# Organometallic compounds of group 14
# Organotin (silicon, lead) compounds

$SnR_4$   $SnR_{4-n}X_n$   $SnR_3^-$   $SnR_3\bullet$   $SnR_3^+$   $SnR_2$

$[SnR_{4-n}X_{n+m}]^{m-}$

High electronegativity, complete electronic configuration

**Si**: strong, covalent Si-C bond, small central atom: stable compounds, monomeric, poor electrophiles.

**Sn**: essentially covalent Sn-C bond, low polarity, not very strong. Sn in $SnR_4$ is not electrophilic; mixed derivatives might instead be electrophilic.

**Pb**: weaker, more polar Pb-C bond, larger central atom: less stable compounds, more electrophilic, unstable towards reductive elimination to Pb(II), particularly in $RPbX_3$.

# Organometallic compounds of group 14
# Organotin (silicon, lead) compounds

Organo**silicon** compounds find their main application in the manufacture of silicones, organically modified silicas (Ormosils) and as reagents in organic synthesis (protective groups, reducing agents, cross-coupling).

Organo**tin** compounds have widespread applications in polymer chemistry (PVC stabilizers), in organic synthesis (Stille cross-coupling), and as biocides (fungicides, algicides…).

Organo**lead** compounds have been extensively applied as anti-knock agents in petrols (production up to $10^6$ t/year, 20% of Pb world production), but are toxic and unstable.

# Synthetic methods: $ER_4$

Direct synthesis (industrial):

$Si/Cu + 2RX \rightarrow R_2SiX_2$ Rochow-Mueller process
$Sn/Cu + 2RX \rightarrow R_2SnX_2$

Need for high T (200 °C) and a catalyst (Cu). Product mixtures are obtained, with the diorganoderivative as prevailing one.

$4Et\text{-}Cl + 4Na\text{-}Pb(50:50 \text{ alloy}) \rightarrow PbEt_4 + 4NaCl + 3Pb$
Three quarters of Pb are recovered unreacted in this process…

$EtMgX_2^- \rightarrow MgX_2 + Et\bullet$
$Pb + 4Et\bullet \rightarrow PbEt_4$
Anodic oxidation (on Pb anodes) of Grignard reagents

# Synthetic methods: $ER_4$

Metathesis:

$MX_4 + 4M'R \leftrightarrows MR_4 + 4M'X$

$MR_{4-n}X_n + nM'R' \leftrightarrows MR_{4-n}R'_n + nM'X$

Partial substitution difficult, but no formation of «ate» complexes. Stable heteroleptic compounds accessible. The general instability of $PbX_4$ is a limitation.

Peculiar case with $PbMe_4$ (analogy with Tl).

$PbX_2 + 2MeLi \leftrightarrows 2LiX + [PbMe_2]$

$[PbMe_2] + MeI \rightarrow PbMe_3I$

$PbMe_3I + MeLi \leftrightarrows PbMe_4 + LiI$

Generally: $PbX_2 + 2RM \leftrightarrows 2MX + [PbR_2]$

$3[PbR_2] \rightarrow Pb + Pb_2R_6$ “diplumbane”

$2Pb_2R_6 \rightarrow 3PbR_4 + Pb$ upon CONTROLLED heating

# Synthetic methods: $ER_4$

Hydrometallation:

$R_3MH + CH_2{=}CHR' \leftrightarrows R_3MCH_2CH_2R'$

With Sn, the reaction is often radicalic (weak Sn-H bond, AIBN can be employed as initiator); *cis* stereoselectivity might be lost…
With Si, the reaction is not radicalic but it generally needs a (metal) catalysts (usually a Pt compound), which also imparts regio- and stereoselectivity.
With Pb the reaction can be either radicalic or concerted.

Nucleophilic attack of triorganostannyl anions (Sn):

$R_3SnX + 2M \rightarrow R_3SnM + MX$ M= Li, Na…
$Me_3SnNa + RC_6H_4Br \rightarrow RC_6H_4SnMe_3 + NaBr$

# Synthetic methods: $MR_{4-n}X_n$ (M= Sn, Pb)

Electrophilic substitution on R:

$SnR_4 + \mathbf{HX} \rightarrow SnR_3X + HR \rightarrow SnR_2X_2 \rightarrow SnRX_3$

$SnR_4 + \mathbf{X_2} \rightarrow SnR_3X + XR \rightarrow SnR_2X_2 \rightarrow SnRX_3$

$PbR_4 + \mathbf{HX} \rightarrow PbR_3X + HR \rightarrow PbR_2X_2 \rightarrow \mathbf{PbRX_3} \rightarrow \mathbf{PbX_2 + RX}$

Reactions under stoichiometric control for Sn (the number of R/X substitutions depends on the stoichiometric ratio of the reagents)

Reaction mechanism not fully understood: concerted reaction (potentially solvent-assisted) or radical mechanism (single electron transfer, SET).

