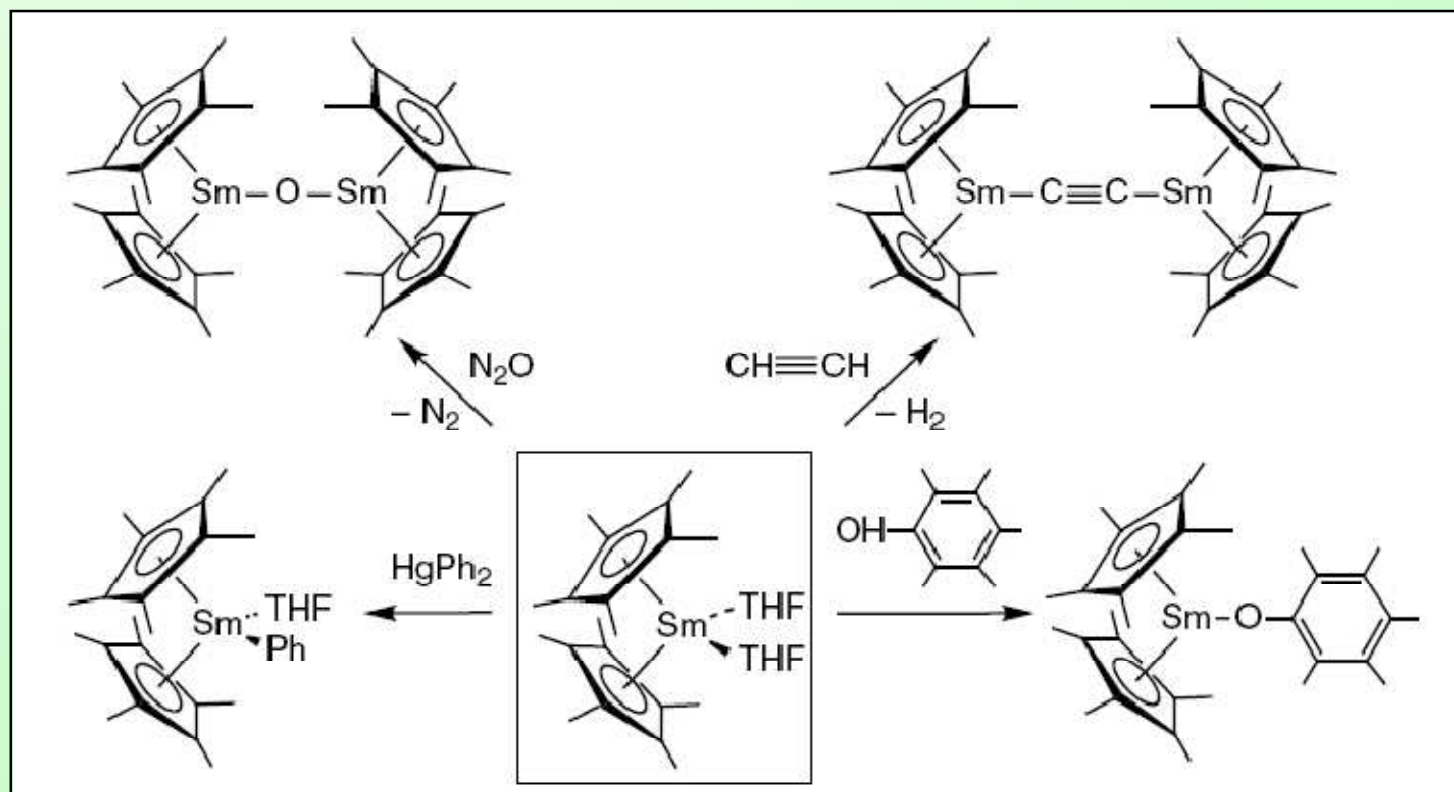
With the ligand C₅-i-Pr₄H, whose electron richness is comparable to that of Cp^{*}, but whose steric constraints are much more demanding, THF cannot coordinate to samarium in the metallocene, even when the synthesis is carried out in this solvent



