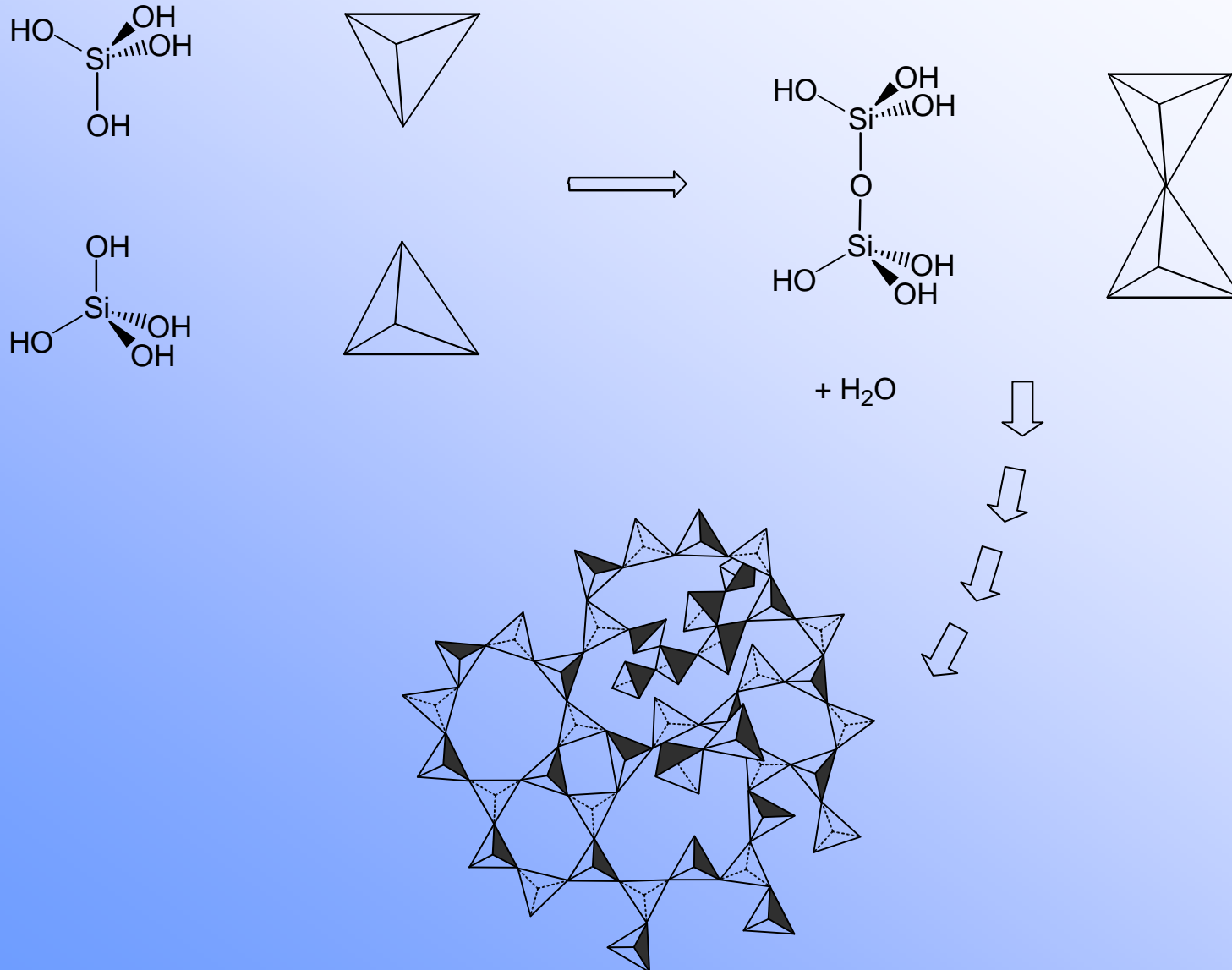


# Molecular Precursors for Sol-Gel Hybrid Materials: Fundamentals

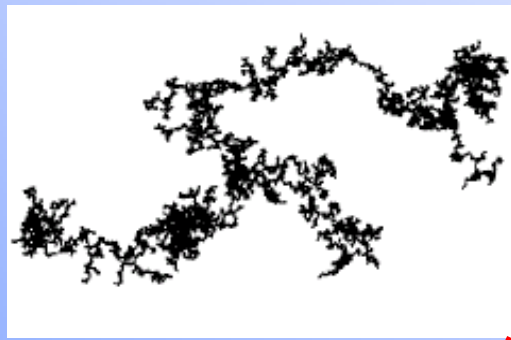
Ulrich Schubert

Institute of Materials Chemistry

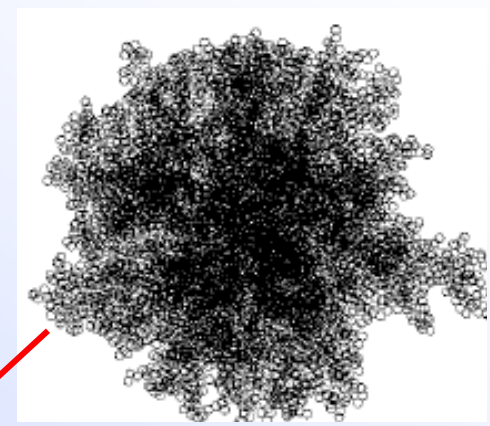
# Sol-Gel Process: Network Formation by Condensation Reactions



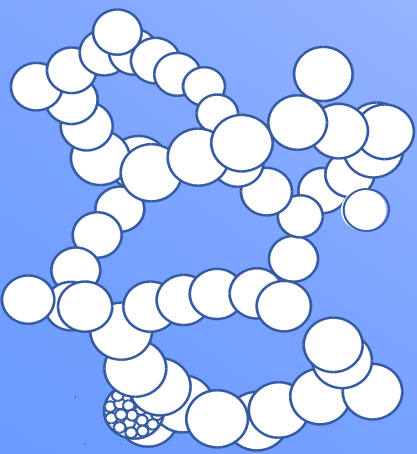
# Sol-Gel Processing: Development of the Network Structure