The reaction with $PbR_4$ is NOT under stoichiometric control: formation of product mixtures. Single products sometimes isolable by selective precipitation but unstable even in the solid state (radical exchange)!

$2PbR_3X \rightarrow PbR_4 + PbR_2X_2$

$2PbR_2X_2 \rightarrow PbR_3X + PbRX_3$

$PbRX_3 \rightarrow PbX_2 + RX$

# Synthetic methods: $SnR_{4-n}X_n$

The Kocheshkov reaction:

$3SnR_4 + SnCl_4 \leftrightarrows 4SnR_3Cl$

$SnR_4 + SnCl_4 \leftrightarrows 2SnR_2Cl_2$

$SnR_4 + 3SnCl_4 \leftrightarrows 4SnRCl_3$

Reaction under stoichiometric control. The mechanism consists in a series of electrophilic substitutions at the C atom bound to Sn (concerted mechanism) in which the relative rates depend on the reactivity of the reagents under consideration (the electrophilicity of $SnR_{4-n}X_n$ decreases with decreasing n…).

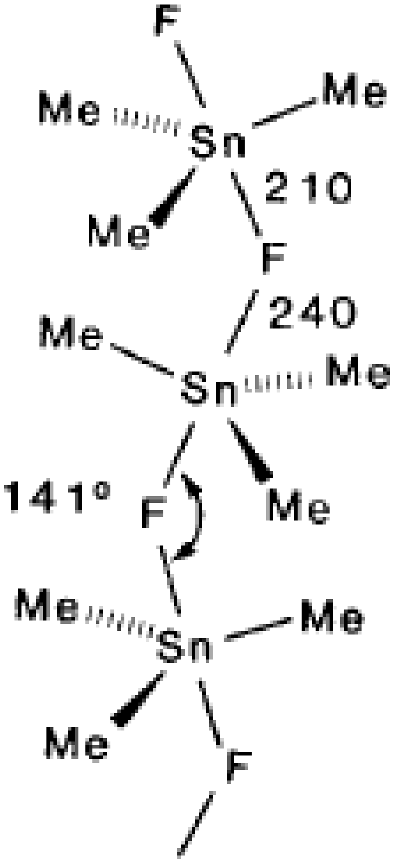
Reaction unsuitable for Pb due to the instability of $PbX_4$.

$SnX_2 + RX \rightarrow RSnX_3$

The stability of inorganic Sn(II) compounds and of $RSnX_3$ is exploited here.

# Structure and aggregation of $SnR_{4-n}X_n$

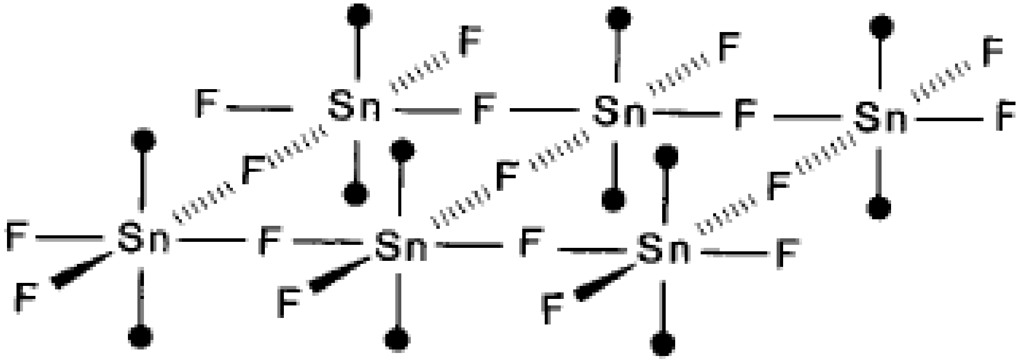
Tin organohalides are soluble in several solvents and exhibit well defined melting points, except when X= F, in which case they are insoluble and decompose before melting. These compounds display polymeric structures in thich F forms asymmetric bridges; consequently, Sn in these compounds behaves as a Lewis acid.