Very interesting is the reaction of Cp^*_2Sm with tetraene. The tetraene takes one electron from each of two Sm(II) units to give two Sm(III) complexes



The reactivity of $[\text{SmCp}^*_2(\text{THF})_2]$ is even more diverse:



Group IVB: Ti, Zr, Hf



-Elements of IVB group has partly ionic character of bonding (but anyway M-C bond is more covalent)

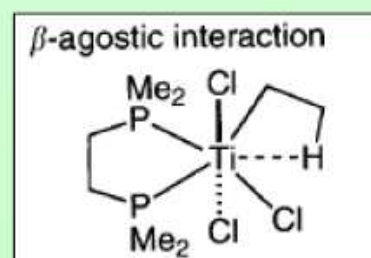
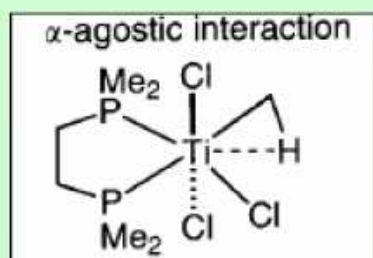
-Oxidation state **+4** for most organometallic compounds of **Ti**, Zr, Hf, even so +2 and +3 possible for Ti

Synthesis:

Using Li, Mg, Zn - organic compounds



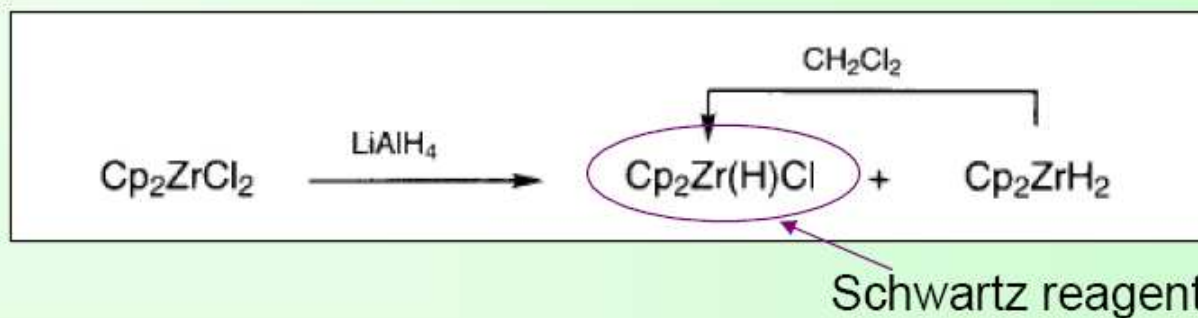
Structure: quite often situation – agostic M-CH bonding



