Organometallic Chemistry

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organosilicon
• The utility of organosilicon compounds in organic synthesis is based on:
  – the **stability of the C–Si bond**
  – the **regio- and stereoselective reactions of organosilanes with both nucleophilic and electrophilic reagents**.

• Focus on: properties of organosilicon compounds: preparation and utilization of alkynyl-, alkenyl-, and allylic silanes in organic synthesis.
Properties of bonds to silicon

❖ Electronegativity

• Si: more electropositive than C. bond is polarized \( \text{Si}^{\delta+} - \text{C}^{\delta-} \)
• polarization: makes Si susceptible to nucleophilic attack
• polarization: imparts stabilization to \( \beta \)-carbocations and \( \alpha \)-carbanions.

❖ Bond length

• The Si–C bond (1.89 Å) is significantly longer than a typical C–C bond (1.54 Å), suggesting that the \( \text{SiMe}_3 \) group is sterically less demanding than a \( \text{tert} \)-butyl group.
Properties of bonds to silicon

- **Bond energy**
  - Organosilicon compounds are much more stable than other typical organometallic compounds.
  - Single bonds from Si to electronegative elements O, Cl, and F are very strong.
  - $p\pi-d\pi$ bonding plays a role in these cases.
  - Since such strong bonds are formed, substitution at Si is especially easy when the nucleophile is O$^-$, Cl$^-$, or F$^-$. 
  - Very strong affinity of silicon for F$^-$. 

<table>
<thead>
<tr>
<th>Bond</th>
<th>Approximate Bond Dissociation Energies.</th>
<th>kcal/mol</th>
<th>kJ/mol</th>
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<tr>
<td>$H_3C-C$</td>
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<td>83–88</td>
<td>347–368</td>
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<td>$H_3C-O$</td>
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<td>$H_3C-F$</td>
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<td>Si–C</td>
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<tr>
<td>Si–O</td>
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<td>127</td>
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<tr>
<td>Si–Cl</td>
<td></td>
<td>113</td>
<td>471</td>
</tr>
<tr>
<td>Si–F</td>
<td></td>
<td>193</td>
<td>807</td>
</tr>
</tbody>
</table>


Properties of bonds to silicon

- **Stabilization of β-Carbocations and α-Carbanions**
  - polarization supports formation of carbocations β-position, a stereoelectronic phenomenon known as the **β-effect**.
  - attributed to stabilizing interaction between Si–C bond and empty $p_{\pi}$ orbital of the β-carbocation ($\sigma_{\pi}$ conjugation).
  - β-effect is conformationally dependent in that the carbon-silicon σ-bond and the vacant p-orbital must be in a common plane.

![Chemical Diagrams](image_url)
Stabilization of β-Carbocations and α-Carbanions

- 2nd-row elements such as Si: known to stabilize α-carbanions with greater effectiveness than first-row elements.
- Early rationalization of this phenomenon favored the $p\pi-d\pi$ model B as a source of the stabilizing influence.
- More recently, stabilization by means of the high polarizability of Si and the presence of an empty $\sigma^*$ orbital on the silicon have been proposed.
- Overlap with the filled orbital of a flanking carbanionic center as in C can account for the observed stabilization.

Properties of bonds to silicon
**Preparation and Reactions**

**Alkynylsilanes**

- **Alkynylsilanes** are readily accessible by metalation of terminal alkynes, followed by addition of the appropriate $R_3\text{SiCl}$.

  \[
  R'\equiv\equiv\text{H} \xrightarrow{\text{a. MeLi or } n-\text{BuLi} \text{ or LDA, THF}} R'\equiv\equiv\text{SiR}_3
  \]

  \[
  \text{b. } R_3\text{SiCl}
  \]

- Reactions of **alkynylsilanes** with $E^+$ in the presence of a Lewis acid catalyst such as $\text{BF}_3$, $\text{AlCl}_3$, or $\text{TiCl}_4$ generally occur **regioselectively at the silicon-bearing carbon** under mild conditions due to the $\beta$-effect.
Preparation and Reactions

