

Group 14 : Tin Chemistry



$\text{Sn} : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^2$



A. G. Massey, *Main Group Chemistry*, 2nd ed., John Wiley, New York, pp. 213 – 264.

- Symbol Sn from Latin *stannum*
- One of the longest known elements
- Tin has more stable isotopes (10) than any other element.
- Bronze items from ca. 3500 B.C.E. contain 10-15% Sn alloyed with Cu.
- Cassiterite, mineral SnO_2 , found in Britain, was an early source.
- Malaysia, Russia, and Bolivia are current principal sources.
- About 40% of tin used in plating to provide a non-toxic coating for sheet metal and “tin” cans.
- Important component of many alloys.
 - Solder 50% Sn, 50% Pb
 - Aluminum solder 86% Sn, 9% Zn, 5% Al
 - Pewter 85% Sn, 6.8% Cu, 6% Bi, 1.7% Sb
 - Bronze 80% Cu, 15% Sn, 5% Zn
 - Bell metal 78% Cu, 22% Sn
 - Babbitt 90% Sn, 7% Sb, 3% Cu

The Group 14 Elements

Element	Electronic Configuration	1 st Ionization Energy (kJmol ⁻¹)	2 nd Ionization Energy (kJmol ⁻¹)	Covalent Radius (Å)
^{12.011} ₆ C	1s ² 2s ² 2p ²	1086	2352	0.77
^{28.0855} ₁₄ Si	[Ne] 3s ² 3p ²	786.1	1576	1.17
^{72.61} ₃₂ Ge	[Ar] 3d ¹⁰ 4s ² 4p ²	761.5	1537	1.22
^{118.710} ₅₀ Sn	[Kr] 4d ¹⁰ 5s ² 5p ²	708.5 ↓	1412 ↓	1.41
^{207.2} ₈₂ Pb	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	715.5 ↑	1450 ↑	1.54

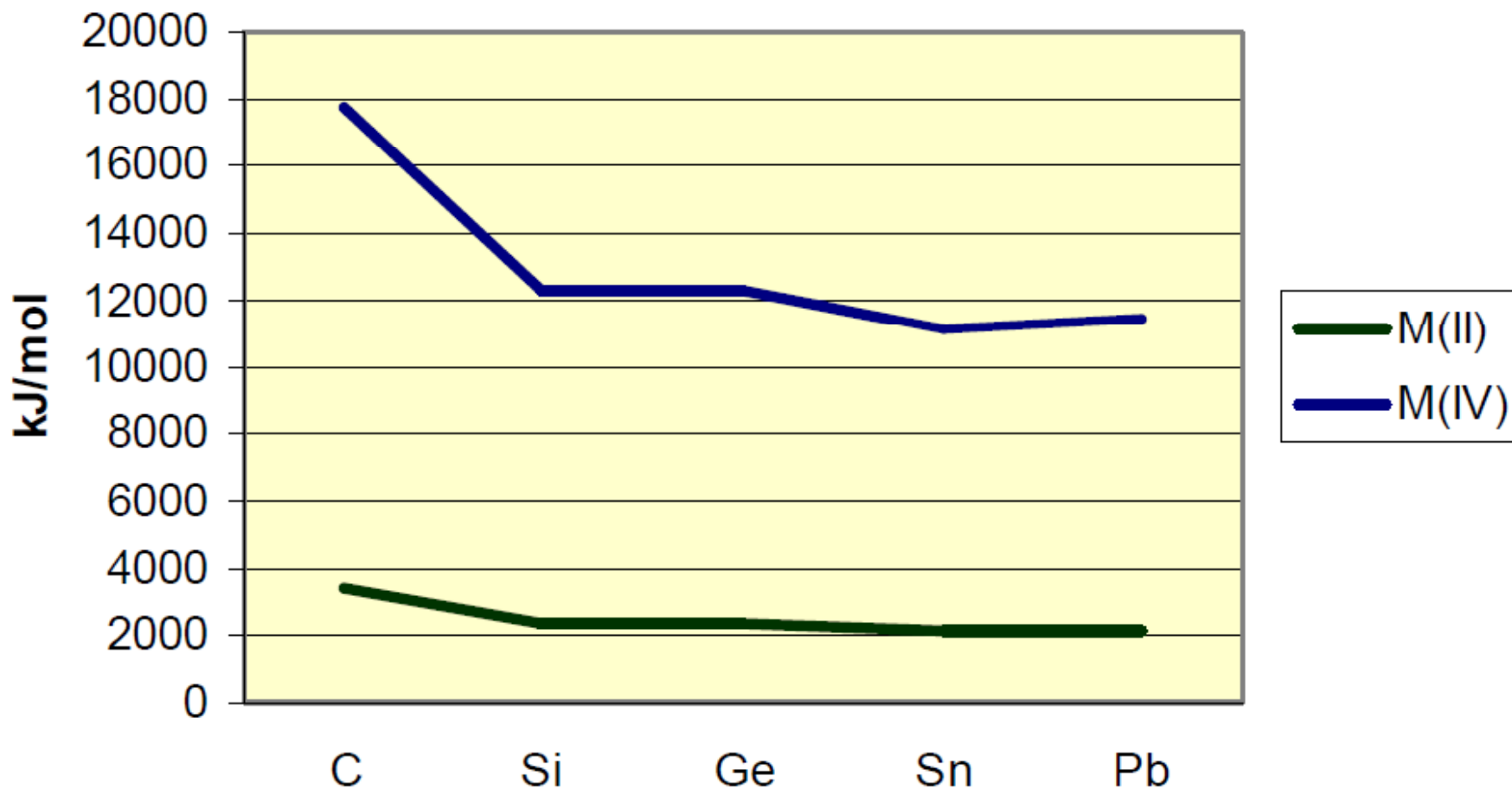
- All Group 14 elements have the valence configuration ns²np².
- Stable carbon and silicon compounds are observed in the +4 state.
- Going down the group the +2 state becomes more stable.

