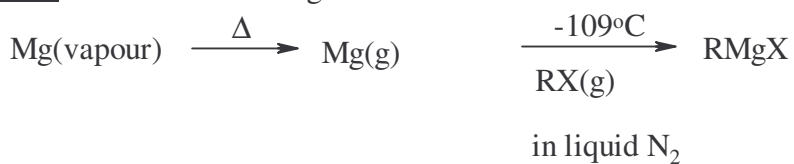


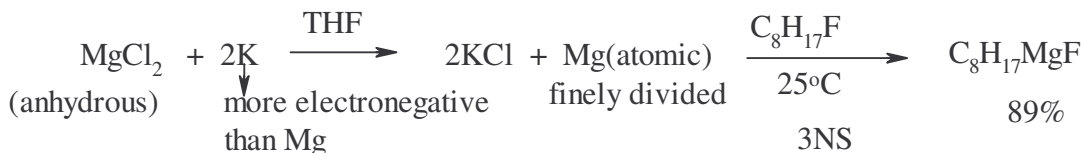
Magnesium

Bulk metal relatively inert as e^- used in bonding.

Preparation of solvent-free Mg



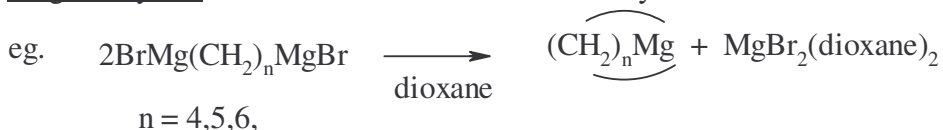
Preparation of fluorogrignards:



Binary Organometallic Compounds

By dioxan displacement of schlenk reaction see earlier or transmetallation with HgR_2 . reactivity of Hg-C bond due to homolytic fission.

Magnesyacycles can result from solvent induced by π shifts.



- Solid Grignard reagents can be 4 coordinated π Be and up to 5, 6 coordinate with donor species.

NB Group 12 transition metals Zn, Cd, Hg have similar reactivity /stoichiometry s^2d^{10} . Form divalent species exclusively - loss / one of s electrons only.

Zinc preparation alkylzinc species

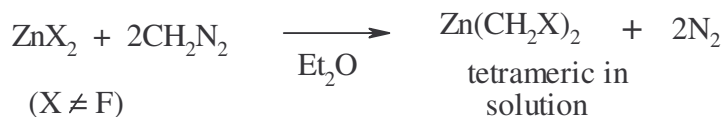


preparation of aryl/zinc species

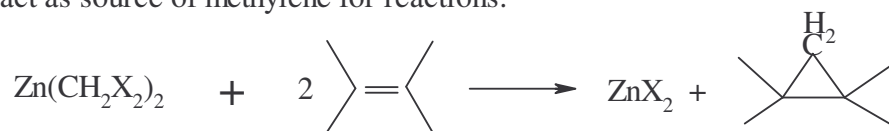


Halomethyl species

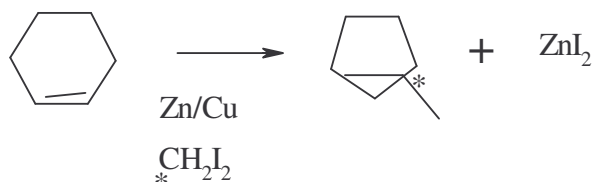
Preparation



act as source of methylene for reactions.



Both Zn-C and C-X bonds are active -reaction occurs via intermediate $\text{H}_2\text{Zn}^+-\text{CH}_2\text{X}$. Evidence for the coordination of Zn occurs when use chiral reagent eg.

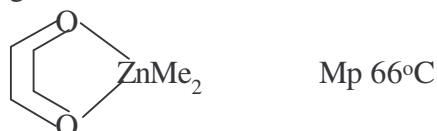


General Properties : very sensitive to O_2 , spontaneously inflammable volatile . Similar reactions but less reactive than Grignards.

eg. no reaction with CO_2 except at high pressure.

Coordination Compounds especially with σ -donor ligands. Chelating ligands give additional stability.

eg.



Unlike $\text{Me}_2\text{Zn-OMe}_2$ which partially decomposes at 44° cubic structures with loss of active H eg. $\text{Me}_2\text{Zn} + \text{MeOH} \rightarrow (\text{MeZnOMe})_4$
 Produces similar compounds to BeR_2 with bipy.

		λ_{max}	$\log \epsilon_{\text{max}}$
ZnBr_2bipy	colourless	310	4.13
$\text{ZnPh}_2\text{ bipy}$	pale yellow	350	2.91
ZnEt_2bipy	orange red	420	2.77
$\text{Zn}^+\text{Bu}_2\text{bipy}$	red	425	2.56
$\text{Zn}+\text{Pt bipy}$	dk red	480	2.63

Looking at transition from $\text{Zn}d$ orbitals .(probably)
 Intensity change due to polarisation.

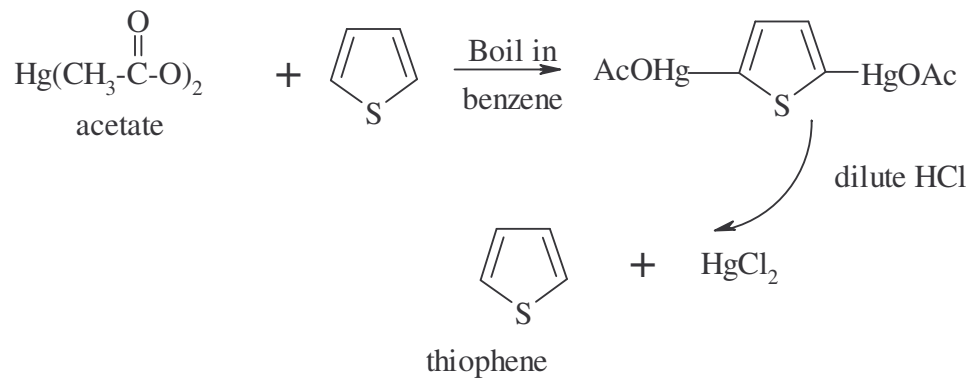
Mercury/Cadmium

far less reactive than Zn

Mercury halides attacked by bacteria → HgR₂ -far more toxic and easily absorbed into food chain