Alkynylsilanes

- AlCl₃-mediated electrophilic substitution of alkynylsilanes with acid chlorides provides a convenient route to alkynyl ketones. Transfer of the acetylenic moiety from silicon to the acyl chloride proceeds via the acyl cation (acylium ion) formed by reaction of the acyl chloride with AlCl₃.

\[
\text{R}^'\text{C}≡\text{C}\text{Cl} + \text{AlCl}_3 \rightleftharpoons \text{R}^'\text{C}≡\text{O} \quad \text{(E}^+\text{= acylium ion)} \quad \text{R}^+\text{C}≡\text{O} \quad \text{AlCl}_4^- \\
\text{a. R}^'\text{SiR}_3 \quad \text{b. workup} \]

\[
\text{R}^'\text{C}≡\text{C}\text{Cl} \quad \text{AlCl}_3 \quad \text{AlCl}_4^- \\
\]

\[
\text{R}^'\text{C}≡\text{C}\text{Cl} \quad \text{AlCl}_3 \quad \text{AlCl}_4^- \\
\text{R}^'\text{C}≡\text{C}\text{O} \quad \text{R} \\
\]

\[
\text{R}^'\text{C}≡\text{C}\text{Cl} \quad \text{AlCl}_3 \quad \text{AlCl}_4^- \\
\text{R}^'\text{C}≡\text{C}\text{O} \quad \text{R} \\
\]

\[
\text{R}^'\text{C}≡\text{C}\text{Cl} \quad \text{AlCl}_3 \quad \text{AlCl}_4^- \\
\text{R}^'\text{C}≡\text{C}\text{O} \quad \text{R} \\
\]
Preparation and Reactions

Alkynylsilanes

- remarkable Si-directing reaction of electrophiles at the α-carbon of alkynylsilanes is further evident when comparing the intramolecular cyclizations of methyl- vs. silicon-substituted triple bonds.

**intramolecular cyclizations of methyl-substituted triple bonds**

![Chemical reaction diagram]

- Protonation of hydroxyl group of A generates carbocation B. In B, attack of the methyl-substituted triple bond leads to formation of the preferred linear vinyl cation. Its trapping by the formate ion furnishes the substituted bicyclo[2.2.2]octene C.
• remarkable Si-directing reaction of electrophiles at the α-carbon of alkynylsilanes is further evident when comparing the intramolecular cyclizations of methyl- vs. silicon-substituted triple bonds.

Protonation of the trimethylsiloxyl group of D generates carbocation E. Attack of the silicon-substituted triple bond in E occurs to form the silicon-stabilized β-carbocation, which, on trapping by formate ion, yields the substituted bicyclo[3.2.2]nonene F.
Preparation and Reactions

**Alkenylsilanes**

- Among the many available procedures for preparing alkenylsilanes are hydrosilylation of alkynes and partial reduction of alkynylsilanes.

- **Hydrosilylation of 1-alkynes** with triethylsilane in the presence of catalytic chloroplatinic acid results in regioselective *syn*-addition of H–SiEt₃ to the triple bond to produce \((E)\)-alkenylsilanes.

\[
\begin{align*}
\text{Et}_3\text{SiH} & \quad \text{H}_2\text{PtCl}_6 \text{ (cat.)} \\
\text{i-PrOH, 0 °C} & \quad \text{H} \\
\text{n-C}_6\text{H}_{13} && \text{n-C}_6\text{H}_{13} \\
\text{H} && \text{H} \\
\text{H} && \text{SiEt}_3 \\
77\% & 
\end{align*}
\]
• **Reduction of 1-(trialkylsilyl)alkynes** with dialkylboranes or with diisobutylaluminum hydride proceeds in a regio- and stereoselective manner to yield, after protonolysis or hydrolytic workup, (Z)-alkenylsilanes.