Group 14 Ionization Energies

- The ionization energies for Group 14 elements are irregular due to inner *d* orbitals (Ge, Sn, Pb), inner *f* orbitals (Pb) and relativistic effects (Pb).
- The exceedingly ***high energies required to form M^{4+} ions*** (next slide), coupled to the fact that such ions would be small and highly polarizing, means that the existence of M^{4+} cations is highly unlikely.
- ***Group 14 compounds are predominantly molecular*** with only SnO_2 , PbO_2 and the Sn, Pb fluorides thought to have significant ionic character.

In all these compounds, the oxidation state is merely a formalism, because all are molecular (not ionic) compounds.

Group 14 Ionization Energies

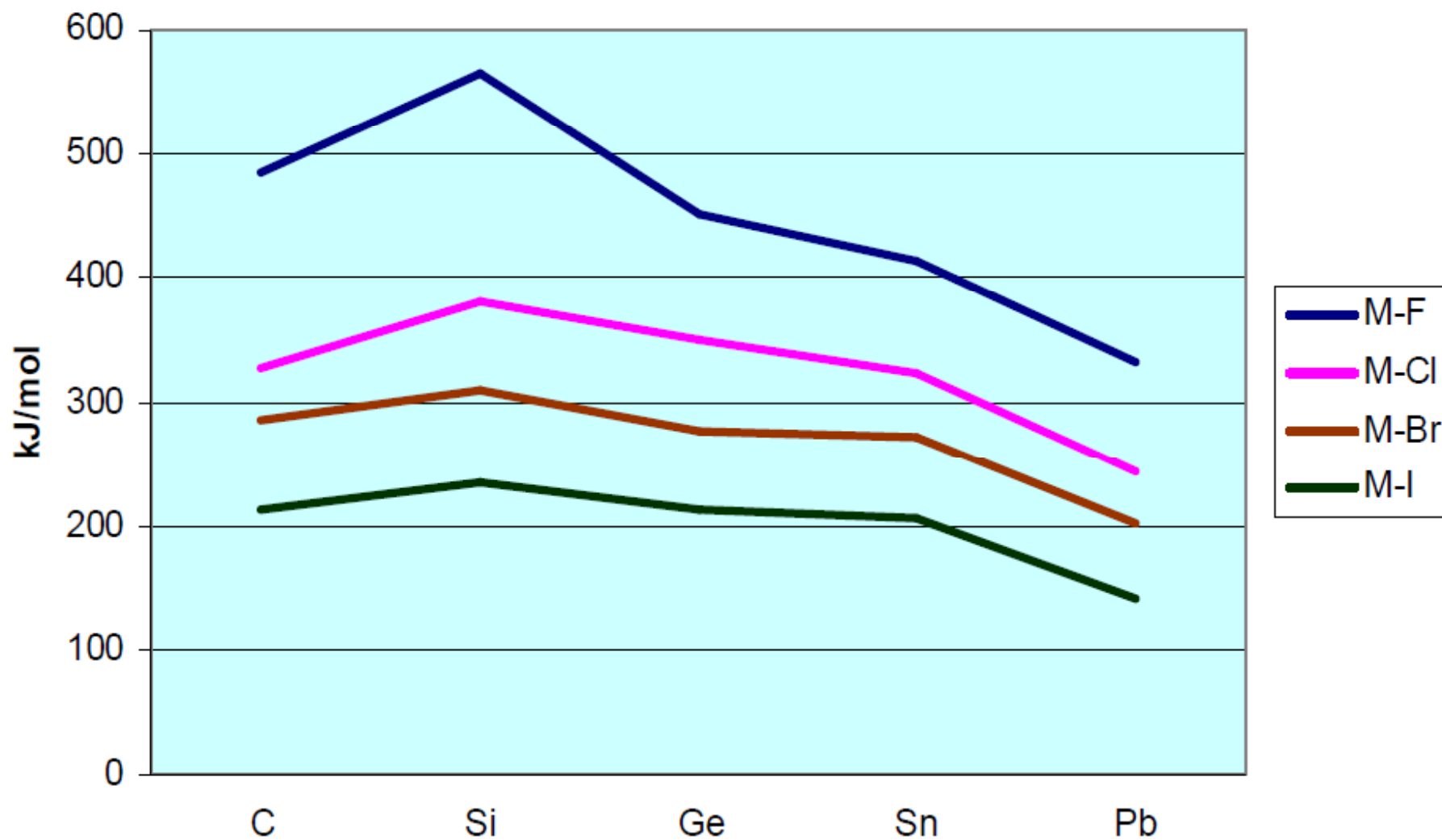


- Ionization energy drops dramatically after C, declining slowly through the rest of the group with Pb breaking this trend due to decreased shielding and enhanced relativistic effects.

Inert Pair Effect

- ***The increasing stability of the lower state (+2) as we descend the Group*** has been called the “inert pair effect” for the tendency of the ns^2 configuration to be retained (*most prominent for Sn and Pb*).
- This has nothing to do with inherent “inertness” of the ns^2 configuration, but rather ***simply a consequence of thermodynamics***.
- Although the energy “cost” of forming M(IV) is high for the lighter elements, the “pay-back” of bond formation is high, too.
- Bond strengths peak at Si, slowly decline through Sn, and then drop off significantly at Pb.
- At Ge and Sn, both M(II) and M(IV) states are stable.
- At Pb, the bond strength is too low to compensate for the slightly higher ionization energy requirement of the Pb(IV) state in many cases. Hence, the +2 state is favored.
- A similar “inert pair” effect is found in groups 13 and 15.

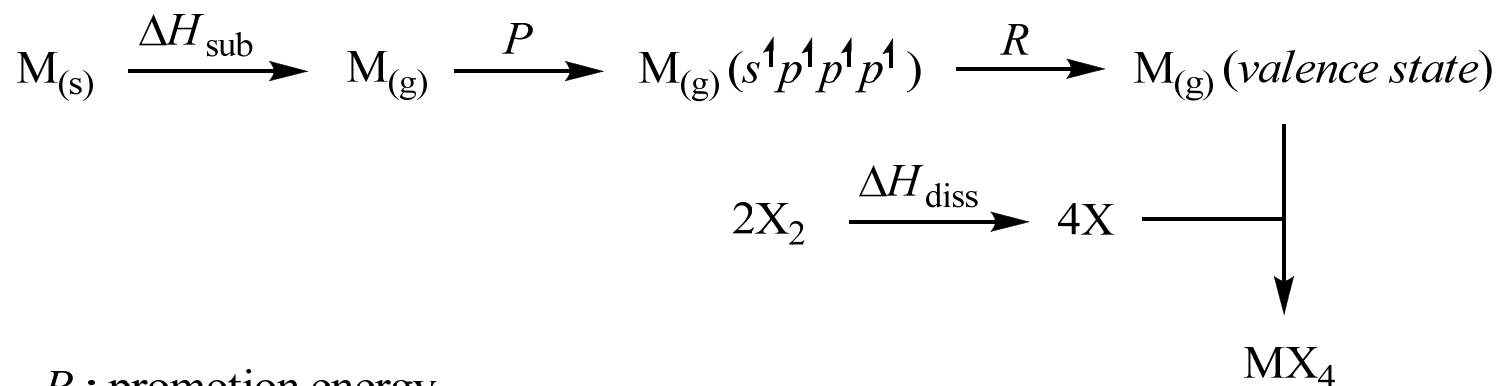
Group 14 MX_4 Bond Enthalpies



Tetravalency of the Group 14 Elements

- From their outer electron configuration of ns^2np^2 , one might expect the Group 14 elements to form covalent compounds on which they bond only to two other atoms using their half-filled p -orbitals.
- However, this is contrary to observation because, in the vast majority of their compounds, **the Group 14 elements (especially carbon) are tetrahedrally surrounded by four other groups.**
- This occurs because it is relatively easy for an ns electron to be promoted to the unfilled np orbital.
- For C the $2s \rightarrow 2p$ promotion energy is $405.8 \text{ kJ mol}^{-1}$, with the $ns \rightarrow np$ promotion energy decreasing slightly as we descend the Group.

- Although the $ns \rightarrow np$ promotion certainly leaves the element with four unpaired electrons, the electron have all their spins parallel. To obtain the element in its *valence 'reacting'* state work must be done to randomize the electron spins.*
- Therefore to form MX_4 ($X = \text{halide}$) from the Group 14 element M and X_2 the following energy steps must be considered:



P : promotion energy

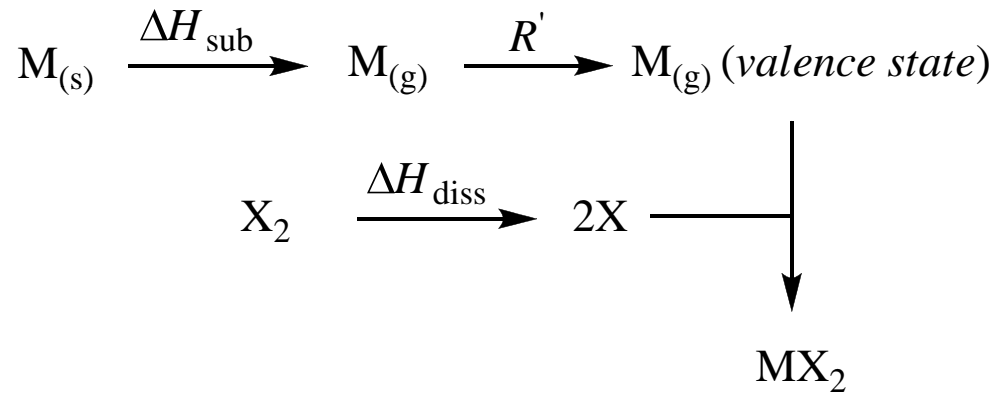
R : electron spin randomization energy

$$\text{Total energy input} = \Delta H_{\text{sub}} + P + R + 2\Delta H_{\text{diss}}$$

*The hypothetical process of hybridization from $s p_{x,y,z} \rightarrow$ four sp^3 orbitals is a mathematical step and requires no energy input.

$$\text{Total energy input} = \Delta H_{\text{sub}} + P + R + 2\Delta H_{\text{diss}}$$

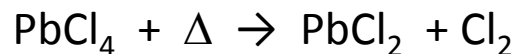
- This *energy has to be regained by the formation of four strong M-X bonds*.
- However, the production of MX_2 requires fewer energy-consuming steps:



$$\text{Total energy input} = \Delta H_{\text{sub}} + R' + \Delta H_{\text{diss}}$$

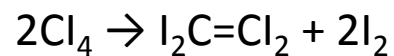
- But only two M-X bonds are formed to compensate for the required energy input.

