

# Traditional Aqueous Routes

## Advantages

Simple Equipment

Inexpensive Materials

Well Studied

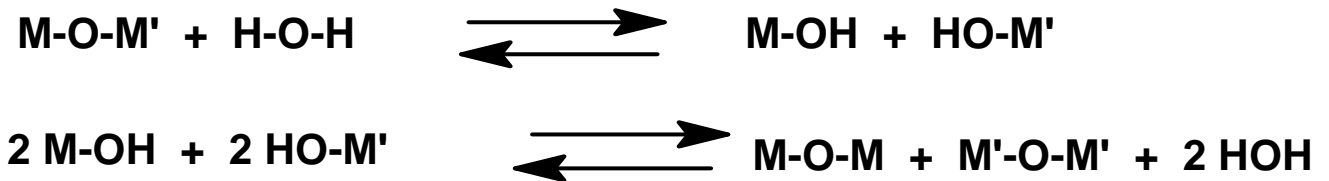
## Disadvantages

Difficult control of hydrolysis and condensation rates

Inhomogeneity introduced by homocondensation

Reversibility of condensation step

Phase Separation



# **Nonaqueous – Nonhydrolytic – Organometallic Methods**

## **Advantages**

**Inhomogeneity and phase separation prevented  
absence of water, volatile organic byproducts cannot cleave M-O-M' bonds  
and cause homocondensation, irreversible condensation step**

**M = mononuclear, polynuclear clusters, building blocks**



**Chemical control of reactivity by selecting X, Z groups**

**Wide choice of solvents, medium polarity, reaction temperature**

**Simplified drying to aerogels, lower surface tension**

# **Nonaqueous – Nonhydrolytic – Organometallic Methods**

## **Advantages**

### **Synthesis of hybrid materials**

**incorporation of water sensitive and water insoluble compounds:  
organometallics, coordination compounds, long aliphatic chains, clusters  
hydrophobic hybrid materials**

### **Template syntheses**

**use of water sensitive and water insoluble compounds, polymers  
microporous and mesoporous**

**Retention of lower coordination numbers (Al, TM), low-hydroxyl surfaces – catalysis**

# **Nonaqueous – Nonhydrolytic – Organometallic Methods**

## **Disadvantages**

- Elaborate procedures and expensive precursors**
- Organic solvents**
- Exclusion of moisture**
- Ligand scrambling vs. elimination**

# **Nonaqueous – Nonhydrolytic – Organometallic Methods**

**Solid-state: solid-state thermolysis**

**Liquid-state: sol-gel, solventless, sonochemical reactions,  
solution thermolysis**

**Gas-phase: CVD, pyrosol**

# Preparation of Oxides, Mixed Oxides, and Silicates

**Alkylhalide Elimination**

**Ether Elimination**

**Ester Elimination**

**Ketene Elimination**

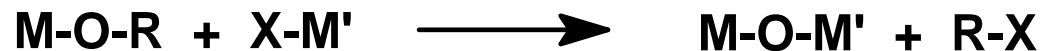
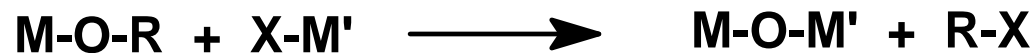
**Alkene Elimination**

**Ketimine Elimination**

**Acetamide Elimination**

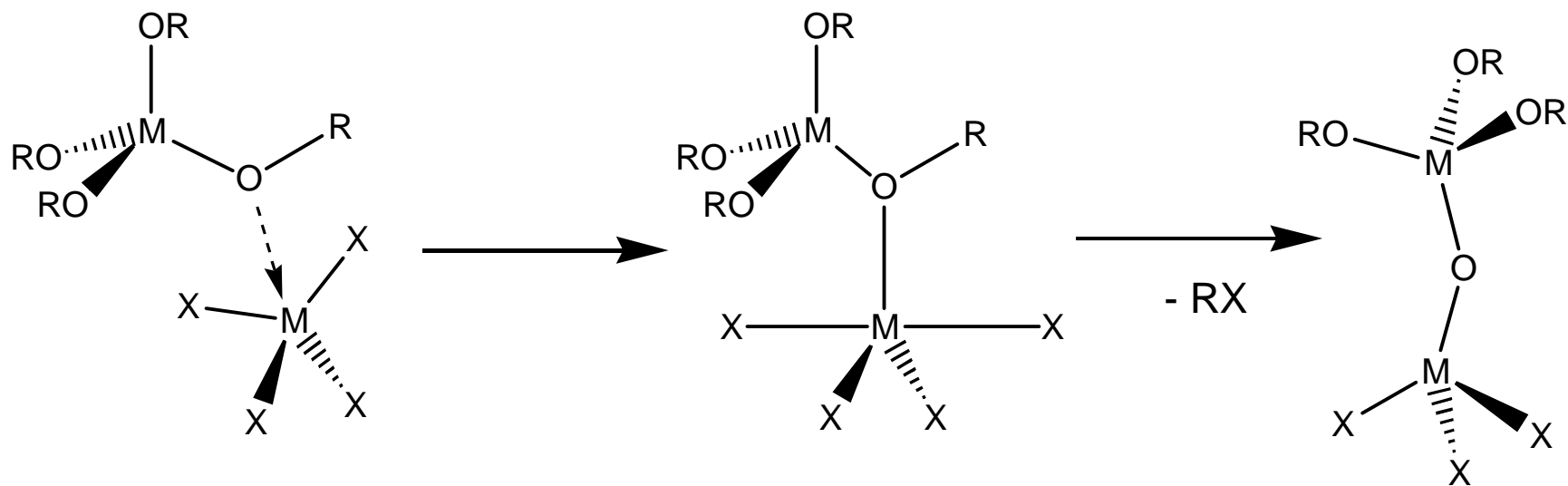
# Alkylhalide Elimination Reactions

M = Si, Al, Ti, Zr, V, Nb, Mo, W, Fe



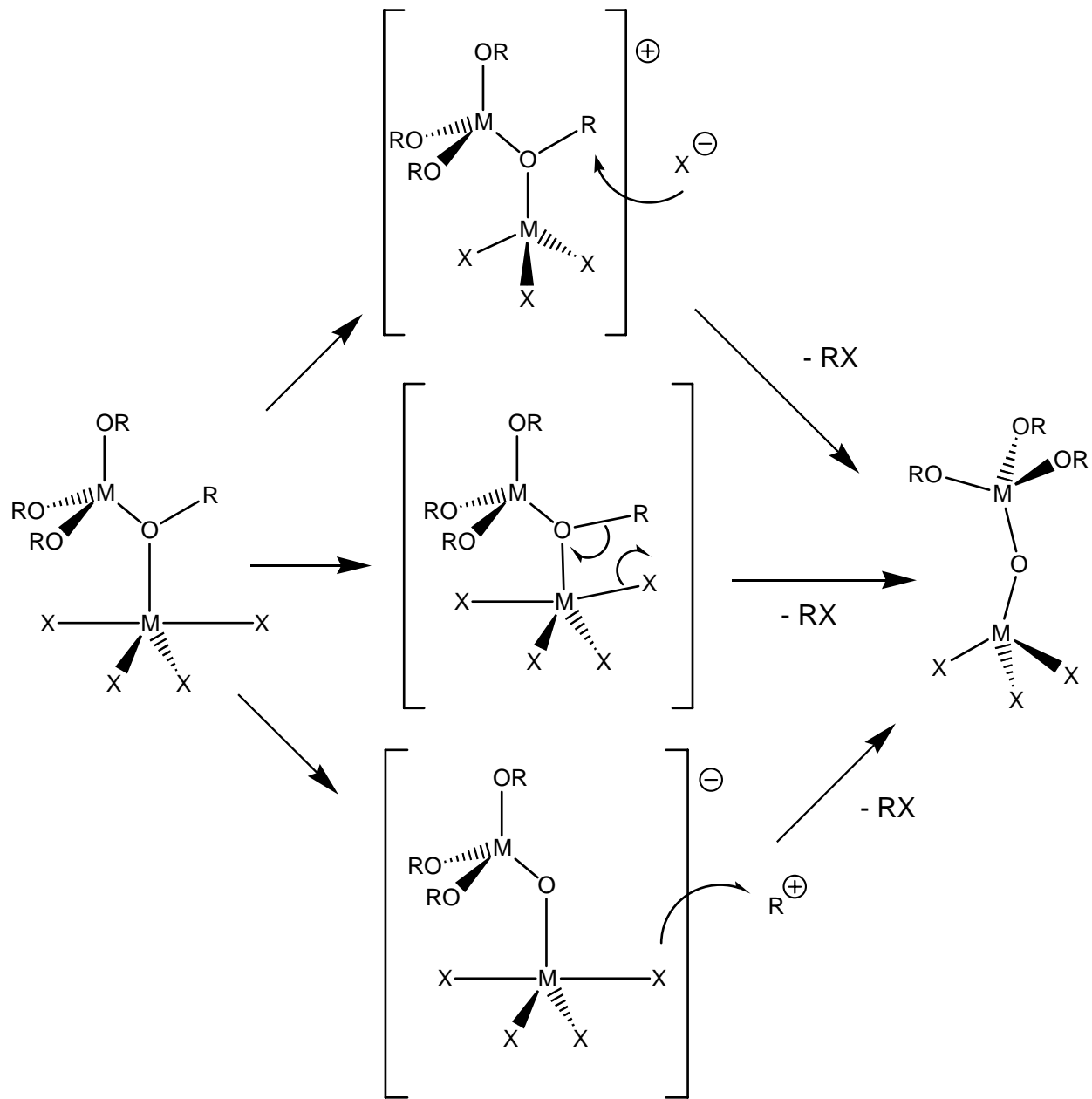
Corriu, Vioux, Leclercq, Mutin, Montpellier  
Hay et al., Surrey