![Chemical reactions and structures](attachment:image.png)
Vinylsilanes react with a variety of electrophiles to give substitution or addition products. In substitution reactions, the silyl group is replaced by the electrophile because formation of the carbon-carbon π-bond is faster than capture of the incipient β-carbocation by the nucleophile.
In addition reactions, the nucleophile reacts with the carbocation before collapse of the Si–C bond. The resultant adduct can be induced to undergo syn- or anti-elimination depending on the reaction conditions. With few exceptions, electrophilic attack on the vinylsilyl moiety is highly regioselective, placing the developing carbocation at the β-position (β-effect).
Preparation and Reactions

Alkenylsilanes

- Acylation of vinylsilanes with acid chlorides in the presence of a Lewis such as AlCl₃ provides a route to α,β-unsaturated ketones.

  ![Chemical Reaction Diagram]

  ```
  \[
  \text{SiMe₃} \quad \xrightarrow{\text{CH₃COCl, AlCl₃, CH₂Cl₂}} \quad \xrightarrow{\text{H⁺, H₂O}} \quad \text{CH₃}
  \]
  77%
  ```

- The reaction is **regioselective and stereospecific**. Stabilization of the incipient carbocation occurs only if the C–Si bond is correctly aligned with the developing vacant p-orbital. Thus, **parallel alignment of the C–Si σ-bond dictates the stereochemistry** of the substitution product.
Preparation and Reactions

Alkenylsilanes

- Acylation of vinylsilanes

$$\text{R}^1\text{C}==\text{SiR}_3 \xrightarrow{\text{R}^3\text{COCl}, \text{AlCl}_3} \xrightarrow{\text{rotation}} \text{R}^1\text{C}==\text{SiR}_3 \xrightarrow{\text{rotation}}$$

$$\xrightarrow{-\text{R}_3\text{SiCl}}$$

$$\text{R}^1\text{C}==\text{C}(\text{O})\text{R}^3$$

$$\text{R}^1\text{R}_2\text{SiR}_3 \xrightarrow{\text{R}^3\text{COCl}, \text{AlCl}_3} \xrightarrow{\text{rotation}} \text{R}^1\text{R}_2\text{SiR}_3 \xrightarrow{\text{rotation}}$$

$$\xrightarrow{-\text{R}_3\text{SiCl}}$$

$$\text{R}^1\text{R}_2\text{C}(\text{O})\text{R}_3$$
Isomerically pure vinyl halides are important starting materials for preparation of the corresponding vinyl lithium species and for use in Pd-catalyzed coupling reactions.

Halogenation of vinylsilanes offers a valuable route for the synthesis of both (E)- and (Z)-vinyl halides.

The reactions involve addition of the halogen to the double bond, followed by elimination of Si and halide moieties.

The stereochemical outcome of the reaction will depend on both the mode of addition and the mode of elimination.
Preparation and Reactions

Alkenylsilanes

- For example, bromination of (Z)-vinylsilanes with Br₂ in CH₂Cl₂ proceeds via an *anti*-addition. Treatment of the bromine adduct with sodium methoxide results in *anti*-desilicobromination. The conversion of the vinylsilane into the vinylbromide occurs with overall inversion of the double bond stereochemistry.

\[
\begin{align*}
R = Me, Et, s-Bu \\
\text{Br}_2 &\underset{CH_2Cl_2, -78 \, ^\circ C}{\rightarrow} \text{Br} \quad \text{Br} \\
&\underset{\text{CH}_3\text{ONa, CH}_3\text{OH}}{\rightarrow} \underset{(E)-vinylbromide}{\text{H}} \quad \text{Br} \\
&\text{75–93\%} \ (E: Z, 99: 1)
\end{align*}
\]
Allylsilanes play an important role in organic synthesis. Whereas Li-, Mg-, Zn-, and B-allylic species undergo 1,3-shift of the metal, **allylsilanes are stable**.