Hg particular facility to attack aromatic systems

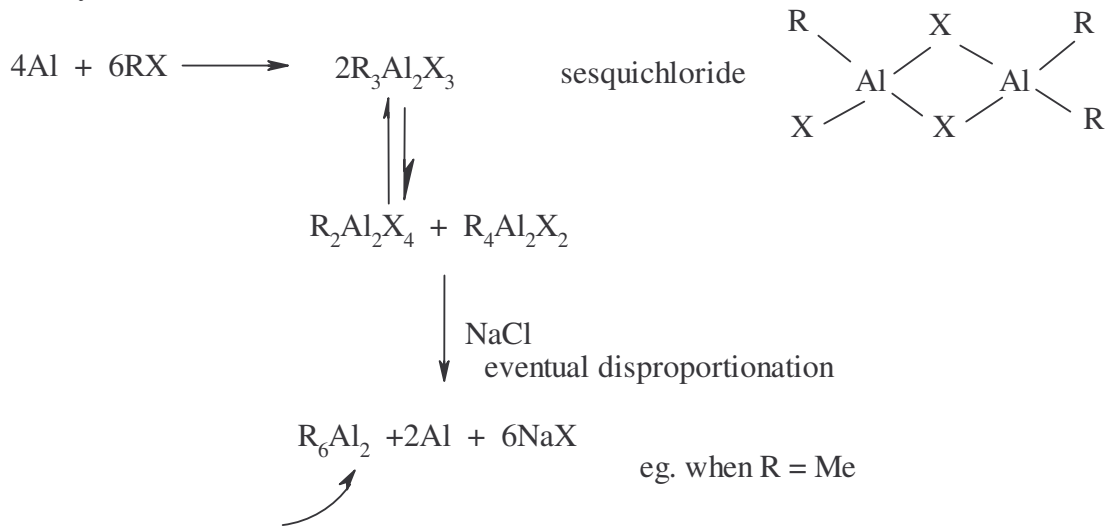
cleaning of coal tar



Aluminium

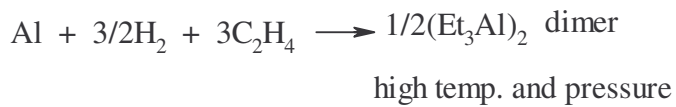
Preparation

1. alkyls industrial



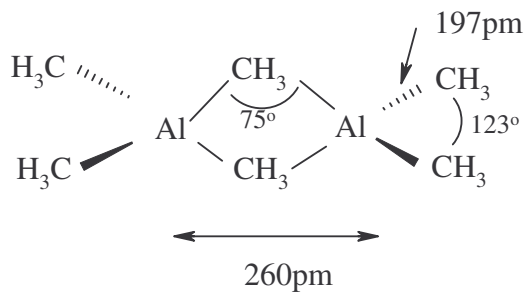
separate by fractional distillation as most volatile.
use aprotic solvent. N₂

2. Also direct processing using Zeigler method



Structure of Me₆Al₂ :

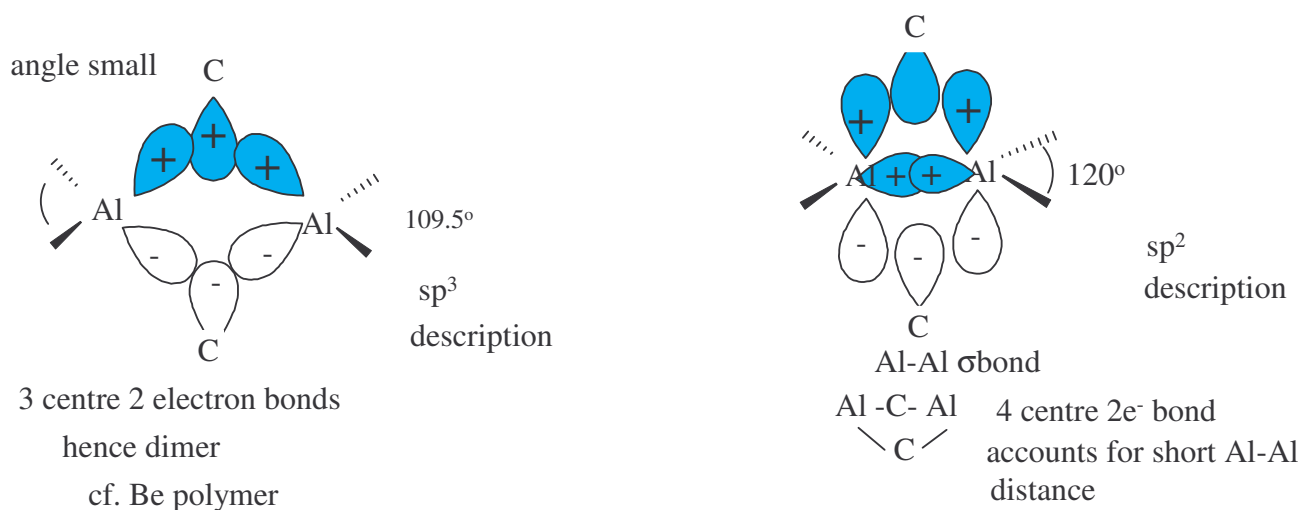
dimeric detailed analysis of bond lengths and angles → conclusion that bonding scheme for Al is intermediate between sp³ and sp²



Al-Al distance short

N.B. covalent radii of Al + Al = 2 x 126pm

Two bonding descriptions



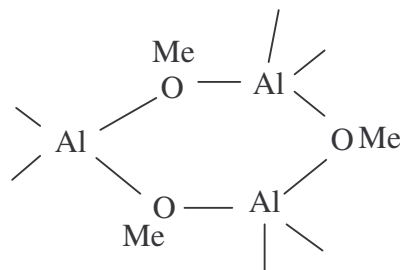
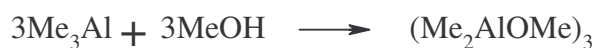
Aluminium -hard metal and AlR_3 are Lewis acids forming Lewis base adducts with donor ligands.

Hard base	Me_3P	↓	ΔH heat of complexation
increases	Me_3As		
	$\text{Me}_2\text{O} \geq -19$		form most stable
(thermodynamically)	$\text{Me}_2\text{S} -19$		compounds with hard bases.
	$\text{Me}_2\text{Se} -16$		
Soft Base	$\text{Me}_2\text{Te} \ll -16$		

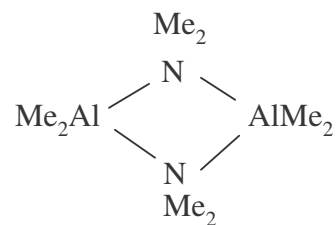
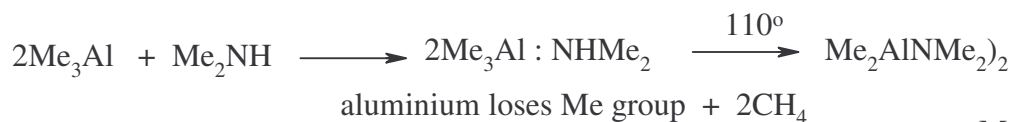
cf remember Zinc - $\text{ZnMe}_2 + \text{MeOH} \rightarrow (\text{MeZnOMe})_4$

cf remember Be - $(\text{BeMe}_2)_n + \text{Me}_2\text{NH}$ trimers/dimers

When an active H is present on the donor the 1:1 adduct is generally non isolable and elimination occurs.



Secondary amines give a similar reaction but give the dimer

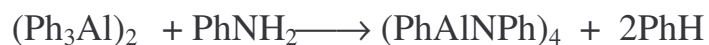


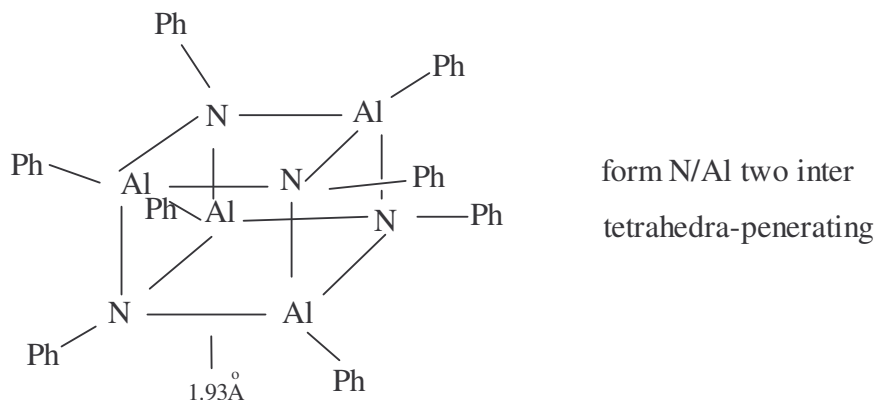
Dimer/trimer relationship determined as before: bond strain vs entropy.

eg. (Me₂Al-OMe)₃ yet (Me₂AlSMe)₂ steric interaction of Me groups

S larger than O can accommodate methyl groups and reduce steric strain.

System with 2 active hydrogens eg. aniline PhNH₂ -cubic structures





H atoms cleaving two Ph groups

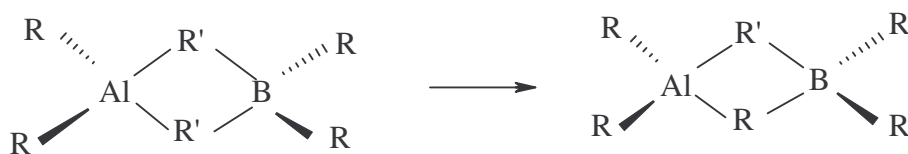
Very Brief Comparison of Chemistry of Al and B

1. Both form organyls when in oxidation state +3.
2. BR_3 do not form dimeric species possibly due to steric bonding (although B_2H_6 -boranes)

BR_3 not hydrolysed by water due to low B-C bond polarity but low molecular weight organyls e.g. BMe_3 do react readily with O_2

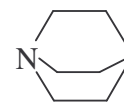
The lack of hydrolysis contrasts with $AlR_3 \Rightarrow Al(OH)_3$

3. AlR_3BR_3 dimers like $(AlR_3)_2$ show rapid inter- and intra- molecular exchange. This can be detected in the NMR ie.



4. Both AlR_3 (see earlier) and BR_3 form adducts with donor species.

eg. A table of the formation adducts with Me_3B using amines

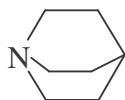


donor	NH_3	MeNH_2	Me_2NH	
ΔH_f^\ominus	-13.75	-17.64	-19.26	-19.94

—→ increasing donation as increase no. of Me substituents and then alkyl groups.

(purposely missed out Me_3N).

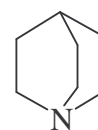
Me_3N would be expected to have ΔH_f^\ominus intermediate between Me_2NH and



actually it is -17.62 (i.e increased) due to some steric interaction of between the three methyl groups.

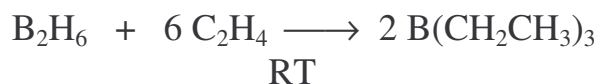
If starting BR_3 is tri-(1-naphthylboron) steric strain is so great that electronic effects are outweighed by steric arguments.

eg. The order of ease of complexation is now:



$\text{NH}_3 > \text{MeNH}_2 > \text{Me}_2\text{NH} > \text{Me}_3\text{N}$ and no reaction with

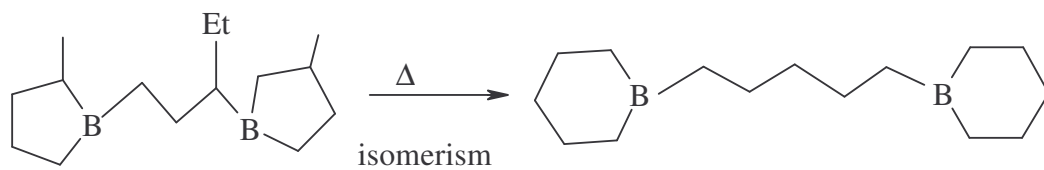
6. Both undergo hydroboration v hydroalumination



Readily undertaken even for sterically hindered alkenes.

7. Boron (not Al) hydrides are e^- deficient and give a range of cage structures all e^- deficient clusters. B_2H_6 , B_4H_{10} , B_5H_9 , $\text{B}_{10}\text{H}_{14}$

8. Boron forms ring complexes which are extremely stable. In reaction below might expect the formation of small volatile B-containing species, actually the alkyl chain rearranges.

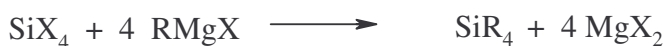


GROUP 14

Chemistry of Si, Ge, organometallic compounds v. similar but as descend the group the element-C bond strength decreases as increasing metallic character. Main difference between these species and Group 1-13 is that here we have a sufficient no. of e⁻ to have classical bonding.

Preparation of Organo-Silicon Compounds

1. Grignard reagent

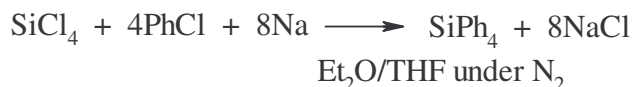


X = halogen preferably Cl or alkoxyl group

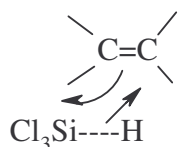
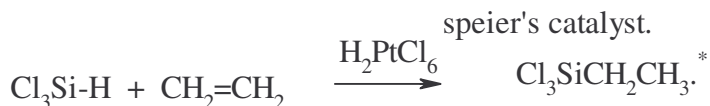
2. Lithium organyl.



3. Wittig Coupling (unlike above two reactions does not require preformed R-M)

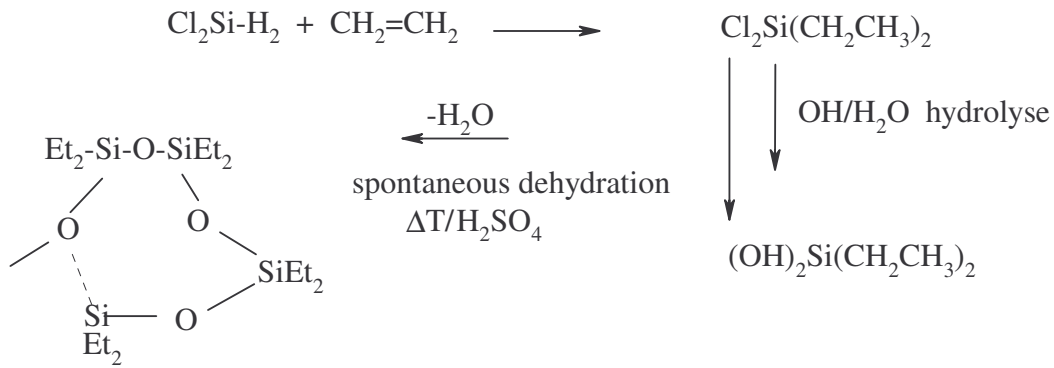


4. Hydrosilation



most efficient with electron withdrawing groups on the Si ⇔ polar Si-C bond

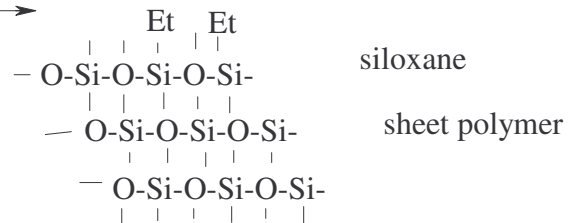
On hydrolysis this reaction can lead to Polymer formation



polymer chain or rings

supposing start with monoethyl cmpd instead

if hydrolyse* and dehydrate \longrightarrow



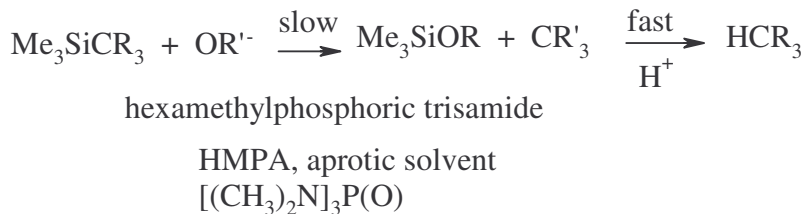
Siloxanes v. important depending on structure \Rightarrow oils, elastomers, resins. High thermal stability, corrosion resistance, flexible due to low barriers to conformational change. Low temp. coefficient of viscosity . High vacuum lubricants.

Reactions at Si-C bonds

Si-C bonds estimated to have only 10% ionic character: nucleophilic and electrophilic attack requires harsh conditions.

Nucleophilic attack (at Si)

1. alkyl silanes



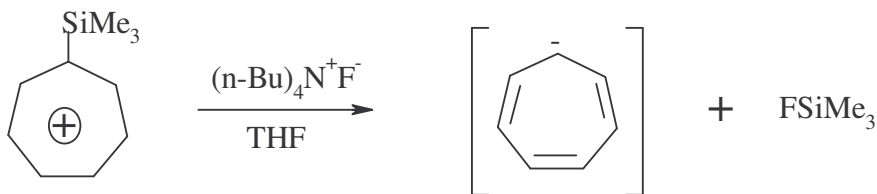
Reaction is faster if desilylation relieves ring strain in the starting material or if good leaving groups are present. ie. one in the β-position

e.g. the ripening of bananas can be hastened artificially using



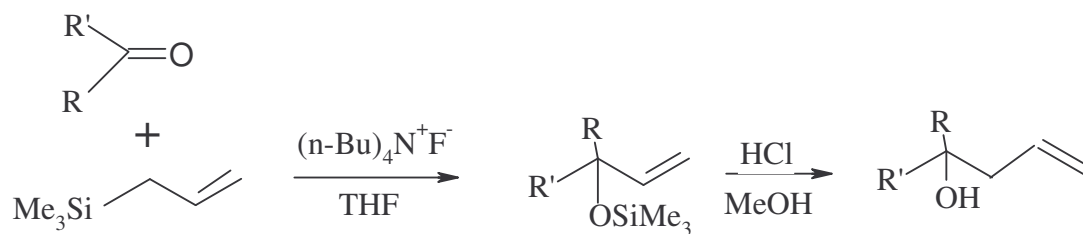
2. aryl silanes

Fluoride ion used as nucleophile (Si-F) $\Delta H_f = 565 \text{ kJmol}^{-1}$ (strongest known single bond)



3. allyl silanes

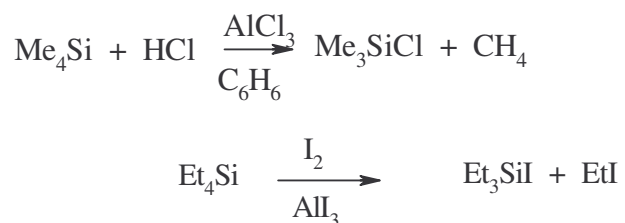
Sakurai reaction nucleophilic attack of F^- at Si \Rightarrow allyl anion as intermediate.



Regiospecific attack of allyl anion on carbonyl

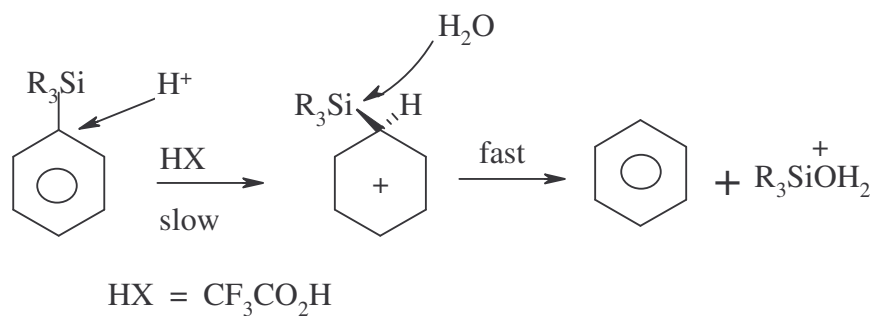
Electrophilic attack at C

1. allyl silanes in presence of strong Lewis acid as catalyst.



concentrated H_2SO_4 gives Si-C bond cleavage but \rightarrow siloxanes.

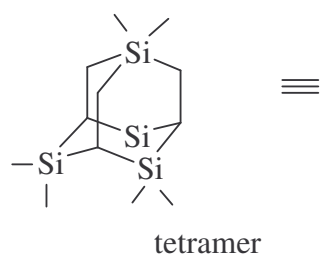
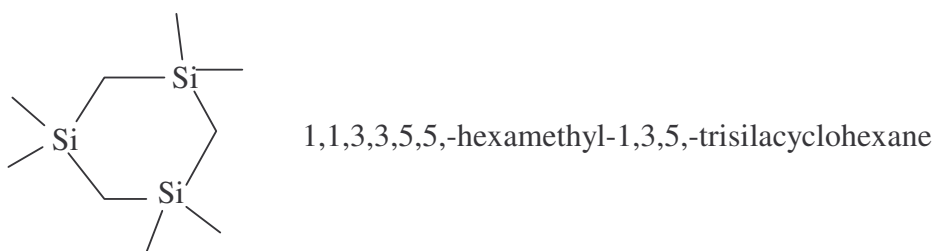
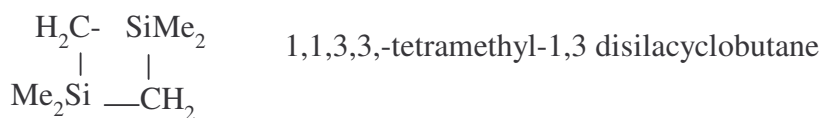
2. Aryl silanes protodesilylation



Cyclocarbosilanes

Generally SiMe_4 is stable and unreactive, obtainable pure, thermally stable to $700^\circ\text{C} \Rightarrow$ used as reference in ^{29}Si , ^1H , ^{13}C NMR - all give one signal sharp singlet.

However if Me_4Si is heated $> 700^\circ\text{C} \longrightarrow \sim 45$ compounds with $\text{bp} < 110^\circ/2\text{mmHg}$ 1 min. these include cyclic carbosilanes



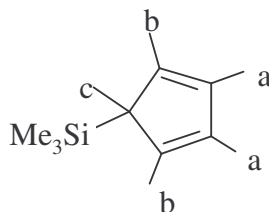
Adamantane.

3 cyclohexane rings in fused chair configuration.

(smallest hydrocarbon with diamond lattice). v. stable symmetrical

Fluxional organosilanes

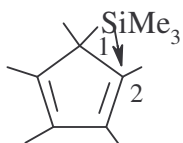
Result from a series of Si-C bond cleavages and reformations.



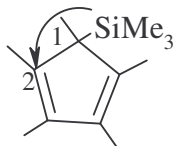
Expected ^1H NMR data 3 Cp signals - actually produces one signal.

Reason : molecule undergoing a fluxional process called ring whizzing

1) metallotropic 1,2-shift



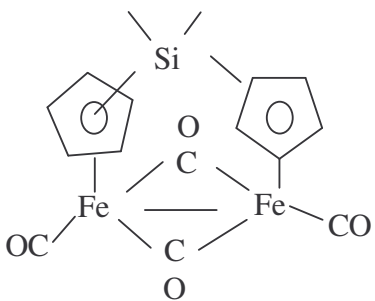
2) prototropic 1,2-shift $\sim 10^6$ times slower.



If ^1H NMR spectrum is cooled to -100°C then fluxional process is slowed down and expected signals observed.

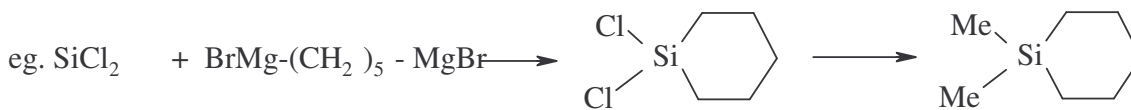
The slow prototropic shift is such that each isomer exists long enough for a mixture of products to be formed in the Diels-Alder reaction with $\text{RC}\equiv\text{CR}$

Me_2SiCp_2 gives an interesting complex with $\text{Fe}_2(\text{CO})_9$, that has analogous structure to one isomer of $(\text{CpFe}(\text{CO})_2)_2$.



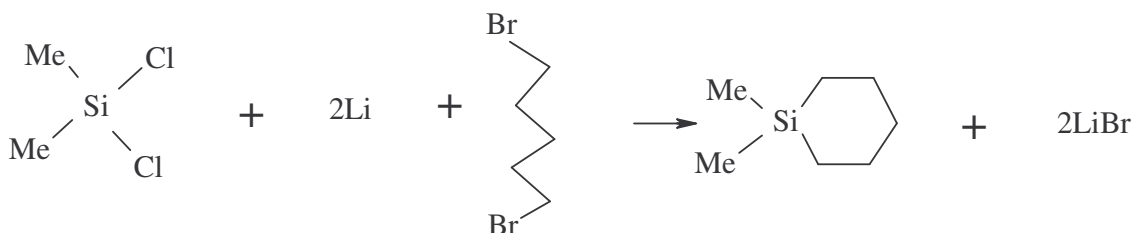
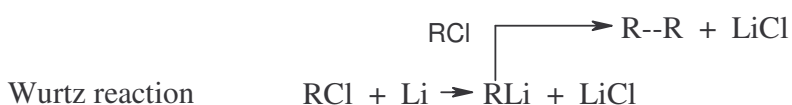
Formation of Cycloheterosilanes –saturated

-usually prepared from di-Grignard reagents or dihalides and metal.



Si-Cl bonds weak/polar easily hydrolysed

6-membered ring



Some known small cycloorganic compounds – silacycloalkanes

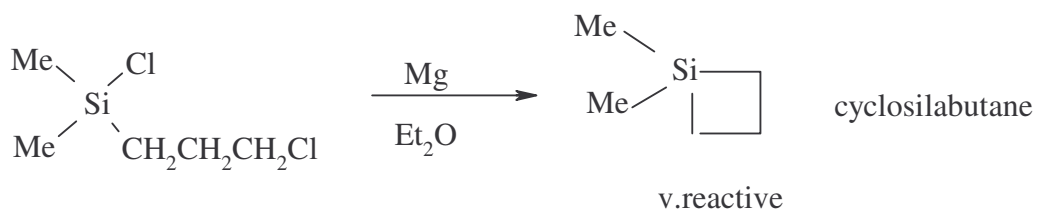


cyclobutane 90° average bond angle



cyclopropane 60° very reactive

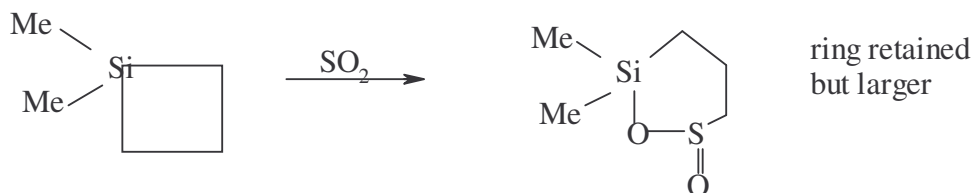
Silicon larger than C \Rightarrow increase in ring strain - observed in reactivity.



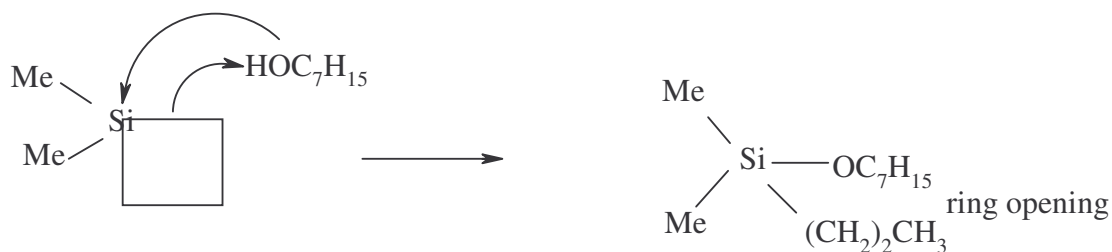
2 examples where reactions occurring predominantly to reduce the ring strain

(not due to Si-C bond polarity which is very low)

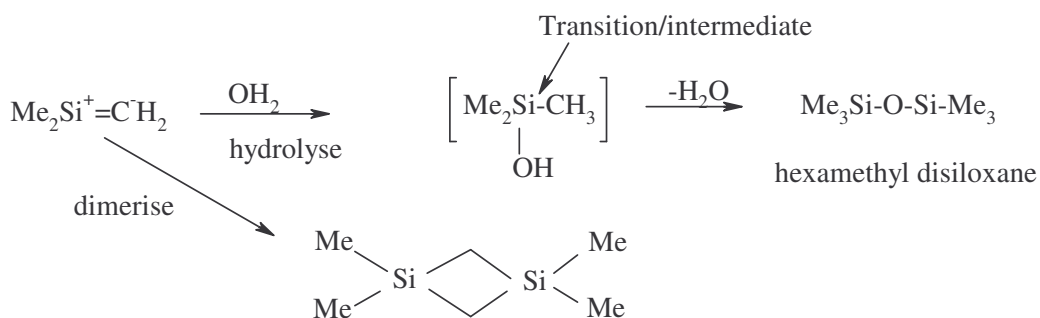
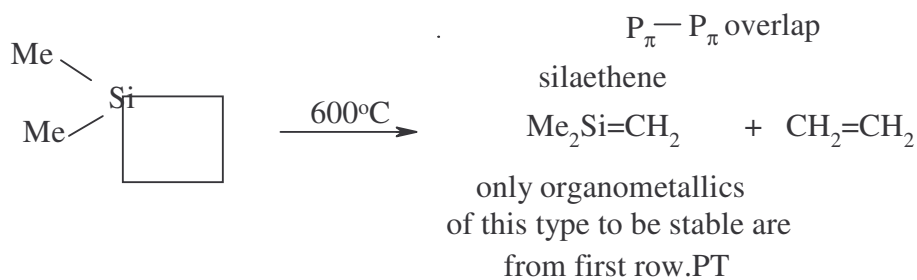
1. insertion of SO_2



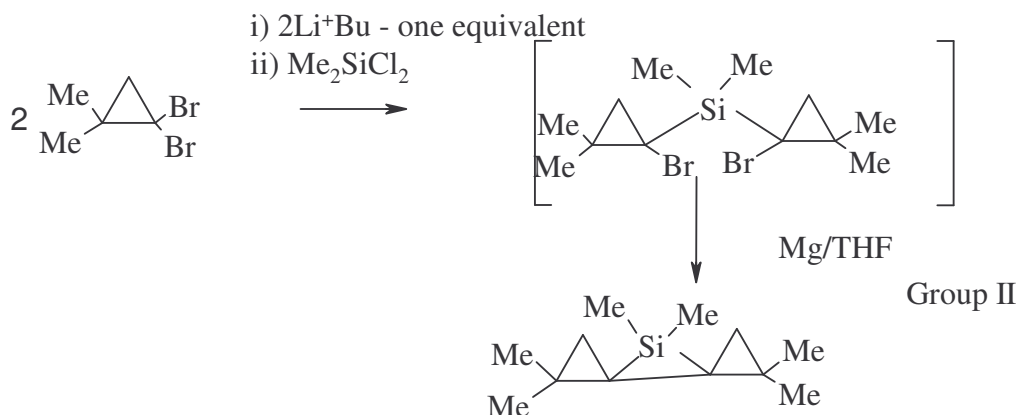
2. Reaction with heptanol -generally unreactive alcohol.



Thermal stability -relatively high 600°C due to necessity for Si-C bond cleavage.