# Alkylhalide Elimination Reactions

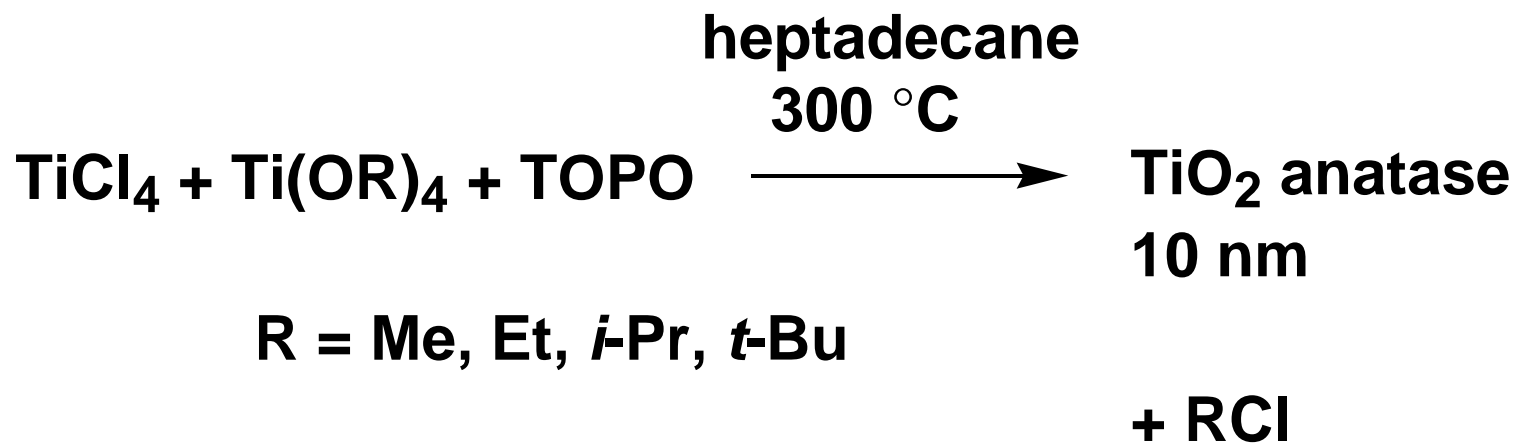


**C-O bond cleavage**



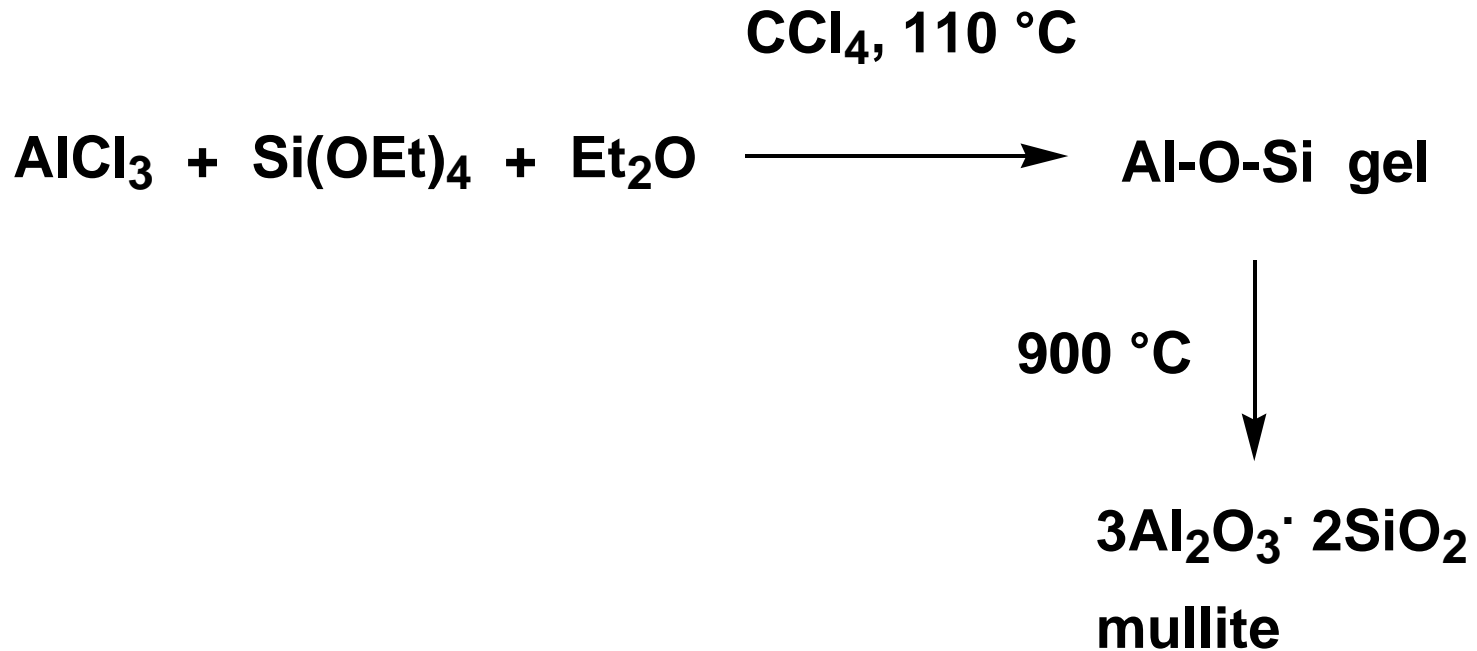


## Alkylhalide Elimination Reactions



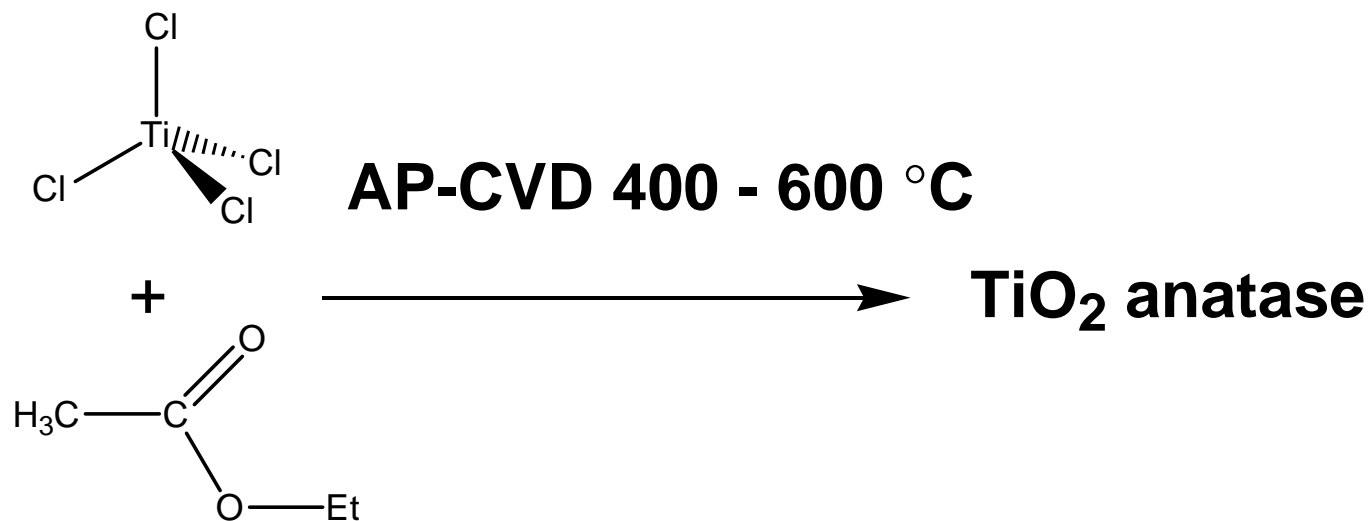
Colvin et al., *J. Am. Chem. Soc.*, **1999**, *121*, 1613

# Alkylhalide Elimination Reactions



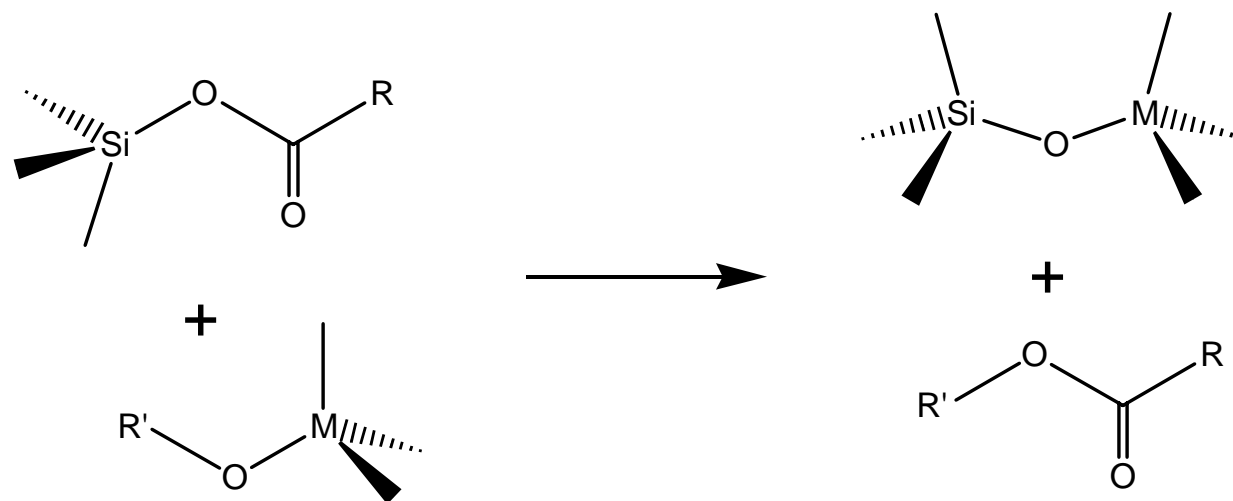
Janackovic et al., *NanoStructured Materials*, **1999**, 12, 147

# Alkylhalide Elimination Reactions



Parkin I. et al., *Chem. Mater.*, **2003**, *15*, 46

## Ester Elimination Reactions: acetates + alkoxides

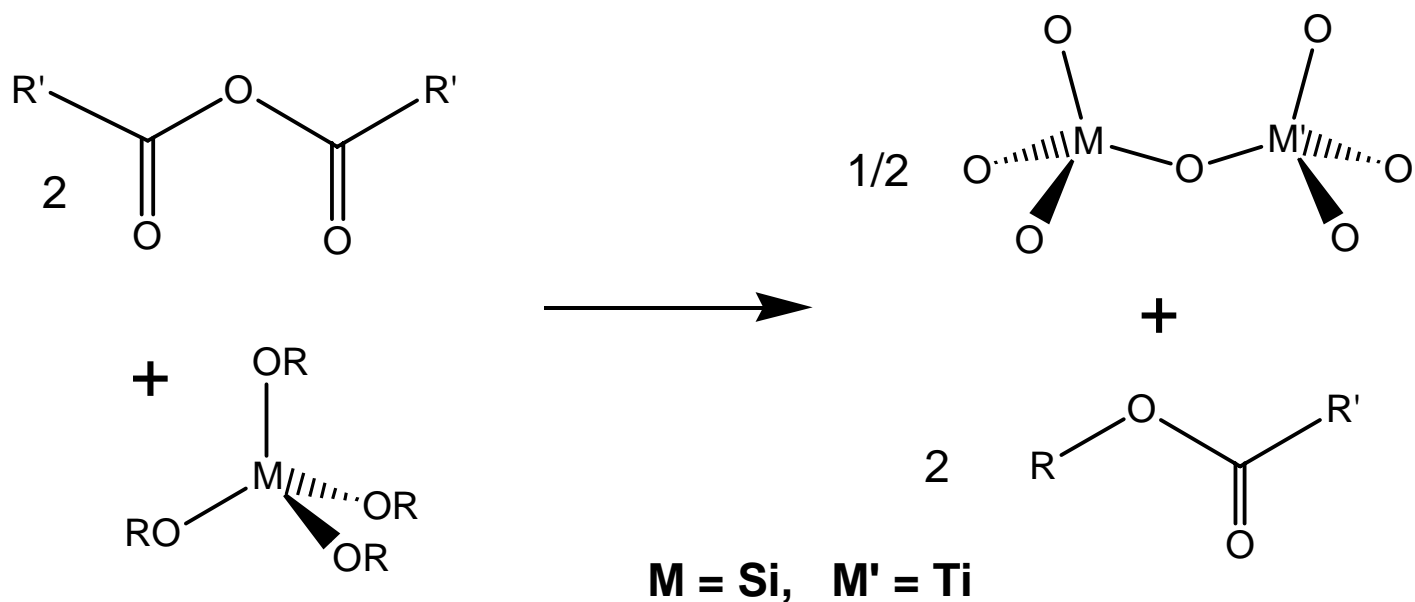


M = Zr, Si, Ti, Ba, Sn, Pb

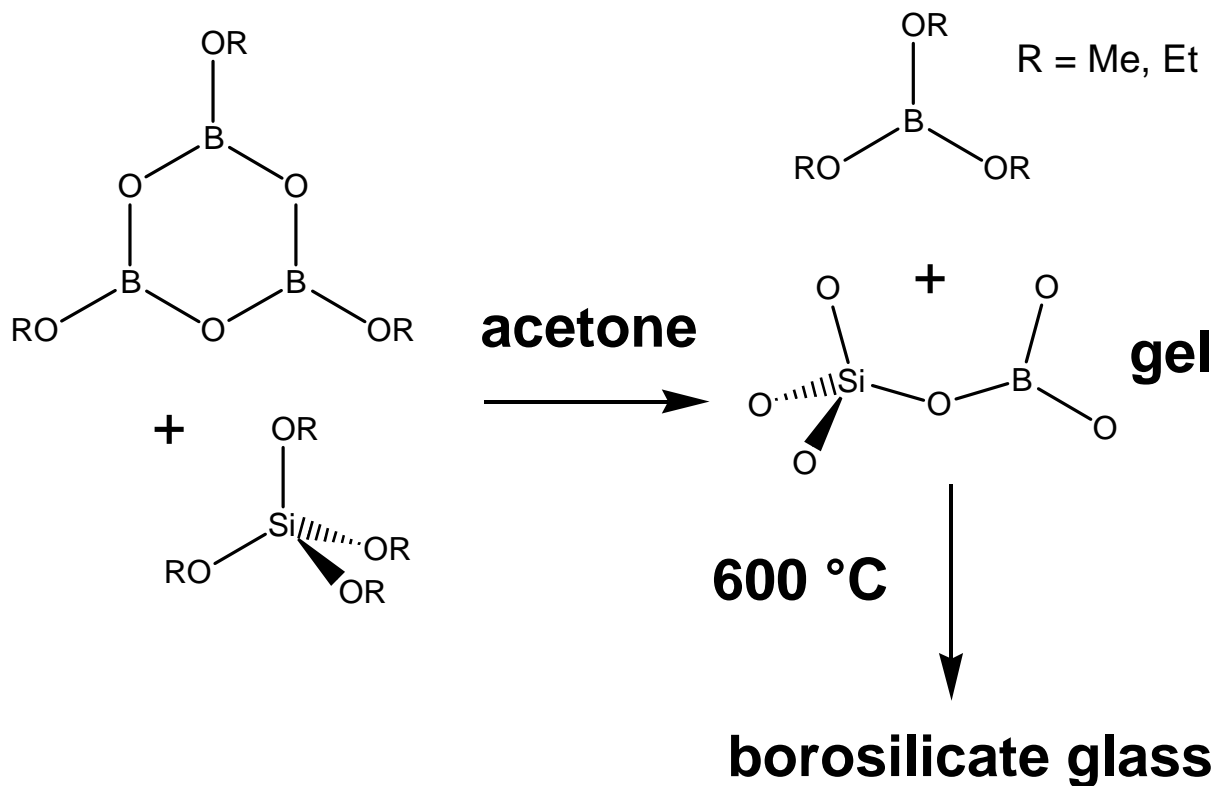
Jansen, Guenther, *Chem. Mater.*, **1995**, 7, 2110