**Polymeric network structures**



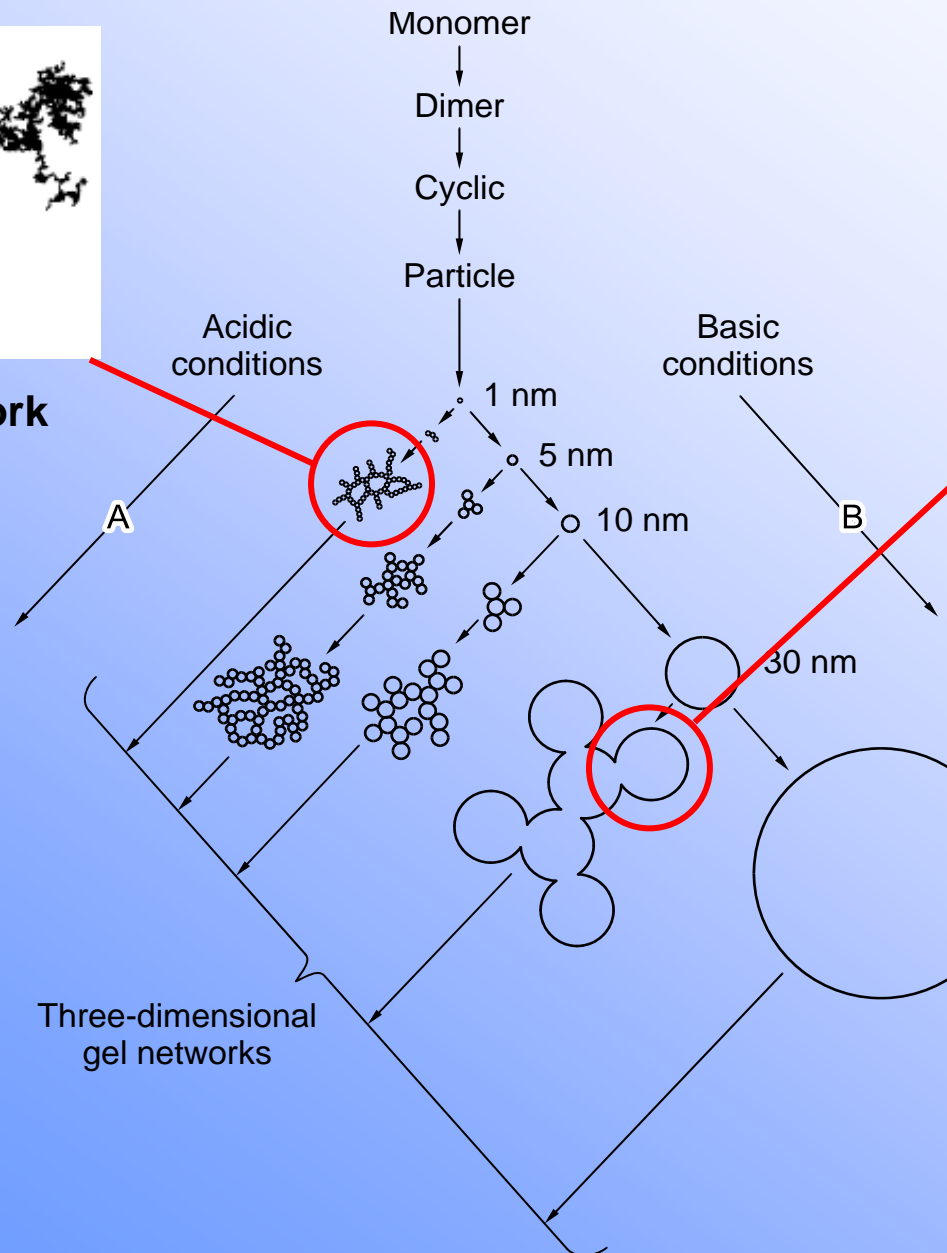
**Colloidal Structures**



**Three-dimensional gel networks**



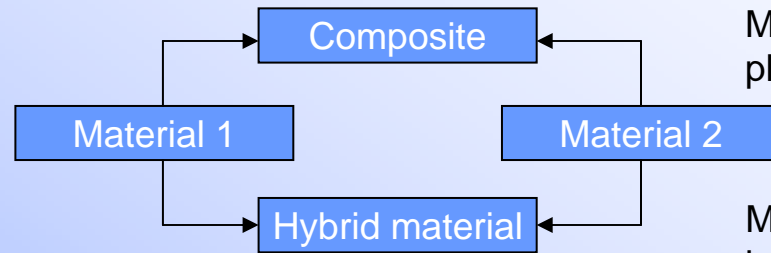
**Stober particles**



1. The precursors are the **building blocks** for the later materials. Multi-precursor mixtures allow combining different building blocks in a deliberate ratio and thus to prepare also materials with non-stoichiometric compositions  
⇒ **Control of the materials properties through the chemical composition.**