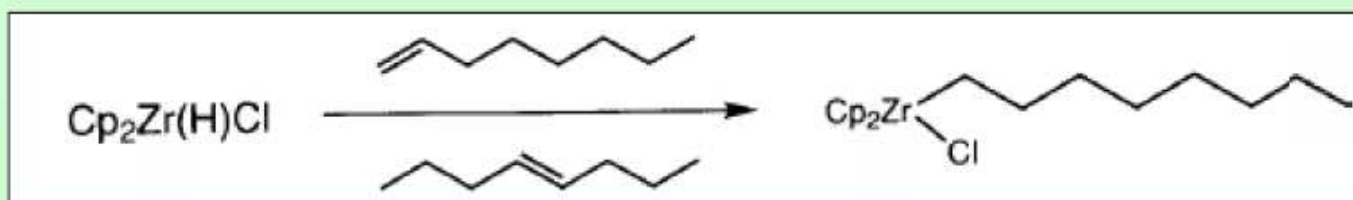
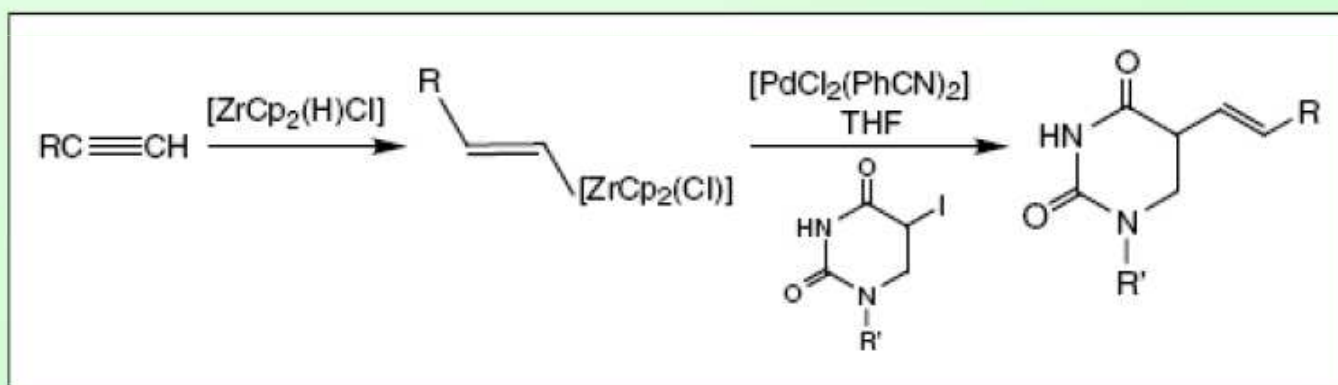
Reactivity:



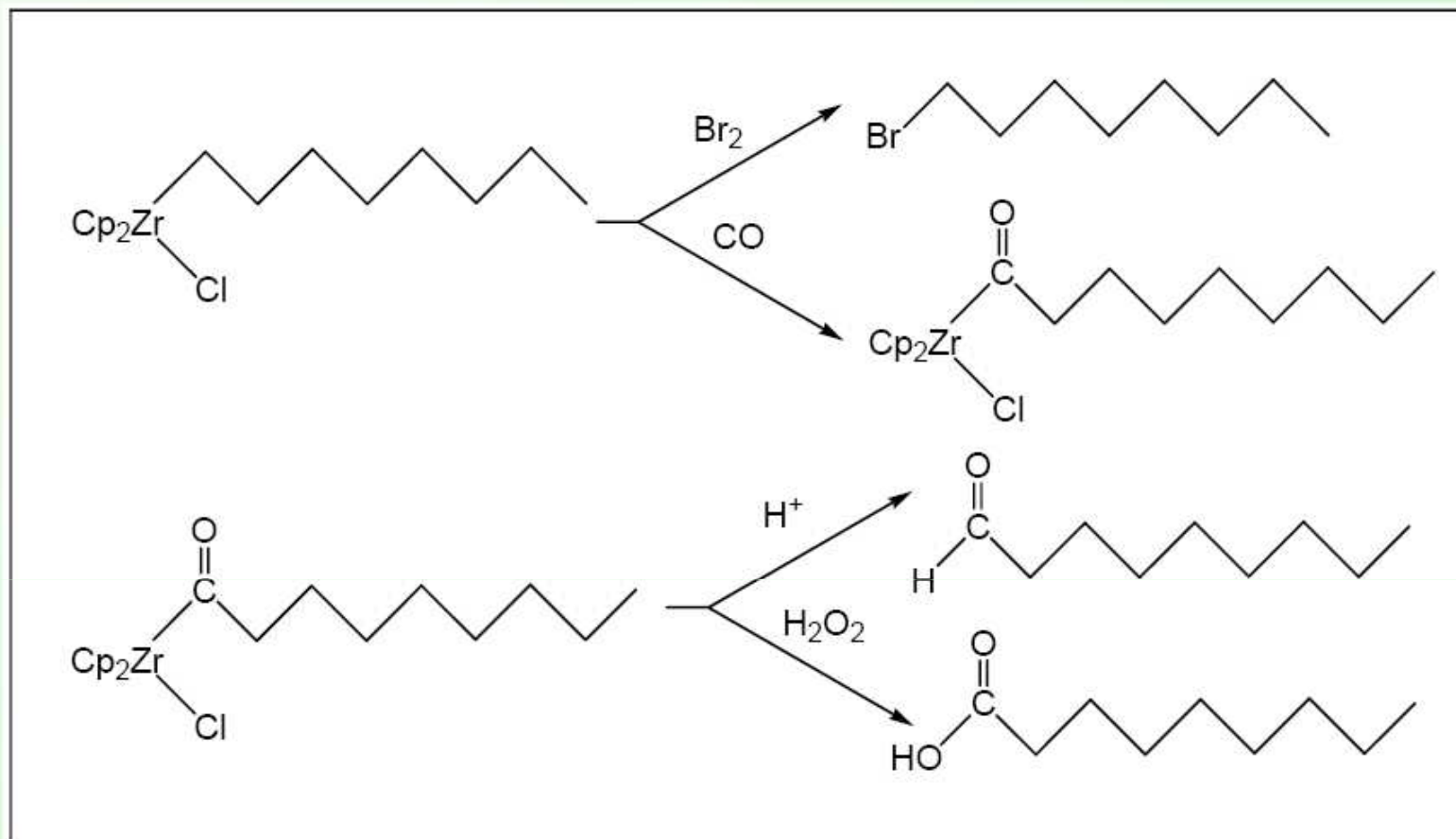
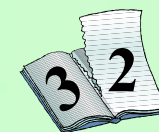
1. Schwartz reagent $[\text{ZrCp}_2(\text{H})\text{Cl}]$:



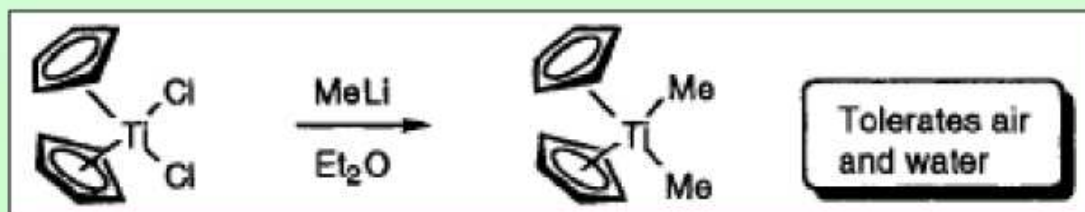
Insertion of C=C and C \equiv C bonds into Zr-H bond of Schwartz reagent:



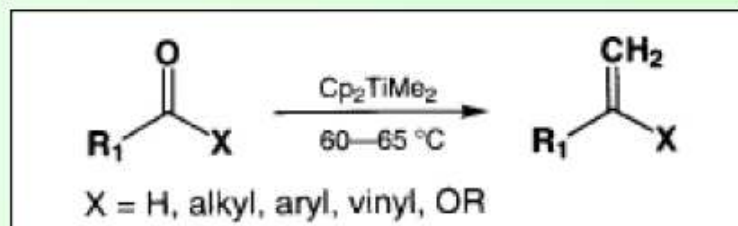
Obtained alkyl-zirconium compound can be used for further transformations:



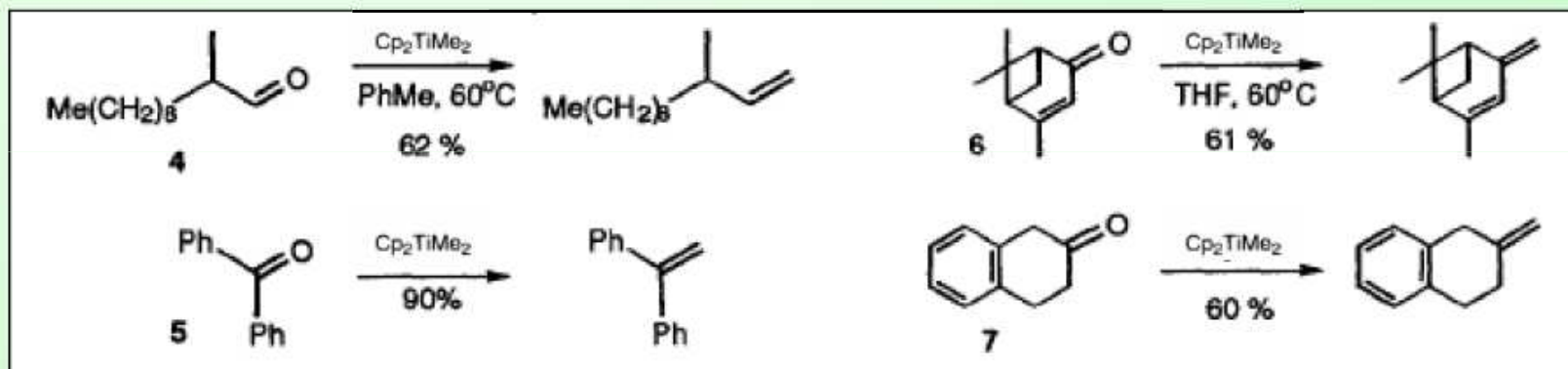
2. Dimethyltitanocene $[\text{Cp}_2\text{TiMe}_2]$ in carbonyl group methylenation:



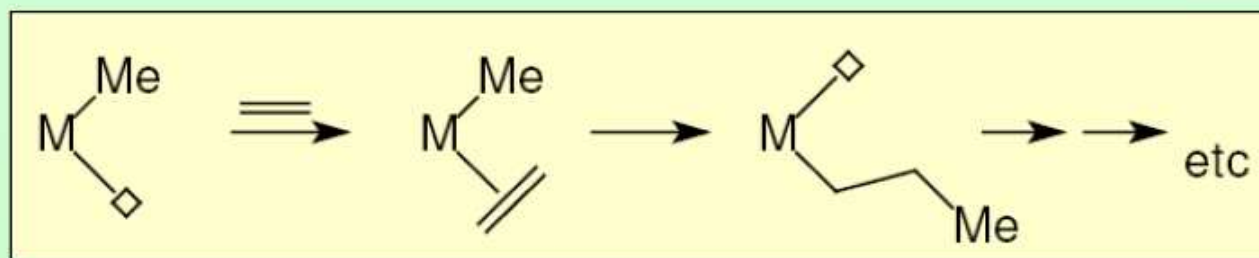
The decomposition of Cp_2TiMe_2 takes place through the formation of carbene complex $[\text{Cp}_2\text{Ti}=\text{CH}_2]$ as an intermediate. That intermediate undergoes metathesis (exchange) with $\text{C}=\text{O}$ group:



Examples:

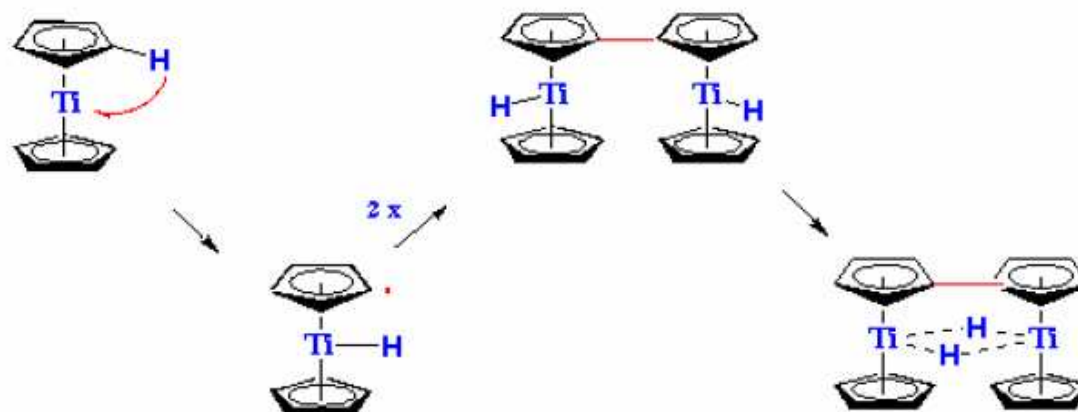


3. Polymerization (usually $\text{M} = \text{Ti, Zn}$ + MAO – methylalumoxane)

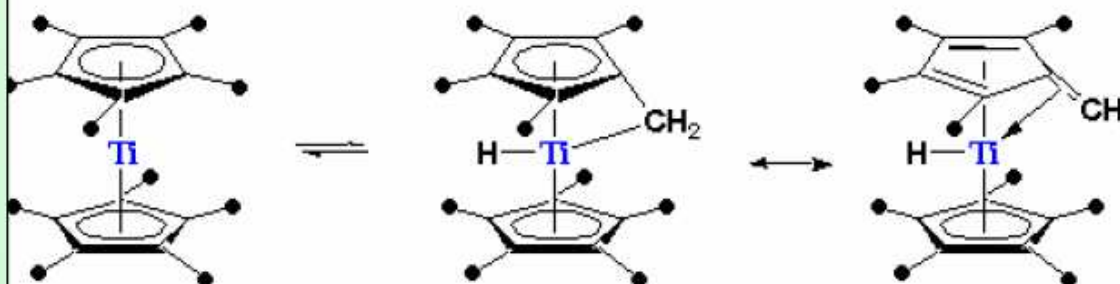


4. Ti(II) metallocenes can undergo intramolecular C-H activation:

14 Valence Electrons and CH-activation



14 Valence Electrons and CH-activation (II)



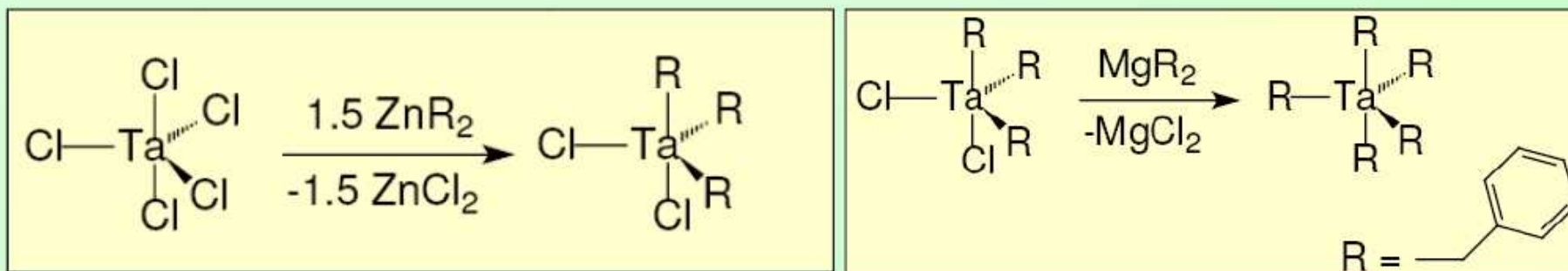
Group VB: V, Nb, Ta



- Many oxidation states are accessible
- Mostly 18e complexes
- Strong, rather unreactive M-C bonds
- Preference for σ -donor/ π -acceptor combinations

Synthesis:

Using Li, Mg, Zn, Sn - organic compounds



Reactivity:

The main application of organotantalum compounds is metathesis reaction.

Usually Ta=C compounds are used as a catalyst:

