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8-2. Chemistry about Group 14 Elements

Si, Ge, Sn, Pb: More electronically positive than carbon (C)

M-C But ionicity of M-C bonds are much lower than that of other organometallics such as alkyllithium.

8-2-1. Substitution at Group 14 Elements



- They has chirality (of course, if A~D are all different).
- Nucleophilic substitution (S_N2-M) is much faster than carbon.
- That's because of stable 5-coordinate intermediate.
- It means stereochemical inversion does not always occur.

(M = group 14 elements)

Tendency of stereochemical inversion or retention

inversion

leaving group: highly polarlized
nucleophile: soft

Tendency of stereochemical inversion or retention

retention

low polarlized
hard

8-2-2. Effects of Substituents

β effect:

Trimethylsilyl (TMS) group shows high electron donating effect when it is at a carbon adjacent to π -electron system (such as benzylic or allylic).



It's due to $\underline{\text{hyperconjugation}}$ between M-C bond's $\sigma\text{-}$ orbital and $\pi\text{-}\text{orbital}.$

Hyperconjugation also accounts for rapid S_N1 reaction.

vertical stabilization

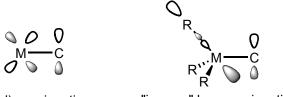
β-effect works against lone pair of oxygen/nitrogen at β-position to decrease oxidation potential.

$$R_3Si$$
 C - e - e - C -Si bond cleaveage

α effect:

- Silyl group combined directly to π -electron system shows relatively strong electron withdrawing conjugative effects.
- This electron withdrawing nature is measured in hyperfine coupling constant of radical anion of mono-substituted benzene.
- Origin of this effect is considered to be σ^* orbital (pseudo π^* orbital) of Si-C bond. ("inverse" hyperconjugation)

(Traditionally, it's considered to be $d-\pi$ conjugation of Si.)



(p-d)π conjugation

"inverse" hyperconjugation

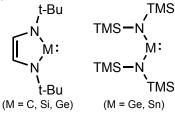
8-2-3. Unstable Spieces of Group 14 Elements

Group 14 elements can form chemical spieces like carbon.

2-coordinate chemical spieces

- Silyrene, germyrene, and stannyrene are generally unstable like carbene.
- Silyrenes or germyrenes are all singlet unlike carbenes.
- Silyrene shows similar reactivity with singlet carbene, but not react with C-H bonds or C-C bonds.
- They form Lewis pair with ethers or amines.

examples:



Cations

3-coordinate silyl cation is too unstable and highly electrophilic

Anions

3-coordinate silyl anion is stabilized by aromatic substituent like phenyl group. Stabilization of silyl anion by phenyl group is considered to be due to π inductive effect.

Radicals

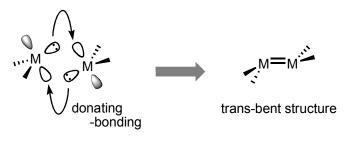
Radicalic reductions by silyl hydride or stannyl hydride are well-known. Pyrmid inversion of silyl radical is slow because of unplanar structure.



Double bonds

H₂M=MH₂ are not planar and take trans-bent structure.

These double bonds are considered to be donating-bonding between two 2-coordinate spieces.



8-3. Chemistry about Group 15-17 Elements

8-3-1. Group 15 Elements (P, As, Sb, Bi)

3-coordinate compounds

trialkylphosphine: R₃P

High ionization potential, low basicity (compared with amine)

This tendency is rationalized by theoretical calculation of hibridized orbital of EH_3 (E = N or P). P-H bond has high p-nature and lone pair has high s-nature.

ER $_3$ compounds : for stabilization of transition metal complex as σ -donating/ π -accepting ligands The higher p-nature of lone pair, the stronger ligand. (R₃P>R₃As>R₃Sb>R₃Bi)

Onium salts and ylides

$$R_2R_1HC-X$$
 $\xrightarrow{+R_3P}$ $R_2R_1HC-PR_3$ $\xrightarrow{\oplus}$ base \xrightarrow{P} $R_2R_1C-PR_3$ $\xrightarrow{\oplus}$ \xrightarrow{P} $\xrightarrow{P$

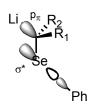
Donation of vlide structure is higher.

8-3-2. Group 16 Elements (S, Se, Te, Po)

Thiol, sulfide, etc.

- Stabilization of adjacent carboanion

Due to p_{π} - σ^* conjugation



- Weaker stabilization of adjacent carbocation than oxygen

R-E-C Because interaction of
$$2p_{\pi}$$
- $3p_{\pi}$ and $2p_{\pi}$ - $4p_{\pi}$ are weak.

- Neighboring group participation

 $\label{eq:hydrolysis} \mbox{Hydrolysis speed}: \mbox{ EtSCH$_2$CH$_2$Cl} >>> \mbox{EtOCH$_2$CH$_2$Cl}$

$$Et-S:$$
 CI
 $S+$
 $Et-S$
 OH

This stabilization is **non-vertical** (different from that of Si's β -cation stabilization).

8-3-3. High-Period Group 17 Elements

High-period halogens (especially iodine) form stable high-coordinate compounds.