Hampden-Smith et al., *Chem. Comm.*, **1995**, 157

# Ester Elimination Reactions: alkoxides + acid anhydrides



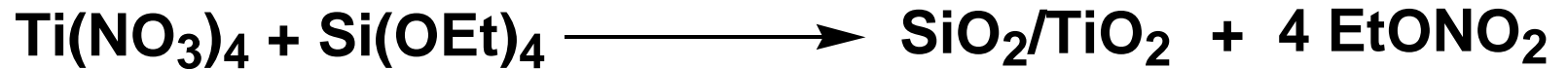
# Ester Elimination Reactions: alkoxides + acid anhydrides



Becket et al., *Chem. Comm.*, 2000, 1499

## Ester Elimination Reactions

**CVD , 300 - 535 °C**

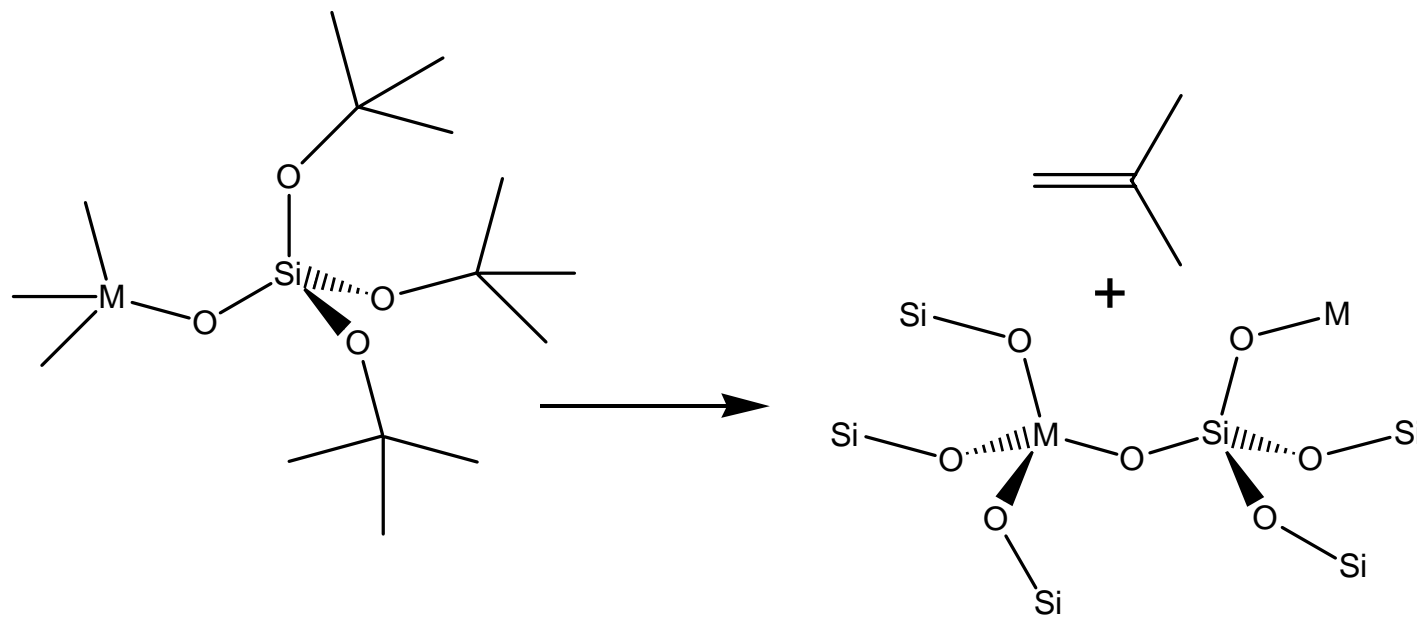


Gladfelter et al., *Chem. Mater.*, **2000**, *12*, 2822



# Alkene Elimination: *tris*(tert-butoxy)silanolates

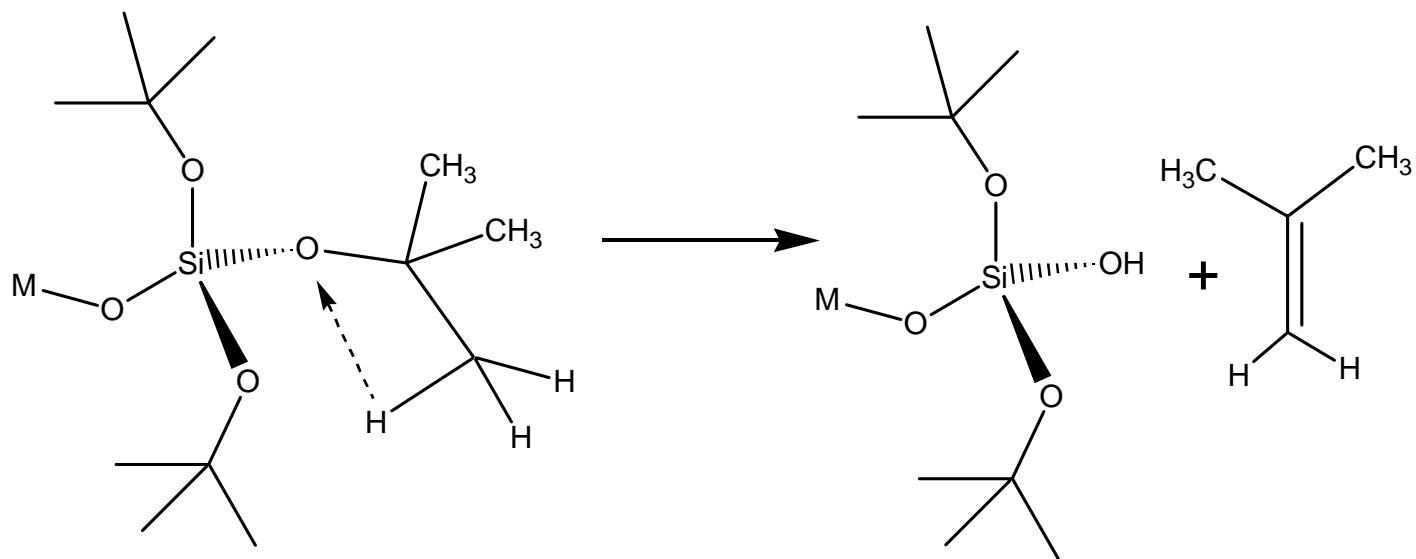
M = Ti, Zr, Hf, Al, Cr, Cu, Zn, Mo, W, V