Allylsilanes: prepared by silylation of allyl-metal species, provided that the carbanions can be trapped regioselectively by $R_3SiCl$.

\[
\begin{align*}
\text{Allylsilane} & \quad \begin{array}{c}
\text{Cl} \\
\text{SiR}_3
\end{array}
\end{align*}
\]

- Allylsilanes: prepared by silylation of allyl-metal species, provided that the carbanions can be trapped regioselectively by $R_3SiCl$. 

\[
\begin{align*}
\text{(Z)-2-butene} & \xrightarrow{n-\text{BuLi, THF, KOT-Bu}} \begin{array}{c}
\text{H}_3\text{C} \\
\text{K}^+
\end{array} \\
& \xrightarrow{\text{Me}_3\text{SiCl}} \text{H}_3\text{C} \\
& \quad \begin{array}{c}
\text{SiMe}_3
\end{array}
\end{align*}
\]
The nickel- or palladium-catalyzed reaction of stereodefined alkenyl halides with trimethylsilylmethylmagnesium chloride (TMSCH$_2$MgCl) delivers allylsilanes with excellent regio- and stereocontrol.

\[
\begin{align*}
n-C_6H_{13} & \quad H \\
H_3C \quad I & \quad \text{ClMgCH}_2\text{SiMe}_3 \\
\text{(Et}_2\text{O solution)} & \quad \text{a. (Ph}_3\text{P})_4\text{Pd (cat.)} \\
& \quad \text{THF, } 0 \, ^\circ\text{C} \\
& \quad \text{b. } H^+, \text{H}_2\text{O} \\
& \quad \text{85\% (95\% E)}
\end{align*}
\]
The hydroalumination-protonation of 1-trimethylsilyl-2-alkynes and the Wittig reaction using silylated ylides are other good approaches for the synthesis of allylsilanes.

\[
\begin{align*}
 & \text{a. } t\text{-BuLi, Et}_2\text{O} \\
 & \quad \text{TMEDA, } -78 \degree \text{C} \\
 & \text{b. } \text{Me}_3\text{SiCl} \\
 & \text{c. } i\text{-Bu}_2\text{AlH, hexane} \\
 & \quad 70 \degree \text{C} \\
 & \text{d. } H^+, \text{H}_2\text{O} \\
\end{align*}
\]

\[
\text{83–85\% (99\% Z)}
\]
Preparation and Reactions

Allylsilanes

• bifunctional reagent 2-bromo-3-(trimethylsilyl)propene represents a synthon for a 1,2-dianion, and offers an opportunity to store chemical reactivity which can be selectively unleashed.
In the presence of a Lewis acid (e.g. Et₂AlCl), allylsilanes react with E⁺ in a regiospecific manner. Intermediate β-carbocation is stabilized by (σ–π)-conjugation with the C–Si bond.

Most important feature of reaction is that E⁺ reacts with the terminus (γ-carbon) of allyl system, and π-system is relocated adjacent to its original position.

Even substituted allylic silanes can be acylated at the more hindered site. Because of this predictability and their high nucleophilicity, allylsilanes are valuable in many syntheses.

There are 2 types of reactions of allylsilanes with E⁺:

– *Lewis acid mediated reactions*

– *reactions involving allyl anions*
Lewis Acid-Mediated Reactions.

- The highly nucleophilic double bond of allylsilanes reacts with a variety of electrophiles provided that the electrophiles are activated by a Lewis acid, such as TiCl$_4$, BF$_3$, or AlCl$_3$. The $\gamma$-position of the allylsilane attacks the electrophile to generate a stabilized carbocation $\beta$ to silicon. Subsequent loss of the silyl group results in the transposition of the double bond.
Both inter- and intramolecular reactions of allylsilanes with enones have been reported. 1,4-Addition of allylsilane to the conjugated enone shown below permits direct introduction of an angular allyl group to a bicyclic enone.

\[
\begin{align*}
\text{ Allylsilane } & \quad \text{ Reaction} & \quad \text{ Product} \\
\text{TiCl}_4, \text{ CH}_2\text{Cl}_2 & & \text{85\%} \\
\text{BF}_3 \cdot \text{OEt}_2, \text{ Et}_2\text{O} & & \text{73\%}
\end{align*}
\]
Preparation and Reactions

Allylsilanes

- Reaction proceeds via an acyclic linear and not via a cyclic six-member transition state. TS A leading to syn-alcohol is sterically favored diastereomeric TS B, which has a gauche Me-Et interaction.

\[
\text{Me} = \text{SiMe}_3 + \text{EtCHO} \xrightarrow{\text{TiCl}_4, \text{CH}_2\text{Cl}_2} \begin{align*}
\text{Et} & \text{OH} \\
\text{Me} & \text{OH}
\end{align*}
\]

\[(E)-\text{crotylsilane}\]

**syn-selectivity** → 95%  5%

\[\begin{align*}
\text{syn-selectivity} & \text{ favored} \\
\text{anti-selectivity} & \text{ disfavored}
\end{align*}\]
Preparation and Reactions

Allylsilanes

- The reaction of \( (Z) \)-crotylsilane furnishes **syn-anti mixtures** of homoallylic alcohols.

\[
\begin{align*}
\text{Me} & \quad \text{SiMe}_3 & \quad + & \quad \text{EtCHO} & \quad \xrightarrow{\text{TiCl}_4, \text{CH}_2\text{Cl}_2} & \quad \text{Et} \quad \text{OH} & \quad \text{Me} \\
& & & & \quad \text{69%} & \quad \text{Et} \quad \text{OH} & \quad \text{Me} \quad \text{31%}
\end{align*}
\]

(\( Z \)-crotylsilane)

**Draw TS!**
Reactions of Allylsilane Anions.

- Generally, deprotonated silanes react in a $\gamma$-regioselective manner with electrophiles to give vinylsilanes.
Reactions of Allylsilane Anions.

- However, if the allylsilane anion is first complexed with certain metals or metalloids, such as B or Ti, \( \alpha \)-regioselectivity then predominates, and high anti-diastereoselectivity is attained with aldehydes as electrophiles.

\[
\begin{align*}
\text{\[\gamma\text{-Li}^+\text{-SiMe}_3\]} & \xrightarrow{(\text{MeO})_3\text{B}} (\text{MeO})_2\text{B}\text{-SiMe}_3 \\
\text{THF} & \quad -78 \, ^\circ\text{C} \\
(\text{MeO})_2\text{B}\text{-SiMe}_3 & \xrightarrow{\text{RCHO}} \text{R}=n-\text{C}_7\text{H}_{15}, \quad 79\%
\end{align*}
\]
Versatile intermediates for C-C bond formations

May serve as precursors for the synthesis of silyl enol ethers, aldehydes, or carboxylic acids.

In the presence of a base or certain nucleophiles, they undergo the Brook rearrangement, where the silyl moiety migrates from carbon to oxygen (see below in this section).

**Preparation**

- several procedures available for the preparation of acylsilanes.
- A general synthesis of acyl silanes is via the dithiane route.
Hydrolysis of 2-silyl-1,3-dithianes which leads to acyl silanes can be accomplished with mercury(II) salts. To repress formation of aldehyde by-products, various modifications for the deprotection of silyl dithianes have been reported, including the use of HgO–F₃B•OEt₂ or chloramine-T.
**Preparation**

**Acyl silanes**

- **alkyl-substituted acylsilanes**

  - Hydroboration of 1-trimethylsilyl-1-alkynes with BH$_3$•SMe$_2$ in a 3:1 ratio, followed by oxidation of the resultant trivinylborane with anhydrous trimethylamine oxide, provides an operationally simple, one-pot synthesis of alkyl-substituted acylsilanes in good yield from readily available starting materials.