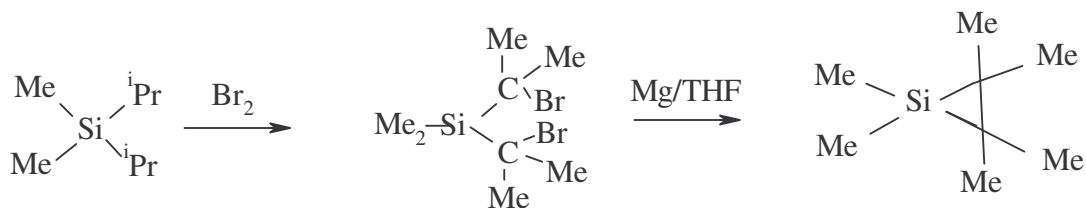


Silacyclopropanes- recent addition to chemistry of heterocycles



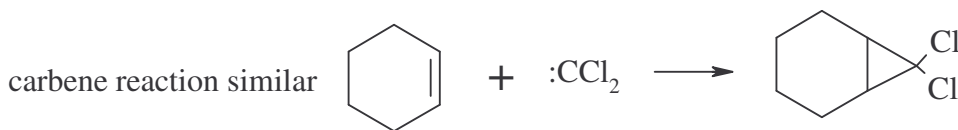
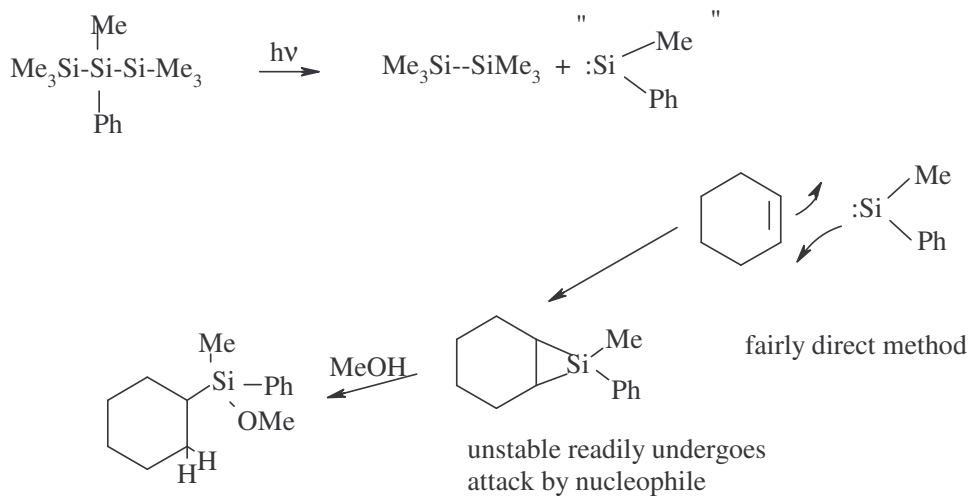
this species extremely reactive Si ring opening
occurs on reaction with O_2 , H_2O , $-\text{OOH}$, CCl_4 , RLi all at RT

Simple **dimethylsilacyclopropane** has been prepared but has a half-life of 81hrs and when impure is rapidly oxidised in air

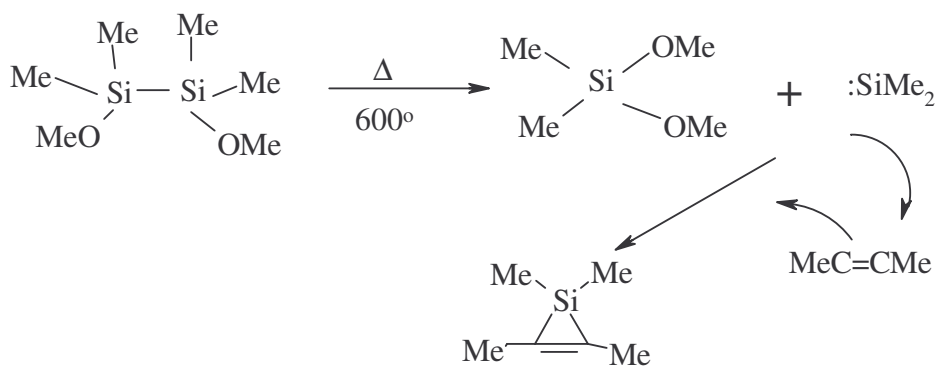


Alternate route for the formation of silacyclopropane rings is from silylene
(analogous to a carbene)

These are prepared photolytically $\text{R}_2\text{C}=\text{R}$



Alternative is to prepare the silylene in situ.



rapidly decomposed in air or water

but stable at RT in solution
thermally more stable with SiMe_3 substituents
on alkane.
double bond imposes 120° angle

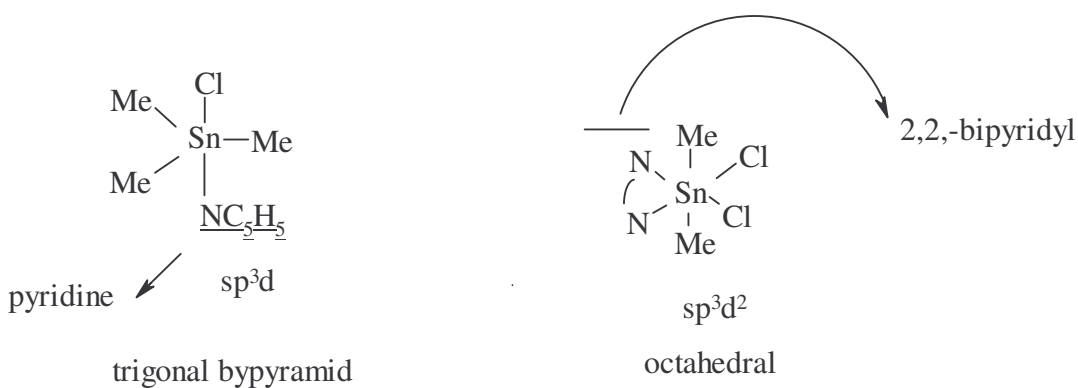
Tin

Advantages of organotin compounds - Mossbauer spectroscopy-
 ^{119}Sn NMR active $I = 1/2$

These techniques enable us to examine ligand interaction with a metal in two OS and coordination no.

Sn - as descend Group 14 stability of lower OS increases - inert pair effect eg. $\text{SnCl}_2(\text{s})$.

Second factor is the greater structural diversity observed for Sn compounds – can actually increase its coordination no. beyond 4. ie. not simply forming sp^3 hybridisation but uses its low-lying d-orbitals.



Mossbauer effect : due to recoilless emission and resonance absorption of γ rays. The ^{119}Sn nucleus emits a γ ray with 23.6eV energy . By moving the source (usually SnO_2 or Mg_2Sn) relative to the sample, the energy of the emergent ray is modulated by the Doppler effect until it matches the nuclear excitation energy of the sample. At this point absorption will occur at a relative velocity called the isomer shift IS.

The energy difference between the ground and excited state is influenced by the electron density about the nucleus. This influence is a result of ground and excited nuclei having different radii and hence differing electrostatic interaction with the surrounding S electrons. The IS is a comparison of the nuclear spin excitation energy of ^{119}Sn in different compounds relative to SnO_2 .

IS reported in mms^{-1} and positive values of IS represent an increase in S electron density relative to SnO_2 .

Mossbauer spectroscopy signals are split when the electronic environment of the nucleus alters from cubic , octahedral or tetrahedral symmetry. QS is the quadrupole splitting.

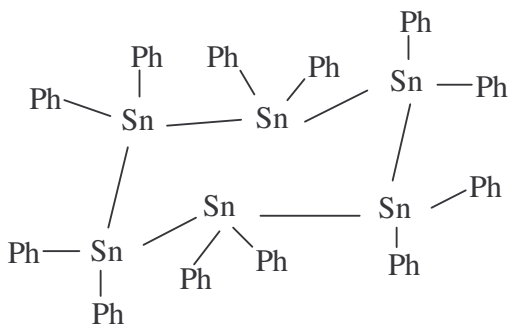
Preparation of SnR₂



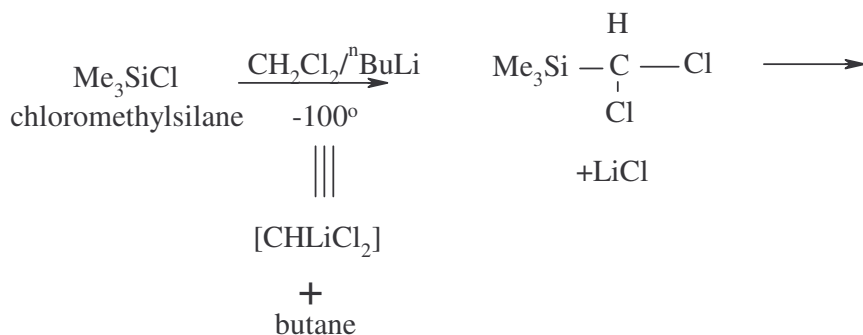
One way to test the formation of Ph₂Sn is to form 4-coordinate compounds by reaction with Br, methyl, or I in an oxidative addition reaction.