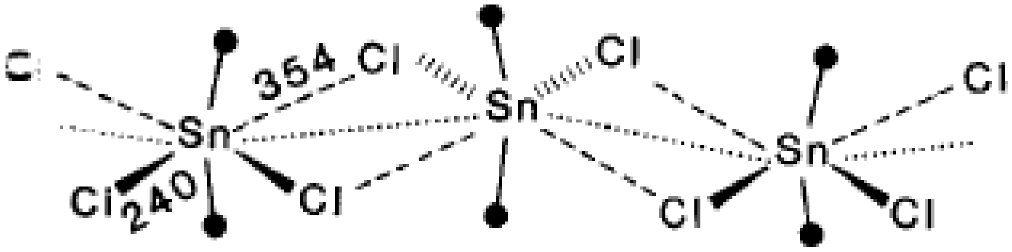
Other monohalides or pseudohalides form similar structures, which are however much less stable.

# Structure and aggreagation of $SnR_{4-n}X_n$

With tin diorganodihalides, more stable strcutres are formed (higher electrophilicity of Sn → hexacoordination)



$d(Sn–F) = 212$ pm —● —$CH_3$



$d(Sn–C) = 221$ pm

# Solution behaviour of $SnR_{4-n}X_n$

In noncoordinating solvents, the fluorides are insoluble, whereas the other halides dissolve. Sn remains electrophilic and promptly coordinates Lewis bases maintaining the coordination geometry that it exhibits in the solid.

In water, the Sn-X bond is hydrolised (it is NOT a simple ionic dissociation):

$SnR_3X + 2H_2O \leftrightarrows SnR_3(OH_2)_2^+ + X^-$

$SnR_2X_2 + 4H_2O \leftrightarrows SnR_2(OH_2)_4^{2+} + 2X^-$

These aquocations are acids, monoprotic when Sn is pentacoordinated, diprotic when Sn is hexacoordinated:
$SnR_3(OH_2)_2^+ + H_2O \leftrightarrows SnR_3(OH)(OH_2) + H_3O^+$

$SnR_2(OH_2)_4^{2+} + 2H_2O \leftrightarrows SnR_2(OH)_2(OH_2)_2 + 2H_3O^+$

# Solution behaviour of $SnR_{4-n}X_n$

If the aquocations are neutralised with NaOH, the corresponding hydroxides are obtained, which spontaneously condense losing water and forming the oxides (stannoxanes):

$$2SnR_3(OH)(OH_2) \leftrightarrows R_3Sn\text{-}O\text{-}SnR_3 + 3H_2O$$

$$nSnR_2(OH)_2(OH_2)_2 \leftrightarrows (R_2SnO)_n + 3nH_2O$$

Such dehydration can be reversed by adding acid.

The corresponding reactions with organosilicon halides does NOT produce the cationic aquocomplexes but the hydroxides, which are unstable and undergo irreversible condensation to (poly)siloxanes (silicones).

# Organometal hydrides

Binary tin(IV) or lead(IV) hydrides are unstable and tend to decompose to the elements. However, di- or triorganometal hydrides decompose only at high T. They are prepared from the corresponding halides via metathesis:

$4SnR_3X + LiAlH_4 \rightarrow 4R_3SnH + LiAlX_4$

The same reaction can be employed also to prepare organosilicon hydrides.

These organohydrides are employed as reagents in hydrometallation reactions or as mild reducing agents:

$R\text{-}NCO + 2R_3SnH \rightarrow R\text{-}NH\text{-}CH{=}O + R_3SnSnR_3$

Interestingly, the Sn-H can break homolitically (under light or in the presence of radical initiators) or heterolitically (in the dark or in the presence of metal catalysts).

# Organotin hydrides

Eterolytic $H^-$: $SnR_3H + MeCOOH \rightarrow SnR_3OOCMe + H_2$

Eterolytic $H^+$: $SnR_3H + Ti(NR'_2)_4 \rightarrow (R_3Sn)_4Ti + 4HNR'_2$

Homolytic H•: $2SnR_3H + HgR'_2 \rightarrow (R_3Sn)_2Hg + 2R'H$

Homolytic scission of the Sn-H bond can be also employed in radicalic hydrostannolysis reactions of organic halides (formal reduction to hydrocarbon):

$SnR_3H \rightarrow R_3Sn\bullet + H\bullet$

$R_3Sn\bullet + R'X \rightarrow R_3SnX + R'\bullet$

$R'\bullet + SnR_3H \rightarrow R'H + R_3Sn\bullet$

# Organotin compounds with Sn-Sn bonds

The tendency to catenation decreases along group 14, since the strength of the element-element bond decreases (C-C 258 kj/mol; Sn-Sn 151 kj/mol), but is present also in organometallic derivatives. Stable compounds are formed when all Sn atoms in the chain are substituted by organic groups (or by H).