8-3-4. Organofluorine Chemistry

Different features from other halogens

- Unreactive for halogen-lithium exchange (due to small atomic radius = unstablity of high-valent spieces).
- Most electronegative element.
- "van der Waals radius" similar to that of H offers intriguing property for bioactivity.

Electronic effects

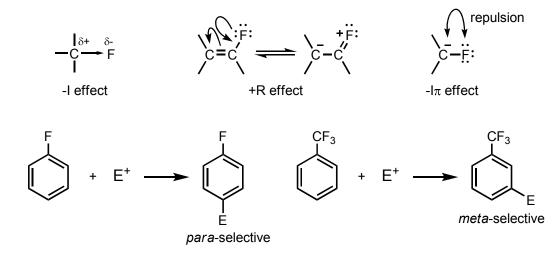
via σ-bond

strong electron-withdrawing inductive effect (-I effect)

via lone pair of p-orbital

electron-donating resonance effect (+R effect) and π -inductive effect (+I π effect)

These orthogonal effects determine the reactivity of floride compounds.



Fluorination reaction

- Nucloephilic fluorination : KF, Et₂NSF₃, etc

- Electrophilic fluorination : FCIO₃, CF₃OF, $(\stackrel{\text{CH}_2CI}{\stackrel{\text{C}_2CI}{\stackrel{\text{C}_2CI}{\stackrel{\text{C}_2CI}{\stackrel{\text{C}_2$

Perfluoroalkylation reaction

 R_f —I Nucleophilic substitution with Nu is unavailable. δ - δ + (Radicalic cleavage, halogen-lithium exchange to generate R_f -)

8-4. Ate Complex and Hypercoordinate Compounds

"Ate complex" = anionic complex salt having hypercoordinate central atom

"Hyper coordinate compounds" = central atom has more electron over Octet Rule.

8-4-1. Bonding of 5-Coordinate Compounds

Muetterties Rule: More electronegative ligands take <u>apical</u> position and more electropositive ligands take <u>equatrial</u> position in TBP structure.

8-4-2. Bonding of 6-Coordinate Compounds

8-4-3. Isomerization of Ate Complex

Isomerization of 5-coordinate compounds

Two hypothetical mechanism is probable: pseudorotation mechanism (Berry) turnstile rotation mechanism (Ugi)

- pseudorotation mechanism

$$X_5 - M \xrightarrow{X_1} X_3 = \begin{bmatrix} X_5 - M & X_1 \\ X_2 & X_4 \end{bmatrix} = \begin{bmatrix} X_3 & X_2 \\ X_4 & X_2 \end{bmatrix}$$

- turnstile rotation mechanism

$$X_5 \xrightarrow{X_1} X_3 \qquad X_5 \xrightarrow{X_3} X_2 \qquad X_5 \xrightarrow{X_3} X_1$$

The former is enagetically advantageous.

Isomerization of 3-coordinate compounds

- vertex inversion

Isomerization of 6-coordinate compounds

- twist mechanism (Bailor): few examples

$$\begin{array}{c} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_6 \end{array} \longrightarrow \begin{array}{c} X_3 \\ X_6 \\ X_6 \\ X_2 \end{array} \longrightarrow \begin{array}{c} X_3 \\ X_4 \\ X_1 \\ X_2 \end{array}$$

- multisteps mechanism : many examples

$$\begin{array}{c} X_4 & X_5 \\ X_3 & X_6 \end{array} \xrightarrow{X_4} \begin{array}{c} X_4 & X_5 \\ -X_6 & X_3 & X_2 \end{array} \xrightarrow{pseudo-rotation} \begin{array}{c} X_1 & X_1 \\ X_2 & X_3 & X_4 \end{array} \xrightarrow{X_1} \begin{array}{c} X_1 & X_2 & X_4 & X_5 \\ X_2 & X_3 & X_6 & X_4 & X_5 \end{array}$$

8-4-4. Reactivity of High-Coordinate Compounds

Roughly devided into two patterns:

- Organo-substituent of e-rich central atom works as nucleophile.
- Organo-substituent works as electrophile and e-rich central atom works as LG.

Example of the former case

Example of the latter case

Other examples: Peterson, Wittig, Corey-Chaykovsky, etc.

8-5. Reaction of Carbon-Metal Bond

8-5-1. Reaction Mechanism

S_F2 reaction (1 step): stereochemical retention or inversion

retention : allowed

inversion : partially allowed

Mechanism via electron transfers (multi steps): stereochemical invertion or racemization

or racemization if these intermediates are diffused (not in solvent cage)

8-5-2. Alkyl-Metal Bonds

Organometallics of Group 1, 2

 $\begin{array}{cc} \text{with Br}_2: & 25:75 \\ \text{with BrCH}_2\text{CH}_2\text{Br}: & 97:3 \end{array}$

Organometallics of Group 12, 13, 14

8-5-3. AllyI-Metal Bonds

Me₃Si Ph Ph TiCl₄ Ph Inversion

SiMe₃ or Me H Strong interaction between alkene's
$$\pi$$
-orbital and C-Si bond's σ -bond offers vertical position of Si group.

8-5-4. Alkenyl-Metal Bonds

Alkenyl silane

Ph SiMe₃
$$\stackrel{+}{D}$$
 $\stackrel{+}{H}$ $\stackrel{+$

Alkenyl borane