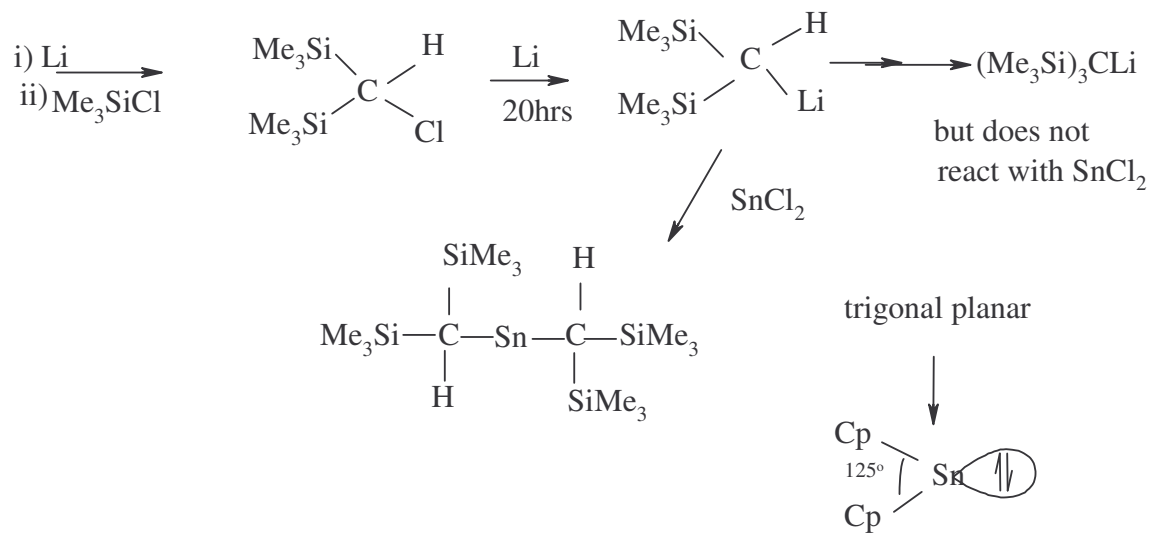
In the above case no reaction occurred. Why?

Reason - actually Ph₁₂Sn₆ from X-ray diffraction.

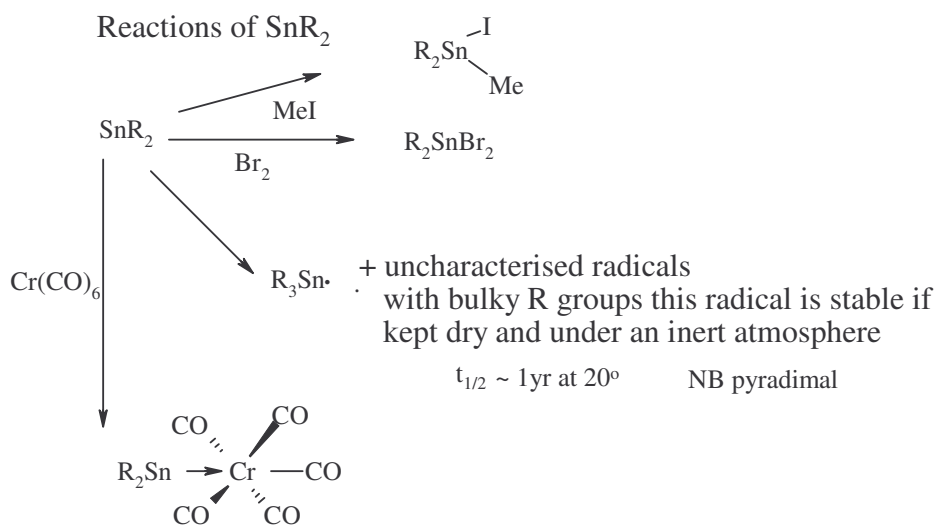


One strategy would be to increase the bulk of the SnR₂ groups so that their interaction prevents oligomerisation.





- Hence in SnR_2
- i) Sn in OS II
 - ii) acts as a donor (lone pair) (e^- donating R groups)
 - iii) add oxidatively



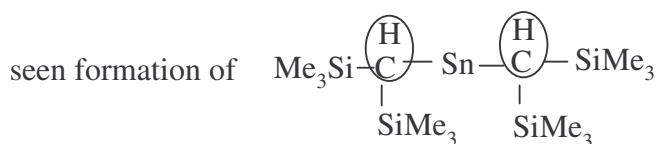
Even if bulky substituents are used oligomerisation/polymerisation can occur e.g. $\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{Sn}$ is monomeric in solution and dimeric in the solid state. The dimer does not possess a planar Sn_2C_4 framework. The $\text{Sn}=\text{Sn}$ bond distance (276pm) is too long. It is proposed that there is overlap of sp^2 hybrid orbitals and the vacant 5p atomic orbitals on the Sn atoms.

SnR_2 compounds are **thermochromic**- characteristic of Sn II compounds

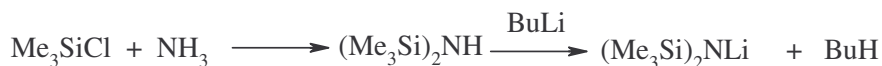


Three energy levels. For thermal reasons the central energy level is occupied at RT and the e^- are excited to higher level giving the compound its deep red colour. At low temp e^- fall in energy and no transitions possible \Rightarrow decolourised at low temperature.

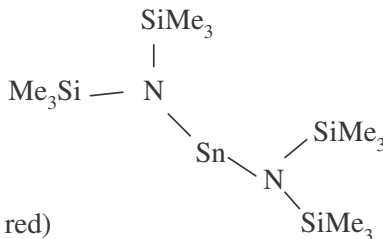
Formation of Sn-N containing compounds



and CH is isoelectronic with N hence we can form nitro compounds



reaction require no O_2
or H_2O



deep orange (rather than red)
because N-R groups less e- donating
than C-R

N more electronegative

Sn(II) amide

expect this cmpd to be less willing to undergo oxidative addition reactions