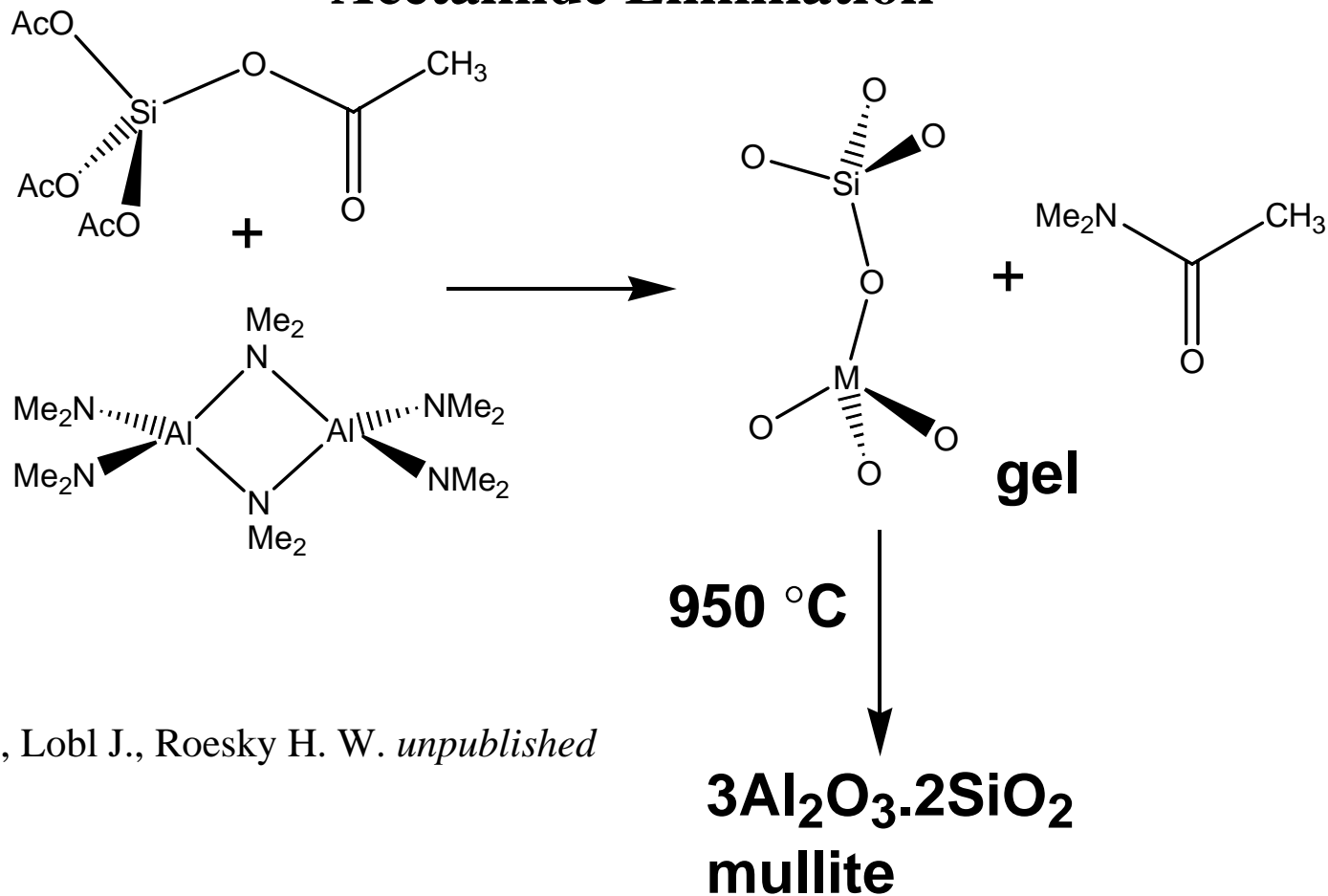
Tilley et al., Berkely

# Alkene Elimination: *tris*(tert-butoxy)silanolates

## $\beta$ -Hydrogen Elimination

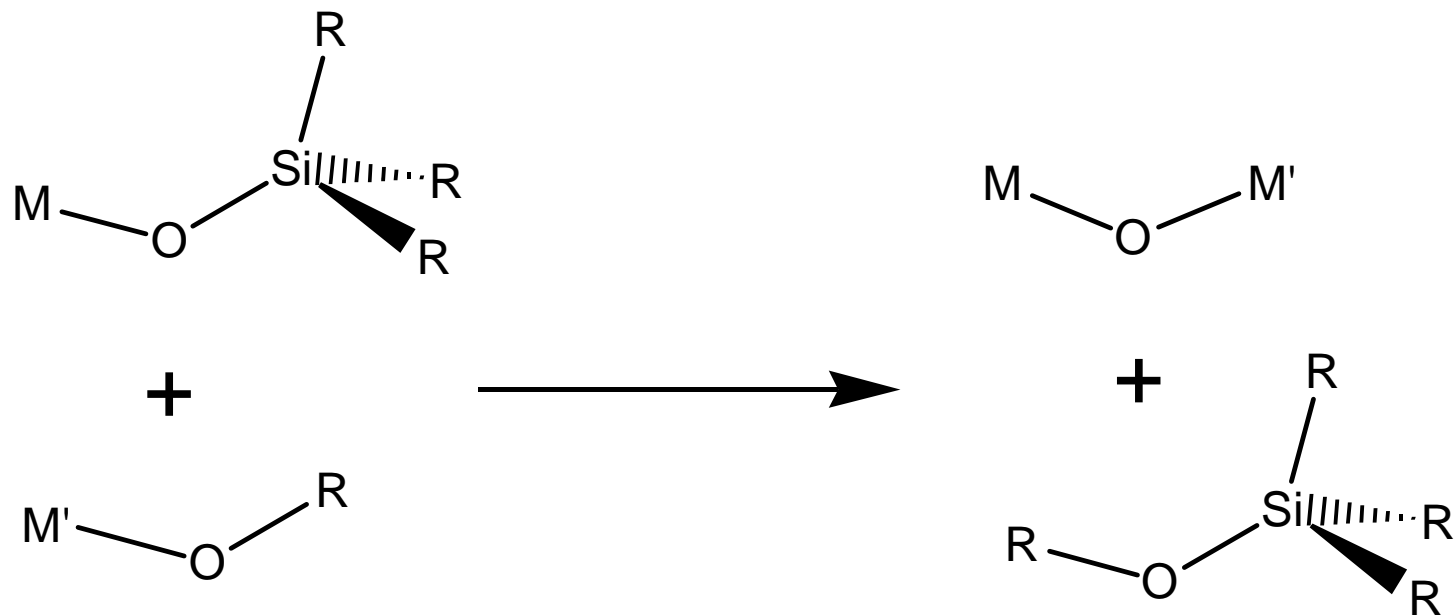


## Acetamide Elimination



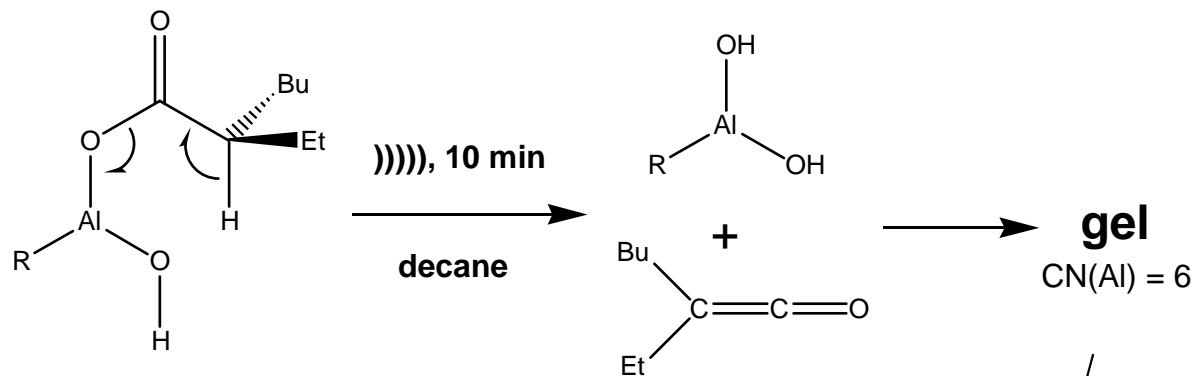
Pinkas J., Lobl J., Roesky H. W. *unpublished*