- ***Which process leads to the more thermodynamically stable molecule?***
- MX_4 is favored for at least C, Si, Ge and Sn. For example, the enthalpy of formation at 25 °C for CH_2 and CH_4 is $+343 \text{ kJ mol}^{-1}$ and $-74.9 \text{ kJ mol}^{-1}$, respectively.
- Thus, although the utilization of the $2s^2$ electrons requires a higher initial input of energy, this is more than offset by the formation of two extra stabilizing C-H bonds.
- However, the ***M-X covalent bond strength decreases as we descend the group***, with the result that not all Pb-X bonds are capable of supplying the energy required to stabilize the Pb(IV) state with respect to Pb(II).
- PbF_4 , PbCl_4 and PbBr_4 readily decompose upon heating, e.g.



- PbI_4 is too unstable to exist at room temperature!!

- Although C–X bonds are strong, carbon tetraiodide C_2I_4 has significant steric crowding and decomposes on heating or exposure to UV light forming C_2I_4 , whose I–C–I angle of 114.2° reduces the strain.

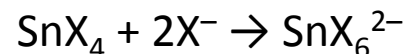


- Except for SnF_4 and PbF_4 , all **Group 14 compounds are very volatile, suggesting covalent bonding with weak van der Waals forces between molecules.**

[For organotin compounds SnR_n and SnH_n ($n = 2,4$) this can render them with a high toxicity]

SnX₄ Halides

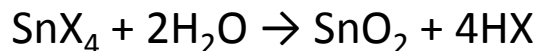
- SnX₄ compounds can act as Lewis acids in the presence of excess halide ion.



- Lewis acid strength is in the order SnF₄ > SnCl₄ > SnBr₄ > SnI₄.
- ***SnI₄ can also undergo redox with I⁻ to give SnI₂.***

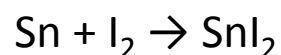
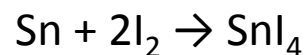


- The resulting solution is brown in polar solvents.
- Except for CX₄, all hydrolyze in water to give various hydrated oxides.
- SnX₄ compounds hydrolyze to give hydrated SnO₂ and HX.



- Similar reactivity occurs with alcohols.

- Direct reaction of tin metal with iodine in methylene chloride yields SnI_4 as the principal product, with formation of SnI_2 as a side reaction.

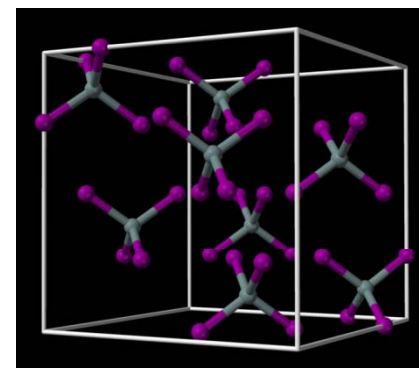


- SnI_4 is a red-orange solid; SnI_2 is a yellow-red solid.
- Color due to polarizability of I^- , probably involving charge transfer ($\text{I} \rightarrow \text{Sn}$).
- SnI_2 is polar, and SnI_4 is non-polar, as a result, SnI_2 is slightly more soluble in CH_2Cl_2 .
- SnI_2 is somewhat more ionic and has a higher m.p.



SnI_2 m.p. ≈ 330 °C

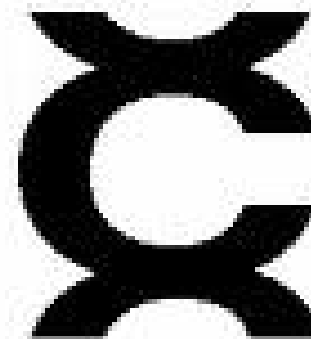
SnI_4 m.p. = 143-144 °C



- **Elemental iodine** is harmful if swallowed, inhaled, or absorbed through the skin.
- It readily sublimates (vaporizes from the solid state) at atmospheric pressure, especially if warmed.
- It is a lachrymating agent (makes your eyes tear up).

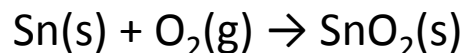


- **Methylene chloride** (b.p. = 40 °C), the solvent in this preparation, is also harmful if swallowed, inhaled, or absorbed through the skin.
- Exposure may cause nausea, dizziness, and headache. It is a narcotic at high concentration and a possible carcinogen. Exposure should be minimized.



