

Main group organometallics

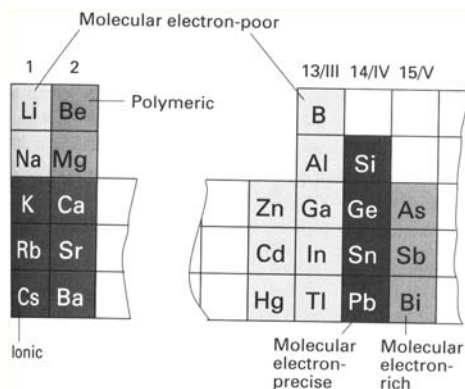
Shriver and Atkins, Chapter 15

Outline

- ◆ Organometallic compounds of alkali metals, alkaline earth metals. Zinc group, boron group and carbon group
 - Structure
 - Synthesis
 - Reactivity
 - Utility

Classification of organometallics

- ◆ An organometallic is a species with a metal (or metalloid) carbon bond
 - bonding is quite varied within the main group organometallics



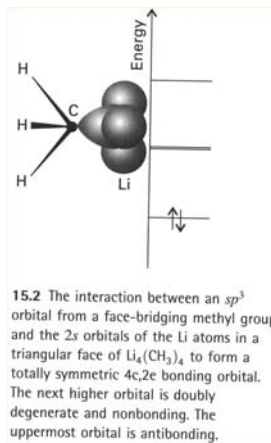
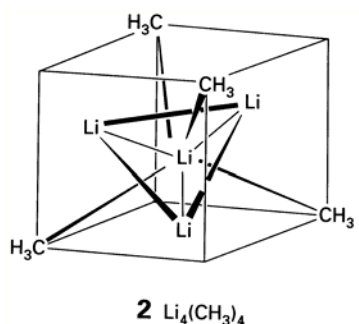
15.1 The classification of methyl compounds of the metals and metalloids.

Structure of alkali metal organometallics

- ◆ Some of them are salt like, KMe has a $NiAs$ structure, sodium naphthalide can be regarded as a salt
- ◆ However, some of them form aggregates with at least partial covalent bonding
 - $MeLi$ is tetrameric in the solid state and solution,
 - $EtLi$ is tetrameric in the solid state but hexameric in hexane

Bonding in MeLi

- ◆ MeLi exists as tetramers in non-coordinating solvents

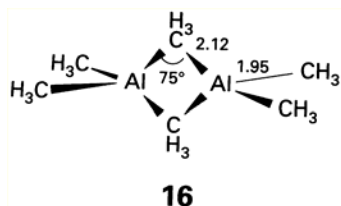


Structures of zinc group organometallics

- ◆ Me_2Hg , Me_2Cd and Me_2Zn are all linear simple molecular species
 - This is typical of d^{10} metals

Boron group organometallics

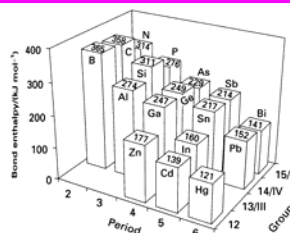
- ◆ AlMe_3 is dimeric. Dimer formation makes use of the empty orbital on the metal center
 - Dimer formation is common for aluminum organometallics
- ◆ BMe_3 is monomeric. The boron is too crowded to make dimer formation worthwhile



The bridging methyl requires a three center two electron bond like that found in B_2H_6

Stability

- ◆ The thermodynamic stability of various organometallics can be assessed by looking at either heats of formation or M-C bond strengths
 - Species involving heavier metals have weak M-C bonds leading to easy decomposition into radicals
 - » Use of Et_4Pb as an antiknock agent



153 Average M-CH₃ bond enthalpies (in kilojoules per mole) at 298 K. From the data in M.E. O'Neill and K. Wade, in *Comprehensive organometallic chemistry* (ed. G. Wilkinson, F.G.A. Stone, and E.W. Abel), Vol. 1, p. 5. Pergamon Press, Oxford (1982).