## Ether Elimination



Hampden-Smith et al.,

# Ketene Elimination



Ulman et al., *J. Am. Chem. Soc.*, **2003**, *125*, 4010

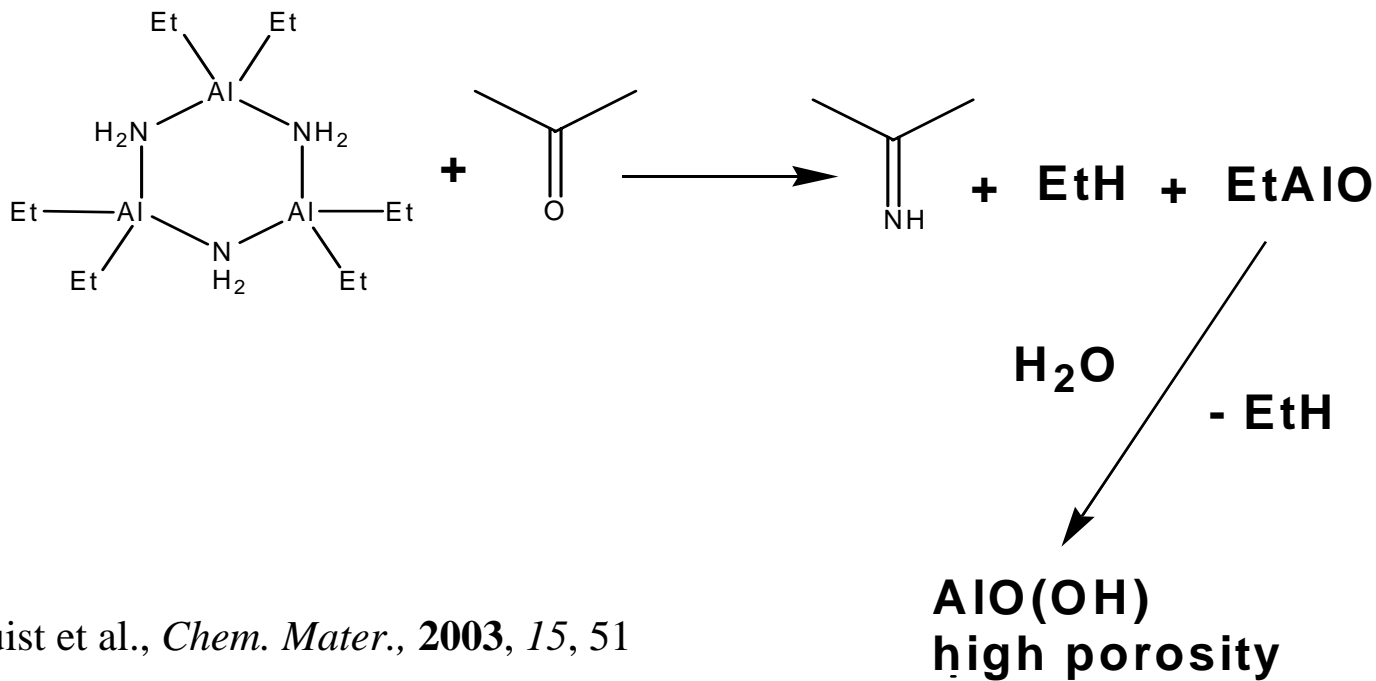
**700 - 900 °C**

**$\gamma\text{-Al}_2\text{O}_3$  (10 nm)**

**$\text{Y}_3\text{Al}_5\text{O}_{12}$**

**$\text{LaAlO}_3$**

# Ketimine Elimination



Lindquist et al., *Chem. Mater.*, 2003, 15, 51

## Thermolysis of a single-source precursor



Fischer et al., *J. Mater. Chem.* **2002**, *12*, 1625

# Preparation of Phosphates and Phosphonates

**Alkane/Hydrogen Elimination**

**Alcohol Elimination**

**Alkene Elimination**

**Ether Elimination**

**Alkylhalide Elimination**

**Chlorosilane Elimination**

**Alkylsilane Elimination**

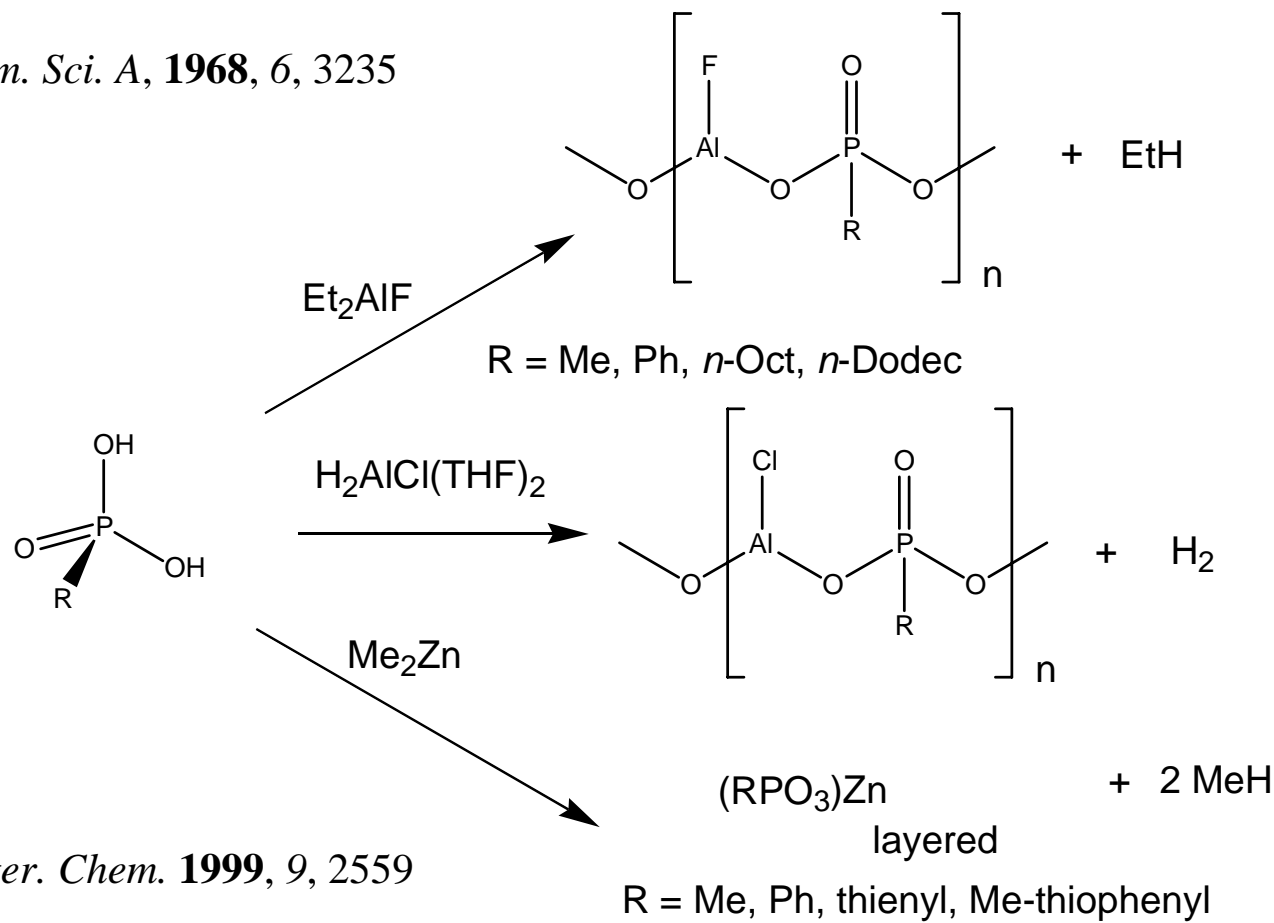
**Diketone/Ester Route**

**Alkylamine Elimination**



# Alkane/Hydrogen Elimination

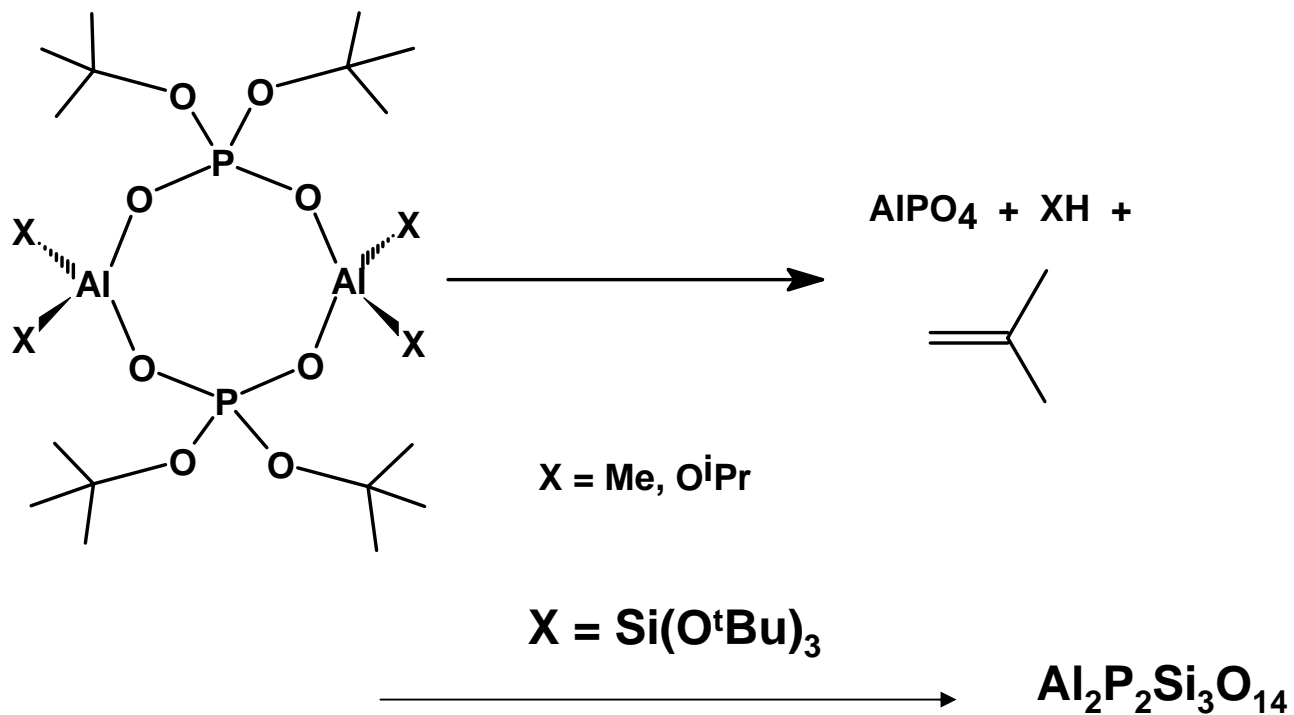
Schmidt et al., *J. Polym. Sci. A*, **1968**, 6, 3235