$2R_3SnX + 2Na \rightarrow R_3Sn\text{-}SnR_3 + 2NaX$ Wurtz-type reaction

However, $R_3Sn\text{-}SnR_3 + 2Na \rightarrow 2R_3SnNa$

It is imperative to work with stoichiometric quantities of Na!

Alternative: reaction between hydrides and oxides:

$2R'_3SnH + R_3Sn\text{-}O\text{-}SnR_3 \rightarrow 2R'_3Sn\text{-}SnR_3 + H_2O$

$R'_2SnH_2 + R_3Sn\text{-}O\text{-}SnR_3 \rightarrow 2R_3Sn\text{-}SnR'_2\text{-}SnR_3 + H_2O$

# Group 14 organometals with M-M bonds

Compounds with Sn-Sn bonds are easily oxidised by $O_2$, and are a practical source of radicals:

$R_3Sn\text{-}SnR_3 \rightarrow 2R_3Sn\bullet$ under irradiation

Stannyl radicals are pyramidal, and depending on the substituents can be also very stable! Chiral stannyls, RR'R''Sn-, can be transferred retaining their configuration.

Organolead compounds are only known to form dimers, which have a tendency to disproportionate:

$R_3Pb\text{-}PbR_3 \leftrightarrows PbR_4 + PbR_2$ much shifted to the left

Evidence: reaction with electrophiles (Pb(II) is attacked!):

$R_3Pb\text{-}PbR_3 + 2HCl \rightarrow PbR_4 + PbCl_2 + 2RH$

Compare: $R_3Sn\text{-}SnR_3 + HCl \rightarrow R_3SnH + R_3SnCl$

$R_3SnH + HCl \rightarrow R_3SnCl + H_2$

# Divalent organotin compounds

$R_2SnX_2$ + 2Na → "$R_2Sn$" + 2NaX

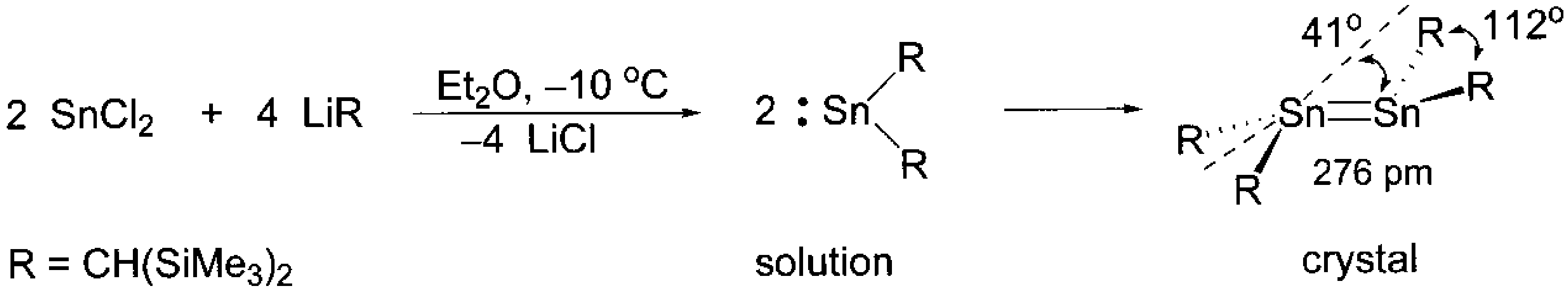
Stannylenes are not stable and usually oligomerize to cyclic compounds, the most stable of which is the six-membered ring. Sn hybridization remains $sp^3$.

If R is a sterically bulky group, monomeric stannylenes can however be isolated ($sp^2$ hybridization, singlet)!

In the solid state, «multiple» Sn-Sn bonds are formed between stannylene units; their structure is however very peculiar (weak interaction between filled $sp^2$ and empty p orbitals on the Sn atoms).

Stannylenes are Lewis bases (electron doublet in the $sp^2$ orbital) and form very stable adducts with Lewis acids such as $BF_3$: the empty p orbital on Sn becomes saturared by electron donation from the filled p orbitals of F.

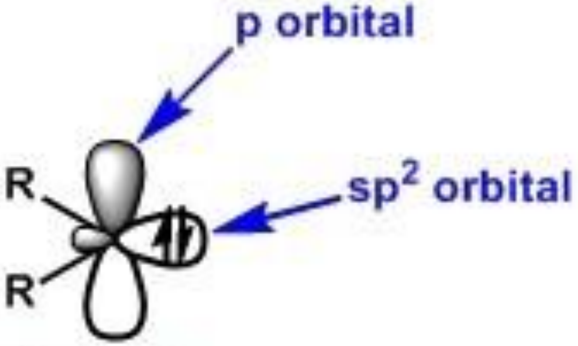
# Divalent organometal compounds of group 14



Divalent organolead compounds (plumbylenes) can be analogously prepared, but they tend to disproportionate instead of oligomerizing. They can be isolated and characterized ($sp^2$ hybridization, singlet) only if R is a bulky group (ad es. $–CH(SiMe_3)_2$).