Table 15.2 Standard molar enthalpies of formation of gaseous methyl derivatives of the *p*-block elements ($\Delta_f H^\ominus / \text{kJ mol}^{-1}$)

Period	12	13/III	14/IV	15/V
2		$\text{B}(\text{CH}_3)_3$ -124	$\text{C}(\text{CH}_3)_4$ -167	$\text{N}(\text{CH}_3)_3$ -24
3		$\text{Al}(\text{CH}_3)_3$ -74	$\text{Si}(\text{CH}_3)_4$ -239	$\text{P}(\text{CH}_3)_3$ -101
4	$\text{Zn}(\text{CH}_3)_2$ +53	$\text{Ga}(\text{CH}_3)_3$ -45	$\text{Ge}(\text{CH}_3)_4$ -71	$\text{As}(\text{CH}_3)_3$ +13
5	$\text{Cd}(\text{CH}_3)_2$ +101	$\text{In}(\text{CH}_3)_3$ > 0	$\text{Sn}(\text{CH}_3)_4$ +21	$\text{Sb}(\text{CH}_3)_3$ +32
6	$\text{Hg}(\text{CH}_3)_2$ +94	$\text{Tl}(\text{CH}_3)_3$ > 0	$\text{Pb}(\text{CH}_3)_4$ +136	$\text{Bi}(\text{CH}_3)_3$ +194

Sources: D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Shumm, I. Halow, S.M. Baily, K.L. Churney, and R.L. Nuttall, *J. Phys. Chem. Ref. Data*, 11, Supplement 2 (1982); M.E. O'Neill and K. Wade in *Comprehensive organometallic chemistry* (ed. G. Wilkinson, F.G.A. Stone, and E.W. Abel), Pergamon, Oxford (1982).

Synthetic strategies

- ◆ Most organometallic species can be prepared using one or more of the following strategies
 - Direct reaction of a metal with an organohalide
 - Transmetallation reactions
 - Double replacement reactions
 - Hydrometallation

Direct reaction with an organohalide

- ◆ This approach works for electropositive metals, such as Li, Na, Mg, Zn, Al
 - $8\text{Li} + 4\text{MeCl} \rightarrow \text{Li}_4\text{Me}_4 + 4\text{LiCl}$
 - $\text{Mg} + \text{MeBr} \rightarrow \text{MeMgBr}$
 - » Grignard reagent

Transmetalation

- ◆ $M + M'R \rightarrow M' + MR$
 - The reaction works when M is higher up the electrochemical series than M' (more –ve standard reduction potential)
 - $2Ga + 3Me_2Hg \rightarrow 3Hg + 2Me_3Ga$
 - $4Li + 2Me_2Hg \rightarrow 2Hg + Li_4Me_4$
- ◆ Use of mercury organometallics for these reactions is in many ways convenient, but the mercury compounds are VERY toxic making them impractical for routine use

Double replacement

- ◆ $MR + EX \rightarrow MX + ER$ X - halide
 - These reactions usually work if M is more electropositive than E
- ◆ $4\text{LiEt} + \text{SiCl}_4 \rightarrow 4\text{LiCl} + \text{SiEt}_4$
 - This is in part going to be driven by the high lattice energy of LiCl

$M - R$	+	$E - X$	\rightarrow	$MX + R - E$
↑		↑		
Li	Mg	Al	Zn	Si
χ: 0.98	1.31	1.61	1.65	1.90
				B
				2.04
				As
				2.18
				P
				2.19

Hydrometallation

- ◆ Essentially addition of MH across a double bond
 - $\text{MH} + \text{R}_2\text{C}=\text{CR}_2 \rightarrow \text{R}_2\text{MC}-\text{CHR}_2$
- ◆ Commonly used for the prepⁿ of organometallics with the less electropositive metalloids B and Si
 - Remember hydroboration from your organic chemistry!
 - $\text{SiH}_4 + \text{C}_2\text{H}_4 \xrightarrow{-(\text{H}_2\text{PtCl}_6 \text{ cat})} \text{H}_3\text{SiCH}_2\text{CH}_3$
- ◆ The reverse reaction is called β -elimination and it is a common decomposition pathway for some compound (see aluminum alkyls later)

Susceptibility to oxidation

- ◆ Many main group organometallics are pyrophoric
 - Particularly species with incomplete valence shells on the metal
 - This requires very careful handling in oxygen and water free environments
- ◆ Compounds with complete valence shells such as SiR_4 and SnR_4 are not pyrophoric

Nucleophilic reactions

- ◆ Many of the useful reactions of organometallics employ them as nucleophiles (carbanion reagents)
 - e.g. Li, Al, Zn and Mg compounds

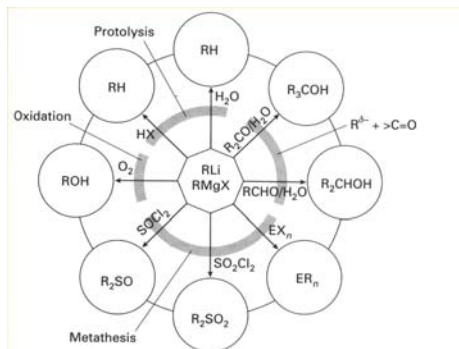
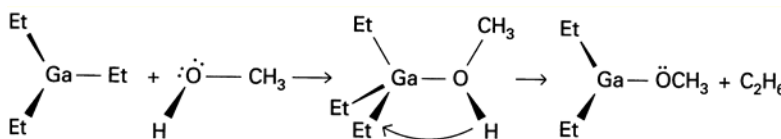
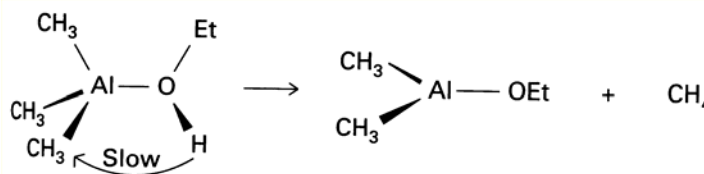


Chart 15.1 Typical protolysis, attack of carbonyl, metathesis, and oxidation reactions of alkyllithium compounds and Grignard reagents; X = halide; E = B, Si, Ge, Sn, Pb, As, and Sb.

Susceptibility to hydrolysis

- ◆ Compounds with Lewis acid character (vacant valence orbital on the metal center) hydrolyze/solvolyze readily



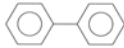



Other reactions of Lewis acids

- ◆ Acidic organometallics can react with bases to form a variety of adducts
- ◆ $\text{BPh}_3 + \text{LiPh} \rightarrow \text{LiBPh}_4$
 - Tetraphenyl borate anion is large enough that it gives low solubility salts with large alkali metal ions such as K^+ , Rb^+ and Cs^+
- ◆ $\text{Al}_2\text{Me}_6 + 2\text{NEt}_3 \rightarrow 2\text{Me}_3\text{AlNEt}_3$

Radical anion salts

- ◆ It is possible to make salts of alkali metals and large aromatic compounds. An electron is transferred from the metal to a π anti-bonding orbital on the organic to make the salt
 - They are soluble in organic solvents and strongly reducing making them useful reagents
 - » e.g. solvent cleaning for sodium naphthalide
 - Reducing power can be controlled by your choice of aromatic

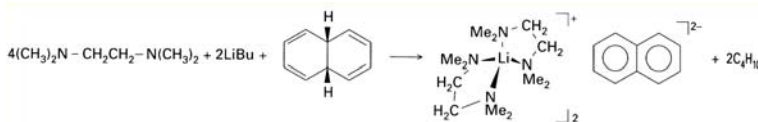
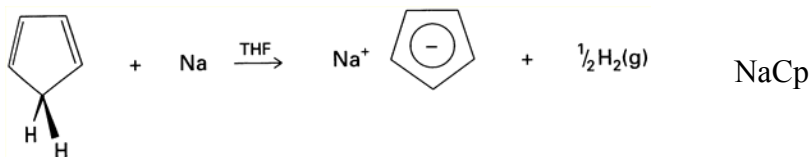
Table 15.3 Standard potentials of some conjugated hydrocarbons*

Compound		E^\ominus/V
Biphenyl		+0.00
Naphthalene		+0.09
Phenanthrene		+0.17
Anthracene		+0.78

*Relative to the value for biphenyl in 1,2-dimethoxyethane. Source: E. de Boer, *Adv. Organometal. Chem.* **2** 115 (1964).

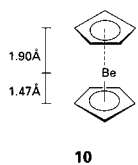
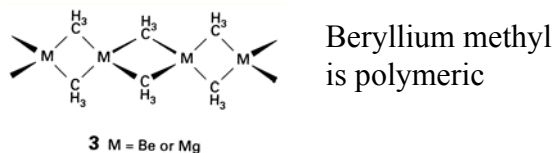
Other delocalized anion alkali metal salts

- ◆ Other salts containing delocalized anions can be prepared by deprotonating appropriate hydrocarbons
 - The best example of this is the cyclopentadienide (Cp) anion. Very widely used as a ligand in transition metal organometallic chemistry

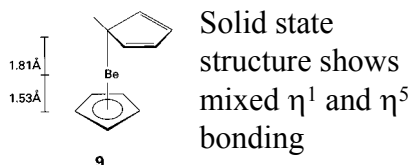


Organoberyllium

- ◆ Not very useful and extremely toxic
 - BeCl₂ + 2NaCp → BeCp₂



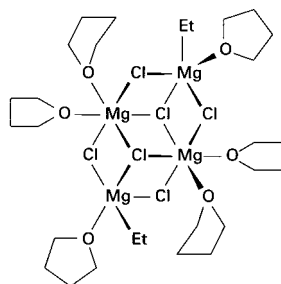
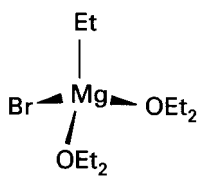
Hapticity is η⁵ in the gas phase



Solid state structure shows mixed η¹ and η⁵ bonding

Grignard reagents

- ◆ Very useful, however the presence of a basic ether can limit their application
 - Ether will react with compounds that are good Lewis acids
- ◆ Grignard reagents exist as a mixture of species due to equilibria in solution
 - $2\text{RMgX} \rightleftharpoons \text{MgR}_2 + \text{MgX}_2$ and more complex processes



Zinc group organometallics

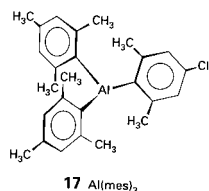
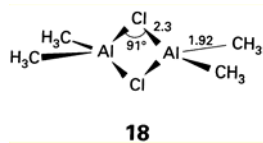
- ◆ Do not behave as good Lewis acids. Lewis acidity decreases on going down the group
- ◆ Decreasing bond polarity and carbanion like behavior on going down the group
 - e.g. Dialkylmercury compounds do not add across ketones
- ◆ On going down the group the softness of the metal center increases
 - Organomercury compounds show a strong tendency to bind to sulfur leading to high toxicity

Organoaluminum compounds

- ◆ Useful commercially for polymer synthesis catalysts
- ◆ Can be made cheaply
 - $2\text{Al} + 3\text{H}_2 + 6\text{RHC}=\text{CH}_2 \rightarrow \text{Al}_2(\text{CH}_2\text{CH}_2\text{R})_6$
 - » This is very important as they could not be widely used if they were expensive!
- ◆ Tend to dimerize

Organoaluminum dimers

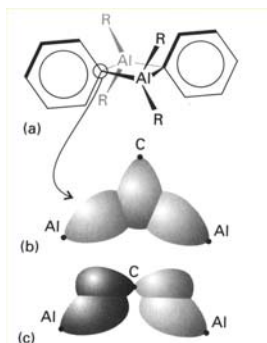
- ◆ Stability of dimers versus monomers depends on the bulk of the ligands
- ◆ Dimers with bridging ligand that have lone pairs tend to be more stable
- ◆ If more than one type of ligand is available the bridging preference is:
 - $\text{PR}_2^- > (\text{RO}^-, \text{X}^-) > \text{H}^- > \text{Ph}^- > \text{E}^-$



Bulk prevents dimerization

Triphenylaluminum

- ◆ The preference of Ph^- to be bridging over say an alkyl group is because the p system of the aromatic ring can be involved in the bridge bonding

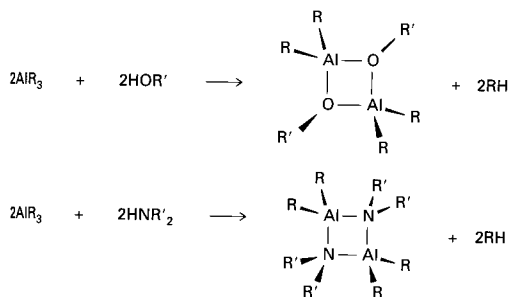


15.4 Structure and bonding of the phenyl bridge in Ph_2Al_2 . (a) Structure illustrating the perpendicular orientation of the bridging phenyl relative to the Al-C-Al plane. (b) The 3c,2e bond formed by a symmetric combination of C and Al orbitals. (c) An additional interaction between the $p\pi$ orbital on C and an antisymmetric combination of Al orbitals.

Routes to aluminum alkoxides and amides

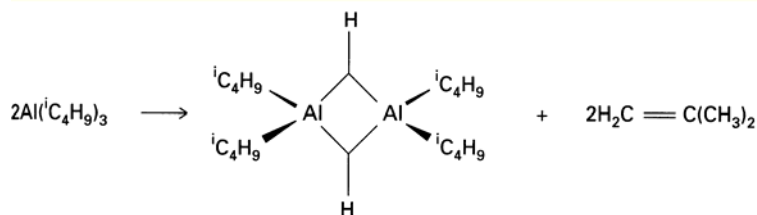
- ◆ Reaction of simple aluminum alkyls with alcohols and amines provides a clean simple route to alkoxides and amides

- Byproducts very readily removed (methane or ethane will just bubble out of solution)
- Much cleaner than say reaction of the alcohol with aluminum chloride



Decomposition of aluminum alkyls

- ◆ Aluminum alkyls with beta hydrogen can undergo thermal decomposition by a process called β -elimination



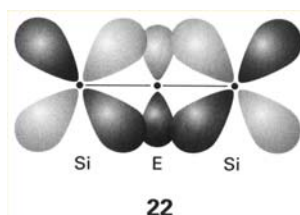
Preferred over decomposition to give radicals

Heavier IIIA organometallics

- ◆ Carbanion character decreases on going down the group
- ◆ Hydrolysis follows trend, $\text{Al} > \text{Ga} > \text{In} > \text{Tl} > \text{B}$
- ◆ Compounds in an oxidation state of I occur for the heavier metals
 - TlCp is a versatile alternative to NaCp
 - » Not reducing and TlX is very insoluble

Organosilicon compounds

- ◆ Commercially important as a consequence of the properties of silicone and perhaps in the future silicon polymers
 - Silicones used as gaskets, waterproofing agents etc.
 - Silicon polymers may find use in electronics as resists
- ◆ Properties of silicone polymers arise due to easy deformation of the Si-O-Si bonds as a consequence of delocalization



Chloroalkylsilanes

- ◆ Key intermediates in the synthesis of silicones and other compounds
 - The halogens can undergo a wide variety of substitution reactions
- ◆ Made on a very large scale
 - $\text{Si} + \text{RX} \text{ (250-550}^\circ\text{C/Cu)} \rightarrow \text{R}_n\text{SiX}_{4-n}$

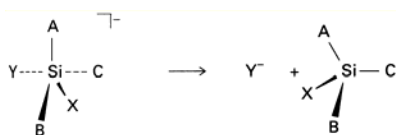
Substitution in silanes

- ◆ All substitution reactions are thought to go via an associative mechanism with a five coordinate intermediate (similar to S_N2)
- ◆ Reactions with good nucleophiles and leaving groups often give inversion of configuration
- ◆ Reaction involving poor leaving groups often give retention of configuration
 - Long lived 5-coordinate intermediate undergoes pseudorotation

Substitution pathways



Pseudorotation prior to loss of the leaving group gives retention of configuration

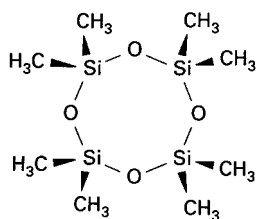


Siloxanes

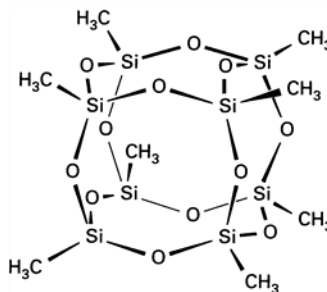
- ◆ Hydrolysis of chloroalkylsilanes produces bridged compounds called siloxanes
 - $\text{Me}_3\text{SiCl} + \text{H}_2\text{O} \rightarrow \text{Me}_3\text{SiOH} + \text{HCl}$
 - $2\text{Me}_3\text{SiOH} \rightarrow \text{Me}_3\text{Si-O-SiMe}_3 + \text{H}_2\text{O}$
- ◆ Hydrolysis of Me_2SiCl_2 can produce ring and chain oligomers
- ◆ Hydrolysis of MeSiCl_3 can produce cages

Siloxane oligomers

- ◆ Siloxanes can be open chain, rings or cages



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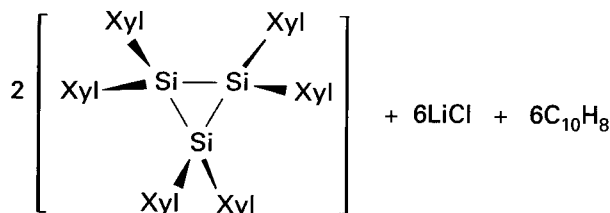
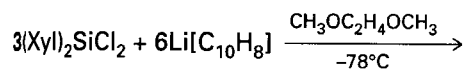
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Silicones

- ◆ Siloxanes can be converted to high molecular weight silicone polymers
 - $[\text{cyclo-Me}_2\text{SiO}]_4 + \text{Me}_3\text{SiOSiMe}_3 \xrightarrow{-(\text{H}_2\text{SO}_4)}$
 $\text{Me}_3\text{SiO}[\text{SiMe}_2\text{O}]_{4n}\text{SiMe}_3$
 - Polymers can be used as waterproofing, seals and implants
- ◆ Note hydrolysis and rearrangement reactions do not result in the breaking of Si - Me bonds

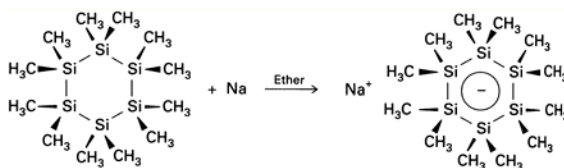
Polysilanes

- ◆ Si-Si bonds can be made by reductive coupling



Bonding in Si-Si backbone polymers

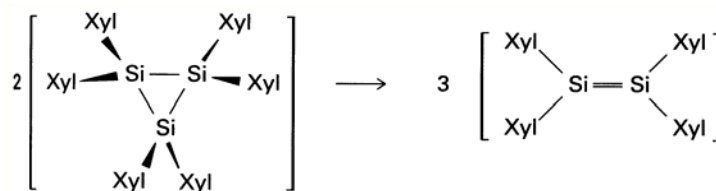
- ◆ Polymers show characteristics of sigma delocalization
- ◆ Near UV absorption $\sigma \rightarrow \sigma^*$ moves to longer wavelengths as polymer increases in length
- ◆ Polymers are being considered as photoresists and for photorefractives
- ◆ Can form delocalized anions



Disilaethenes

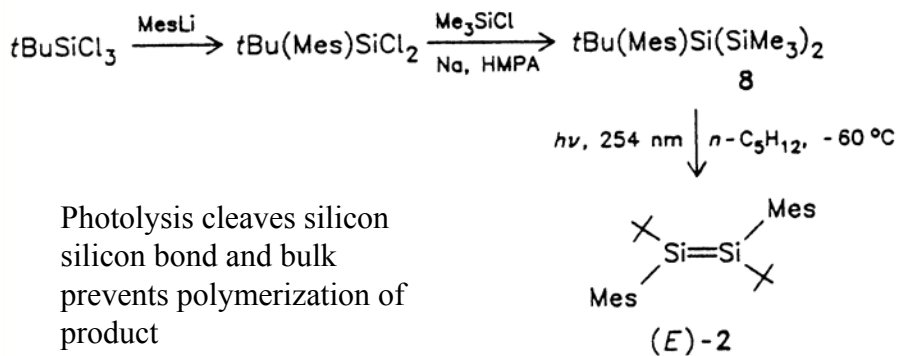
- ◆ Compounds containing Si=Si are not widespread
- ◆ Si=Si is weaker than two Si-Si bonds and the double bond is not usually kinetically stable
 - C=C is also weaker than two C-C, but kinetic helps out!
- ◆ To prepare disilaethenes bulky ligands are required to protect the double bond
- ◆ Rotation around the double bond is easier than for carbon compounds
- ◆ The double bond and its substituents are not always planar

Synthesis of disilaethenes from cyclic trisilanes



Photolysis provides the energy to drive the reaction and steric bulk prevent polymerization

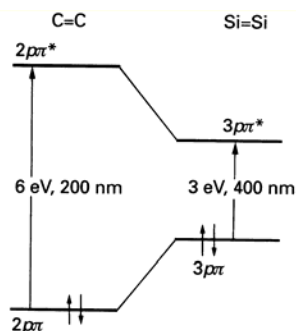
Synthesis of disilaethenes from linear trisilanes



Photolysis cleaves silicon silicon bond and bulk prevents polymerization of product

Bonding in Disilaethenes

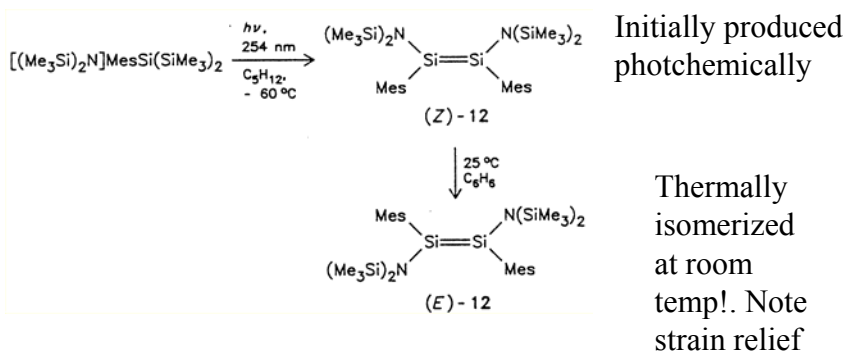
- ◆ Si=Si bond is much weaker than C=C bond consequently the HOMO LUMO gap is much lower leading to absorption in the visible



15.6 Approximate energy levels for alkenes and disilaethenes. The energy separations are obtained from the analysis of UV absorption spectra. (From R. West, *Angew. Chem. Int. Ed. Engl.* 26, 1201 (1987).)