Reactivity

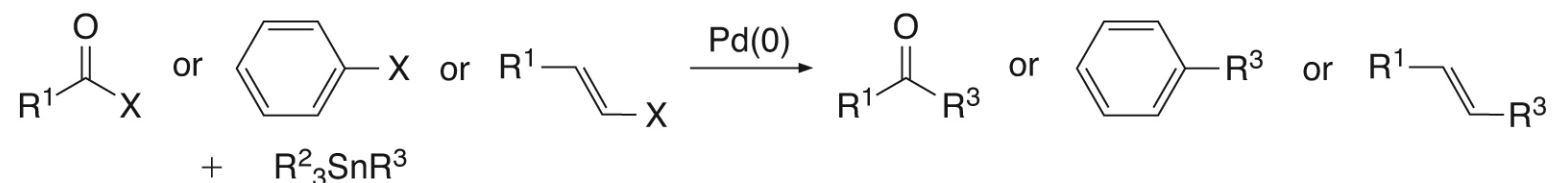
- Tin is stable toward water and oxygen at 25 °C, but reacts with steam or when heated in oxygen to give SnO₂



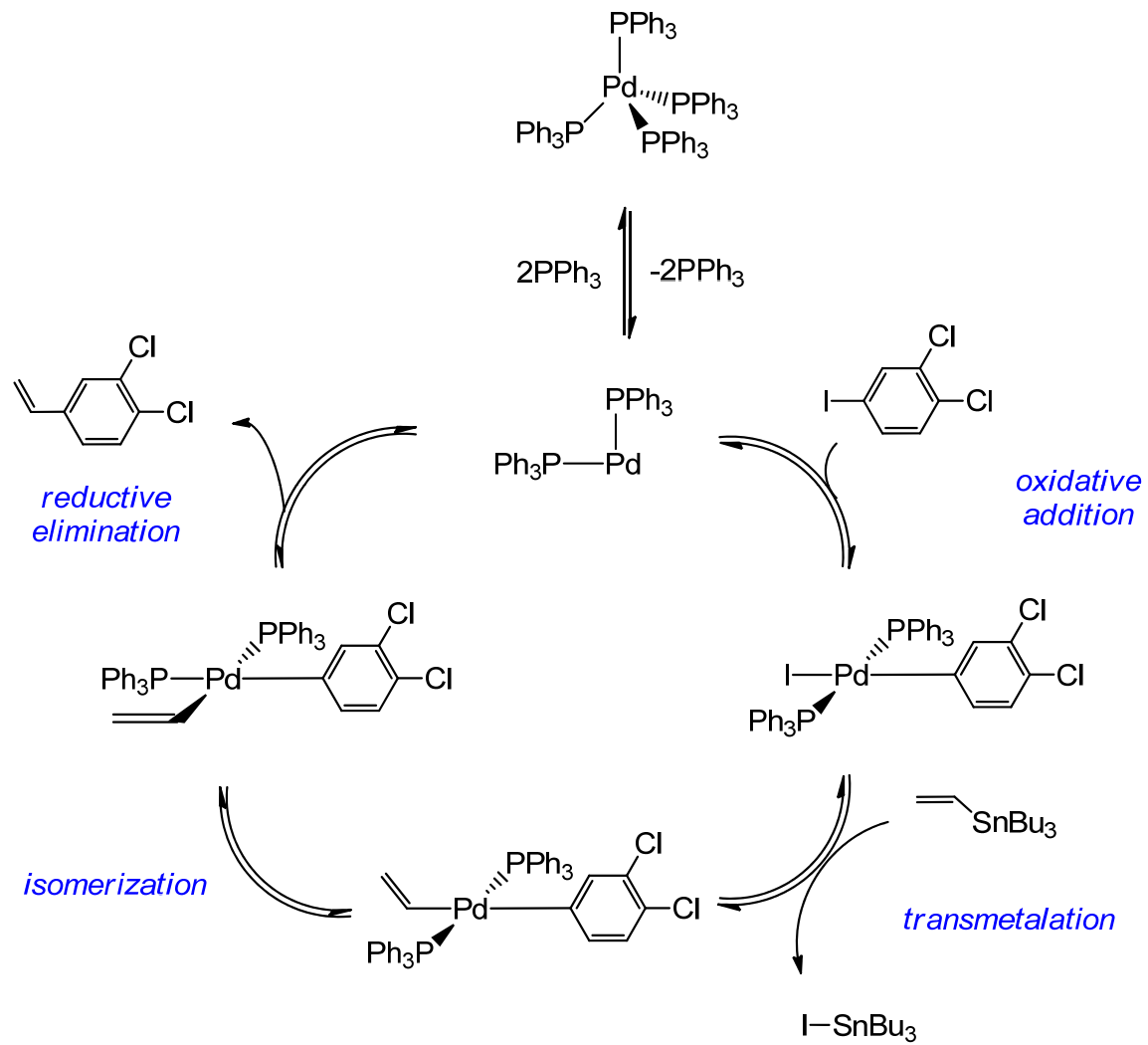
- Tin shows little reaction with dilute HCl or H₂SO₄, but with dilute HNO₃ it forms Sn(NO₃)₂ and NH₄NO₃.
- Hot conc. HCl gives SnCl₂ and H₂, and hot conc. H₂SO₄ gives SnSO₄ and SO₂.
- In hot KOH(aq), Sn dissolves to give K₂[Sn(OH)₆] and H₂.
- Note that both +2 and +4 Sn compounds form, showing that both states have comparable stability.
- Which oxidation state forms depends upon the thermodynamics of ionization versus bond stability.