![Chemical reaction diagram]

- **yields:** 75–91%
Preparation

Acyl silanes

- acetyltrimethylsilane

- By metalation-silylation-protonation of methyl vinyl ether furnishes, the simplest acyl silane.

\[
\begin{align*}
\text{H} = \text{O} & \quad \text{Me} \\
\text{H} = \text{H} & \quad \text{a. } t-\text{BuLi} \\
\text{Me} & \quad \text{b. } \text{TMSCl} \\
\text{H} = \text{O} & \quad \text{Me} \\
\text{SiMe}_3 & \quad \text{88%} \\
\text{H} & \quad \text{H} \\
\text{SiMe}_3 & \quad \text{H}^{+}, \text{H}_2\text{O} \\
\text{acetone} & \quad \text{83%} \\
\text{H}_3\text{C} & \quad \text{O} \\
\text{SiMe}_3 & \quad \text{H}_3\text{C} \text{SiMe}_3
\end{align*}
\]
Preparation

Acyl silanes

- [(trimethylsilyl)acetyl]trimethylsilane
  - Monohydroboration of bis(trimethylsilyl)acetylene and oxidation of the resultant trivinylborane with anhydrous trimethylamine oxide followed by hydrolytic workup affords [(trimethylsilyl)acetyl]trimethylsilane, which contains both α- and β-ketosilane structural features. This reagent is a versatile synthon for stereoselective syntheses of functionalized trisubstituted olefins.

\[
\text{Me}_3\text{Si} \equiv \text{SiMe}_3 \quad \text{bis(trimethylsilyl)acetylene} \quad \xrightarrow{\text{a. } \text{H}_3\text{B} \cdot \text{SMe}_2, \text{THF}} \quad \text{Me}_3\text{Si} - \text{CH}_{\equiv} - \text{SiMe}_3 \quad \xrightarrow{\text{b. } \text{Me}_3\text{NO (anhydr.)}} \quad 75\% \quad \text{Me}_3\text{Si} - \text{CH} - \text{SiMe}_3
\]
Reactions

Acyl silanes

- sensitive to light and basic reaction conditions.
- can be regarded as sterically hindered aldehyde synthons

\[ R'\text{SiR}_3 \text{C} + \text{R''Li or R''MgX} \rightarrow \ \text{R'}\text{SiR}_3\alpha\text{-silyl alkoxides} \]

reversible rearrangement (Brook rearrangement) of silyl gr from C to O (driving force is strong Si–O bond)

rearrangement A → B: rapid only when R or R' is a carbanion-stabilizing group, such as vinyl, aryl, or ethynyl.

- reaction of acylsilanes with organolithium and Grignard reagents frequently gives complex product mixtures
Reactions

Acyl silanes

- potential of acylsilanes as hindered aldehyde synthons is the preparation of the secondary alcohol
- pentadienyl anion possesses the highest electron density at the internal $\gamma$-position (MO calculations)
- Its reaction with acetaldehyde gave a mixture of isomers, favoring bond formation at the more hindered position of the lithium reagent.

\[
\text{(3-methylpentadienyl)lithium with 2 nucleophilic sites} \quad \text{THF} \quad \text{conjugated addition product} \quad 25\% \quad \text{deconjugated addition product} \quad 75\% 
\]
To enhance coupling of the carbonyl carbon with the less hindered site, acetyltrimethylsilane-sterically more hindered synthon of acetaldehyde was used.