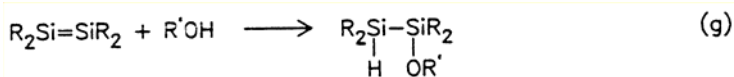
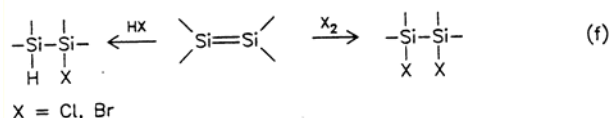
Isomerization of disilaethenes

- ◆ Isomerization of disilenes is much easier than for alkenes because the Si=Si bond is weaker



Reactivity of Disilaethenes: 1,2 - Additions

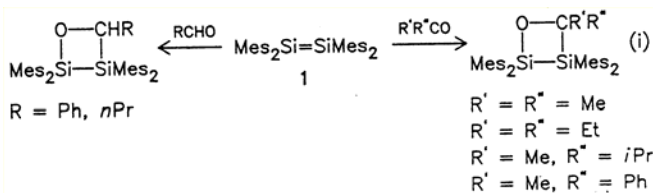
- ◆ The reactivity of disilaethenes has some things in common with alkenes including 1,2 addition processes, but they tend to be more reactive!



This would not go without a catalyst for an alkene

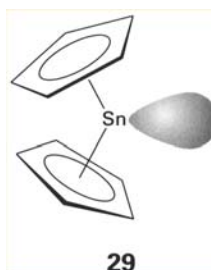
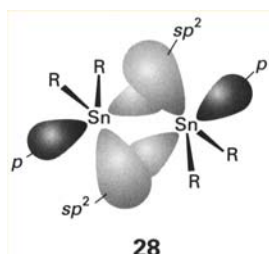
Reactivity of Disilaethenes: 2+2 cycloadditions

- ◆ Unlike simple alkenes, disilaethenes readily undergo a variety of 2+2 cycloadditions



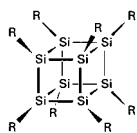
Digermaethenes and distannaethenes

- ◆ Do not have planar geometry
- ◆ Sn(II) or Ge(II) compounds may be preferred over a double bond
 - Due to low strength of M-M bond



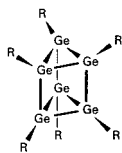
Rings ,chains and clusters

- ◆ As multiple bonds are not favoured by Si, Ge and Sn clusters may be formed rather than unsaturated compounds



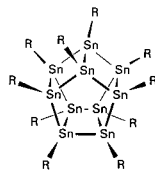
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Note that this is an isomer of a cyclooctene like structure

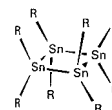


32 R = CH(Si(CH₃)₃)₂

Note that this is an isomer of a benzene like structure!



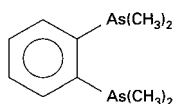
34 R = (C₂H₅)₂C₆H₃



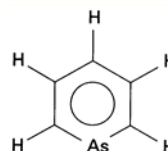
31 R = CH₃, CH₂CH₃

Organoarsenic compounds

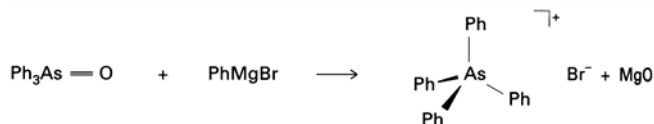
- ◆ Found with oxidation states of (III) and (V).
- ◆ Can form catenated and ring structures
- ◆ Can form multiple bonds



36 $C_6H_4(As(CH_3)_2)_2$, diars



38 Arsabenzene



As - As bonds

- ◆ It is possible to make As-As bond by reductive coupling