Stille Coupling

- The Stille Coupling is a versatile C-C bond forming reaction between **stannanes** and **halides** or **pseudohalides**, with very few limitations on the R-groups.



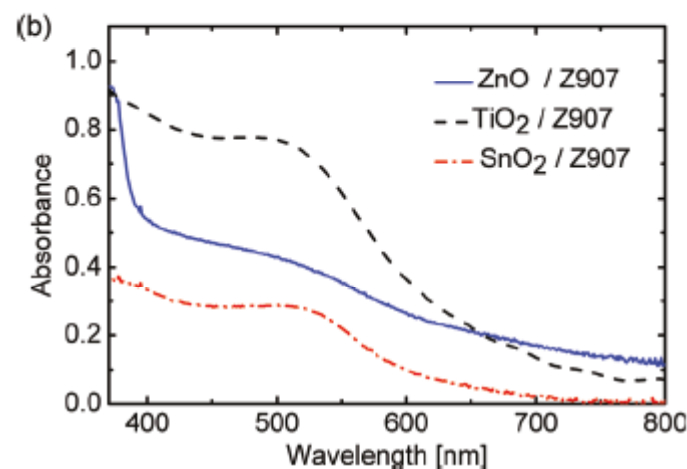
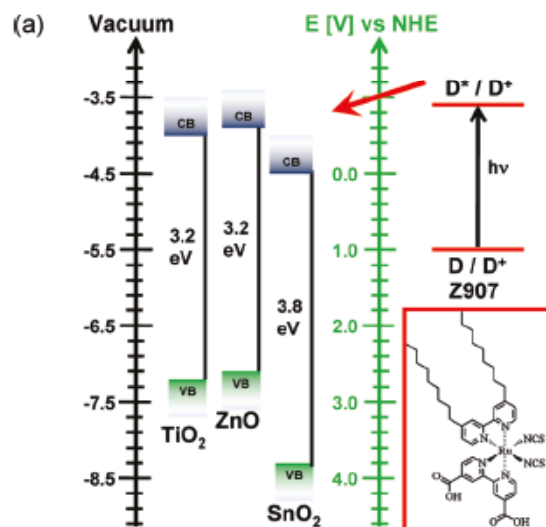
- The main drawback is the **toxicity of the tin compounds** used, and their low polarity, which makes them poorly soluble in water.
- Stannanes are stable, but boronic acids and their derivatives undergo much the same chemistry in what is known as the Suzuki Coupling.
- Improvements in the Suzuki Coupling may soon lead to the same versatility without the safety drawbacks of using tin compounds.



Electron Mobility and Injection Dynamics in Mesoporous ZnO, SnO₂, and TiO₂ Films Used in Dye-Sensitized Solar Cells

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Hierarchical Tin Oxide Octahedra for Highly Efficient Dye-Sensitized Solar Cells

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