Reactions

Acyl silanes

\[
\text{acetyltrimethylsilane} \quad \text{sterically more hindered synthon of acetaldehyde}
\]
Examples of organosilane in coupling reactions

Palladium-katalysierte Akinkupplungen

*Terminale Acetylene*

\[ \text{Br-BHBr-SiMe}_3 + \equiv\text{Si}^\text{Pr}_3 \rightarrow \text{Pr}_3\text{Si}=\text{SiPr}_3 \text{H=H} \]

1) Pd(0) / Cu(I)
2) K₂CO₃, MeOH


\[ \text{Br-BHBr-BHBr} + \equiv\text{SiMe}_3 \rightarrow \text{H=H=H=H=H} \]

1) Pd(0) / Cu(I)
2) KOH, MeOH

28%

Examples of organosilane in coupling reactions

Palladium-katalysierte Akinkupplungen

Terminale Acetylene

\[ \text{RX} + \text{(SiMe}_3\text{)} = \text{Rx-SiMe}_3 \]

\[ \text{PdCl}_2(\text{PPh}_3)_2, \text{ CuI} \rightarrow \text{R-SiMe}_3 \]

\[ \text{NEt}_3 \text{ oder Pyridin, RT bis 60°C} \]

\[ 70-92\% \]

\[ \text{R} \equiv \text{Aryl, Alkenyl} \]

\[ \text{KOH / MeOH} \rightarrow \text{R-H} \]

\[ \text{RT, 1h} \]

\[ 79-94\% \]

[auch Fluorid möglich]

Synthesis **1980**, 627-30

*Tetrahedron Lett.* **1993**, 34, 2071-74

Examples of organosilane in coupling reactions

Alkin/Alken-Trimerisierungen

(1) Alkin-Trimerisierungen

Rhodium

\[ \text{Alkin} + \text{Alken} \rightarrow \text{Trimer} \]

\[ \begin{align*}
\text{CO}_2\text{Et} & + \text{NHAc HO} \\
\rightarrow & \text{HO} \text{CO}_2\text{Et}
\end{align*} \]

\[ \text{(PPh}_3\text{)}_3\text{RhCl} \]

\[ \begin{align*}
80 \degree \text{C} & \quad 81\% \\
\end{align*} \]


(2) Alkin/Alken-Trimerisierungen

Palladium

\[ \begin{align*}
\text{Bn} & + \text{Me}_3\text{Si} \quad \text{SiMe}_3 \\
\rightarrow & \text{Me}_3\text{Si} \quad \text{SiMe}_3
\end{align*} \]

\[ \text{Pd(PPh}_3\text{)}_4 \]

\[ \begin{align*}
65 \degree \text{C} & \quad 86\% \\
\end{align*} \]

Examples of organosilane in coupling reactions

Alkin/Alken-Trimerisierungen

(1) Alkin-Trimerisierungen

Cobalt

\[
\text{CpCo(PPh}_3\text{)₂} + \text{R}^1\text{=C}≡\text{C}-\text{R}^2 \rightarrow \text{R}^3\text{=C}≡\text{C}-\text{R}^4
\]

13-59%


\[
\begin{align*}
\text{MeO} & \quad \text{MeO} \\
\text{MeO} & \quad \text{MeO} \\
\text{Me}_3\text{Si} & \quad \text{SiMe}_3 \\
\text{CpCo(CO)}_2 & \quad 93\%
\end{align*}
\]

References - organometallics

References - organometallics

• **Course materials:** from

  • Dr. Ian Hunt, Department of Chemistry, University of Calgary
    http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch14/ch14-1.html
  • http://depts.washington.edu/chemcrs/bulkdisk/chem238A_win05/notes_14_11_15.pdf
  • http://users.ox.ac.uk/~mwalter/web_05/resources/sil_chem/org_silicon_chem.shtml
Additional References - organolithiums


Additional References - organomagnesium

Additional References – organocopper + organozinc

• Herrmann, W.A. Ed. *Synthetic Methods of Organometallic and Inorganic Chemistry Vol 5, Copper, Silver, Gold, Zinc, Cadmium, and Mercury*, *Efficient Synthesis of Functionalized Organozinc Compounds by the Direct Insertion of Zinc into Organic Iodides and Bromides* 
Additional References - organoboron

Additional References - organosilicon