Gerbier et al., *J. Mater. Chem.* **1999**, 9, 2559

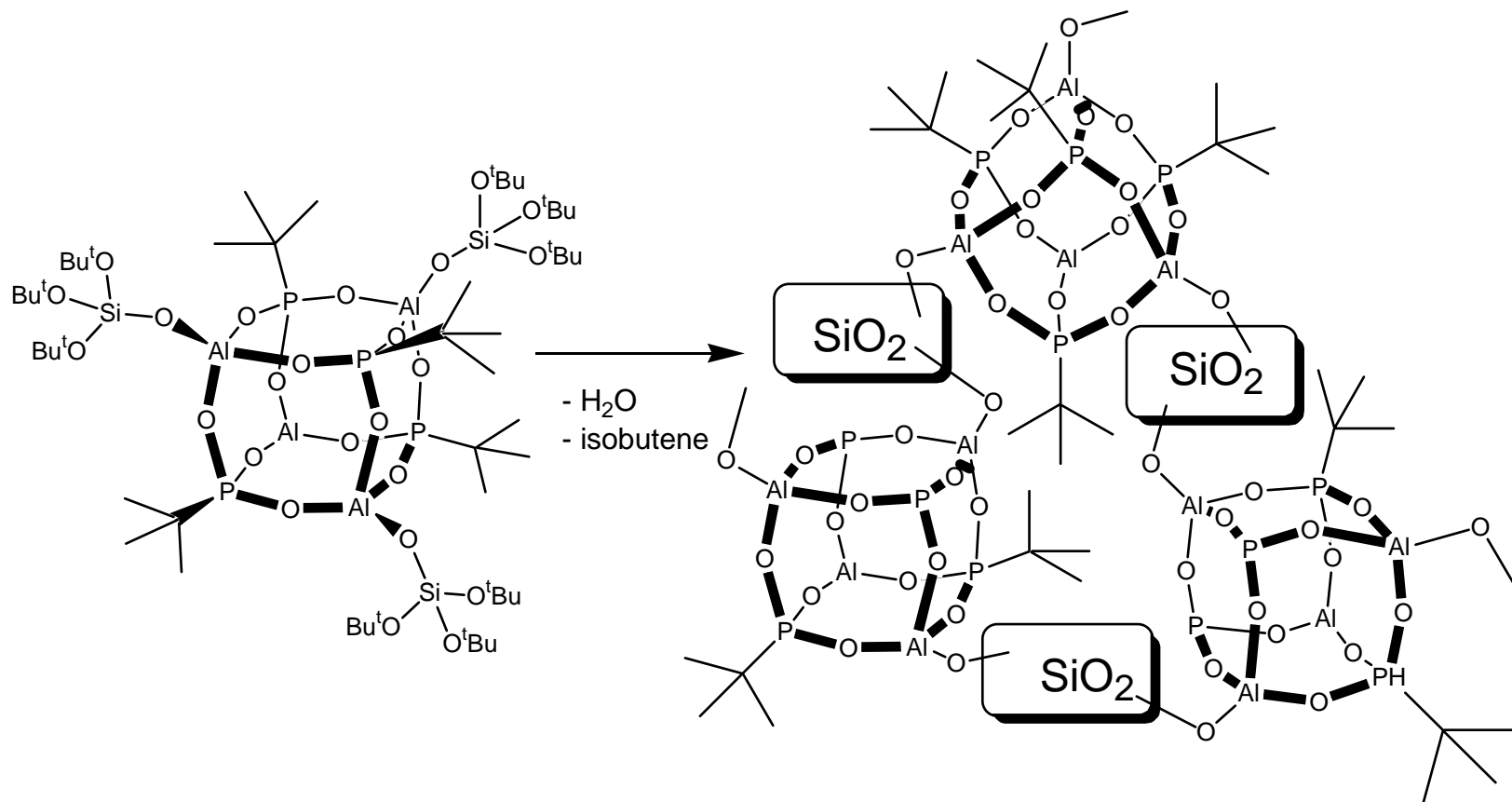
Knight et al., *J. Organometal. Chem.* **1999**, 585, 162

# Alkene Elimination



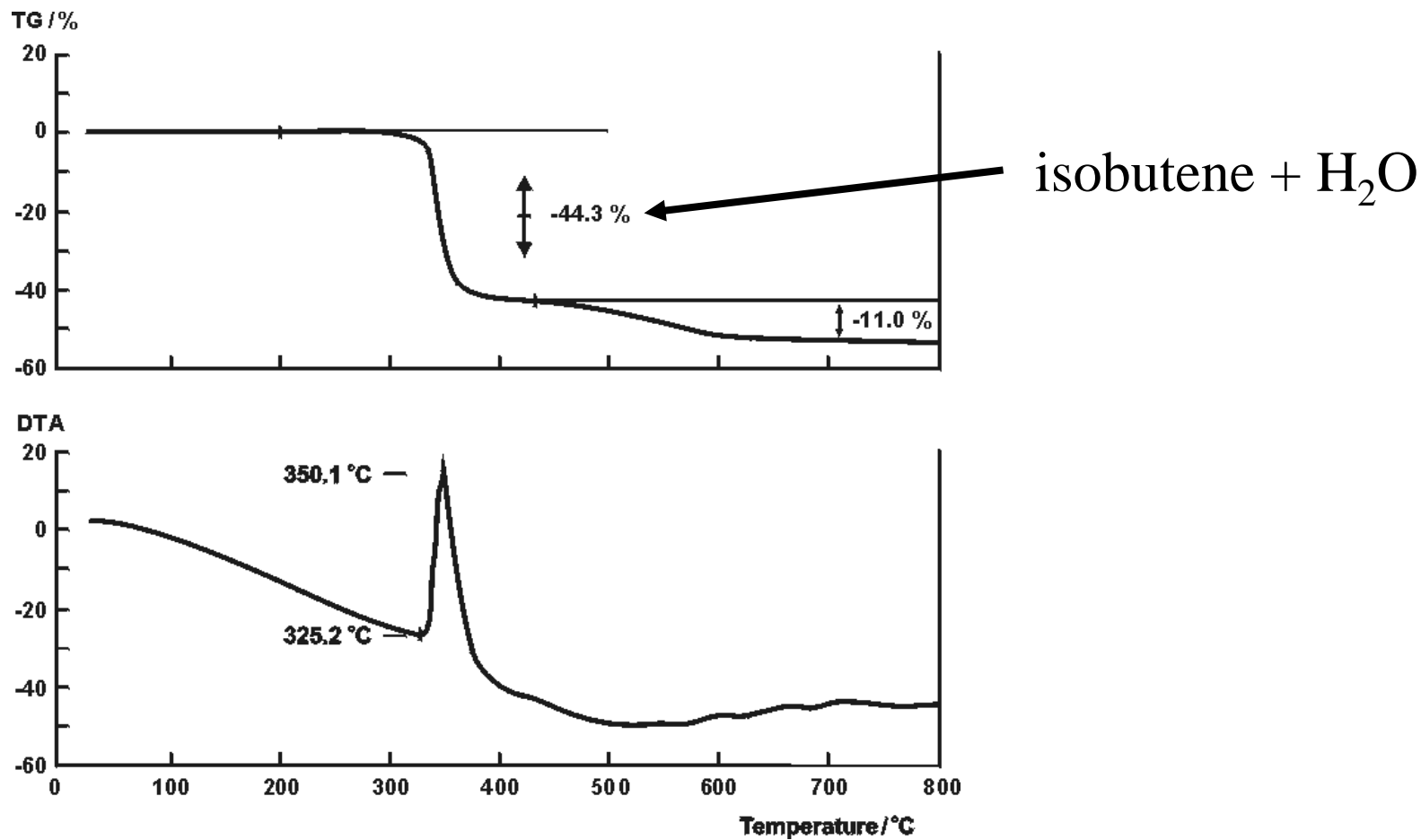
Tilley et al., *J. Am. Chem. Soc.* **2001**, *123*, 10133

# Alkene Elimination: *tris*(tert-butoxy)silanolates



Pinkas J., Brlejova Z., Roesky H. W. *unpublished*

# Alkene Elimination: *tris*(tert-butoxy)silanolates

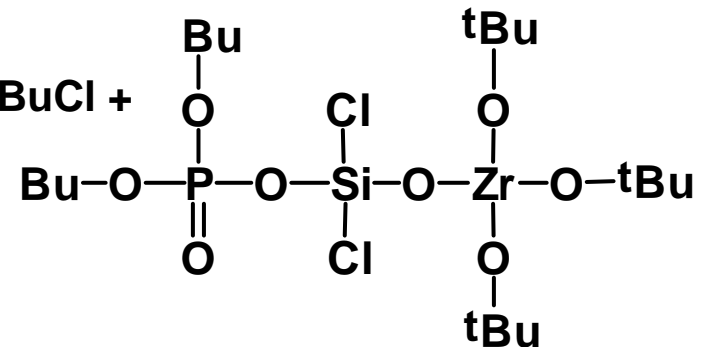
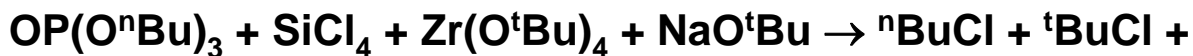


# Alkylhalide Elimination

Nonhydrolytic synthesis of NASICON

$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$  solid electrolyte, high  $\text{Na}^+$  ionic conductivity