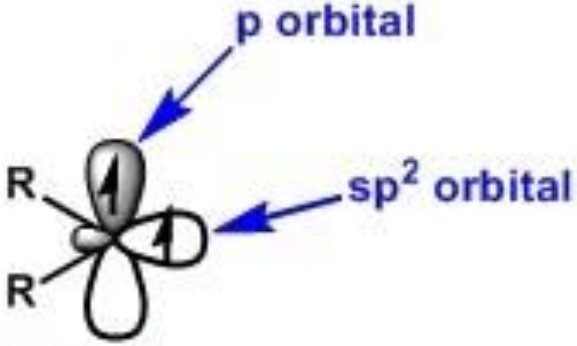
Plumbylenes, like stannylenes, are associated in the solid state and are Lewis bases, forming very stable adducts with Lewis acids such as $BF_3$.

# Divalent organometal compounds of group 14



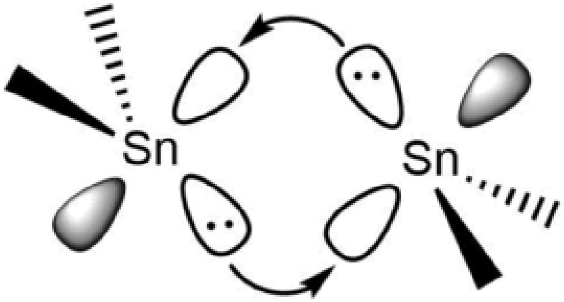
singlet carbene

sp$^2$ orbital contains
2 paired electrons

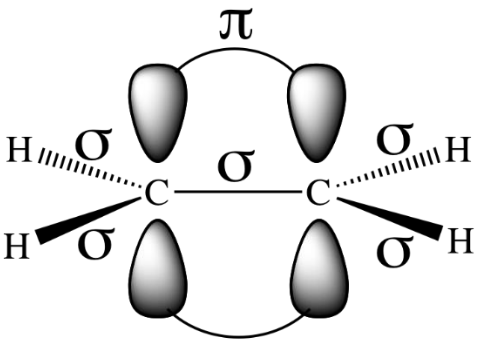


triplet carbene

sp$^2$ and p orbital each
contain 1 electron



**2 donor-acceptor interactions**



**2 covalent bonds (σ + π)**

Carbenes can exist both in singlet and triplet states. Descending in the series silylenes, germylenes, stannylenes and plumbylenes the stability of the singlet state **increases**.

# Synthetic applications

Organoelement compounds of group 14 are poor nucleophiles…

- Addition of allyltin compounds to carbonyl compounds (mechanism analogous to the corresponding reaction with B):

$R'_3Sn\text{-}CH_2\text{-}CH{=}CRR' + R''_2C{=}O \rightarrow R'_3Sn\text{-}O\text{-}CR'_2\text{-}CRR'\text{-}CH{=}CH_2$

- Cross-coupling: Stille (Sn) reaction/Hayashi (Si) reaction:

$R'SnR_3 + R''X \rightarrow R'\text{-}R'' + XSnR_3$ cat.= [Pd]
$R'SiR_3 + R''X \rightarrow R'\text{-}R'' + XSiR_3$ cat.= [Pd]

Migratory attitude: alkynyl > vinyl > aryl > allyl, benzyl > alkyl.

Problem with Si: strong Si-C bond, metathesis difficult. Addition of promoters (fluoride) necessary.

Problem with Sn: triorganotin halides are toxic. It is possible to use $RSnX_3$, but the reactivity is lower.

# Other applications of organotin compounds

- PVC stabilzers

Main application of organotin compounds (60% of industrial production). Compounds of type $R_2SnX_2$ (X= long-chain thiolate) do: 1) suppress the development of HCl from dehydrochlorination of chloroallylic sites in the PVC chains during thermal curing of the polymer (substitution of Cl with X); 2) <u>inhibit the thermal degradation of the polymer</u> (formation of stable Sn radical species);

- Biocides (antifungi, antialgae etc.)

Compounds of type $R_3SnX$. Very efficient and economical, the final decomposition product is innocuous $SnO_2$. However, they also liberate cations $R_3Sn^+$, which are toxic, particularly when R= short alkyl chain. Alternatives are currently sought after.