- Solid state preparation: dissolved  $\text{ZrO}_2$
- Sol-gel from alkoxides: very slow hydrolysis necessary, different hydrolysis rates
- Nonhydrolytic route in  $\text{CH}_3\text{CN}$



Gel formation

Solvent and byproduct evaporation under vacuum

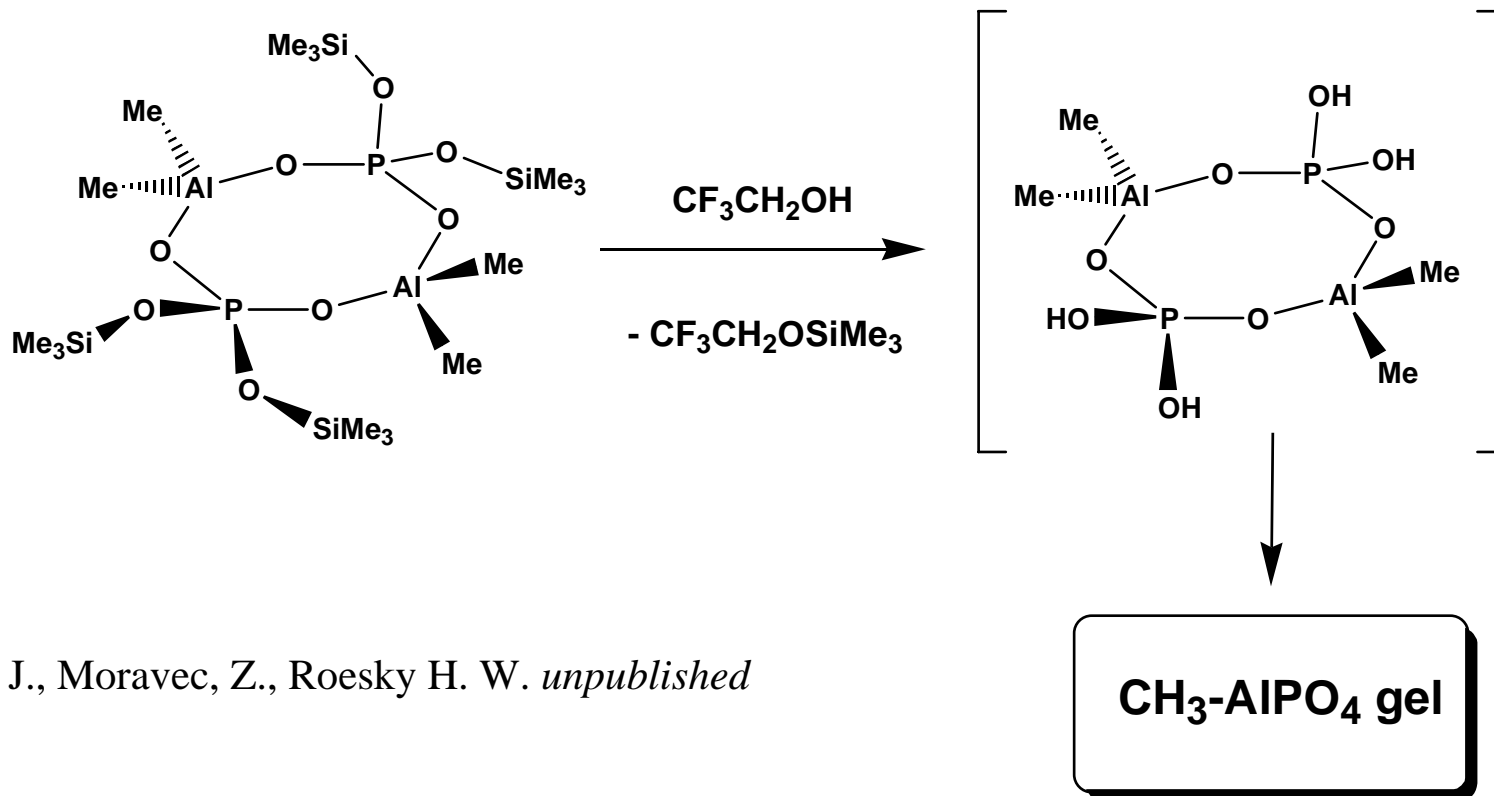
Drying at 120 °C for 15 h

Ball milling

Calcination at 800 °C gives NASICON

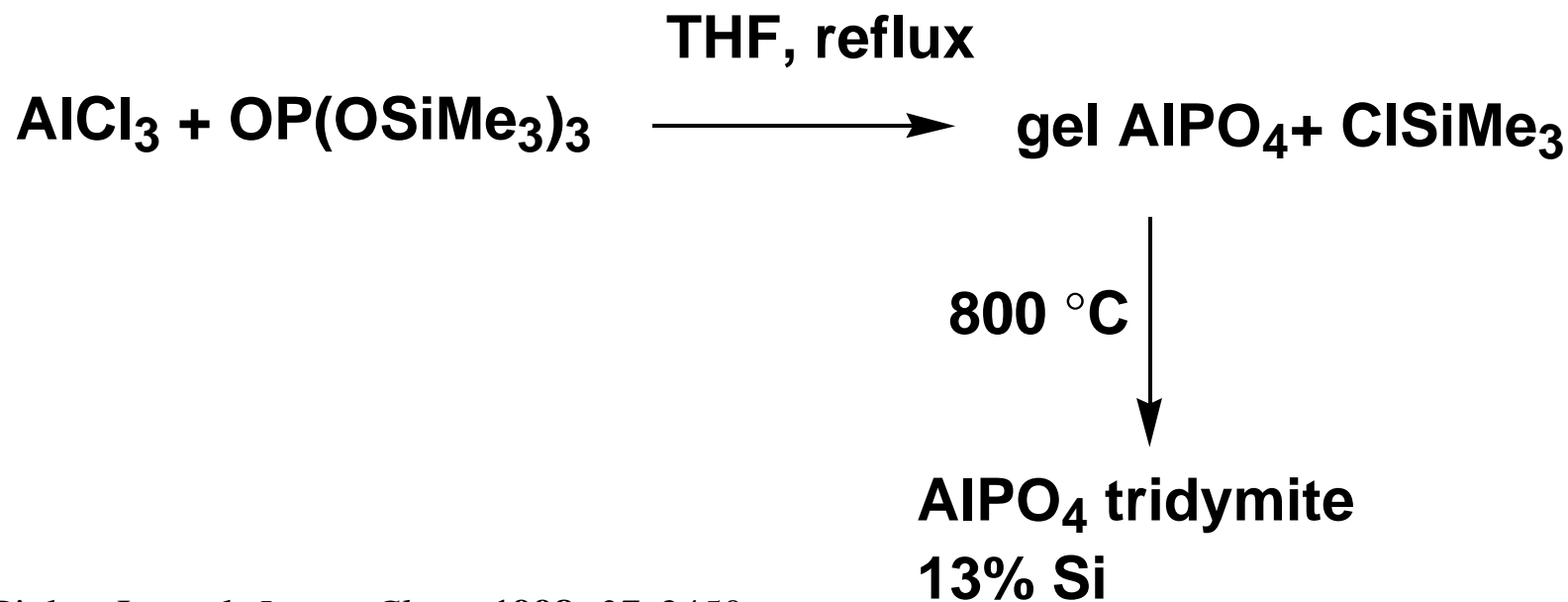
Di Vona et al., *J. Sol-Gel Sci. Technol.*, **2000**, 1/3, 463

# Ether Elimination



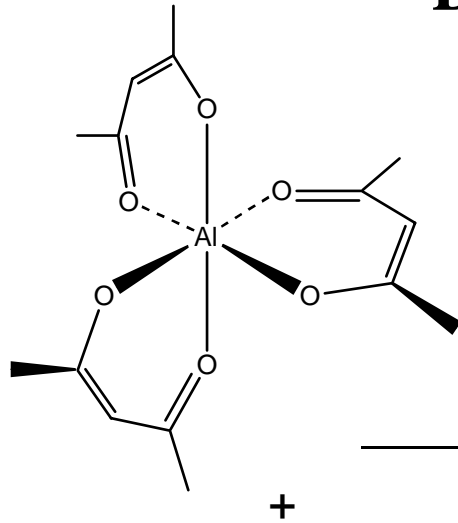
Pinkas J., Moravec, Z., Roesky H. W. *unpublished*

## Chlorosilane Elimination



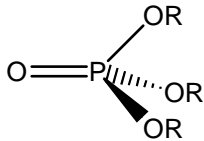
Pinkas J., et al. *Inorg. Chem.* **1998**, 37, 2450

## Diketone/Ester Route



pyrosol CVD process  
in ethanol, 300 – 400 °C

**AlPO<sub>4</sub> amorphous**



Daviero et al., *J. Non-Cryst. Solids*, **1992**, 146, 279, *Thin Solid Films*, **1993**, 226, 207