2. Whether gelation or precipitation occurs is a question of the overall reaction kinetics and is thus influenced by the precursors. **Gels are kinetically controlled solids**, while crystalline precipitates are formed under thermodynamic control ⇒ **Control of the materials properties through the reaction conditions.** This includes the kind of employed precursor.

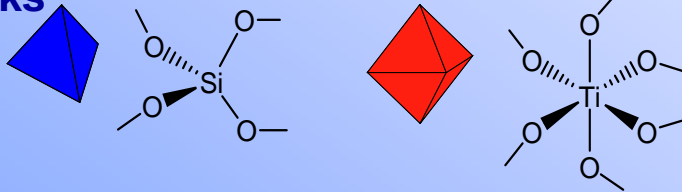


Macroscopic phases

Molecular building blocks

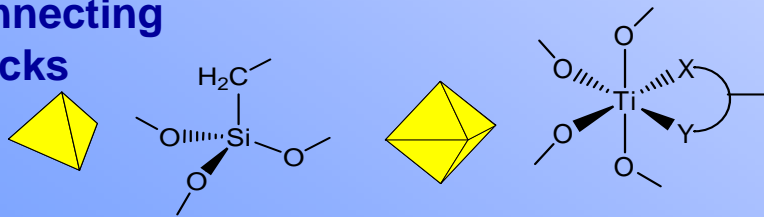


## Inorganic Building Blocks



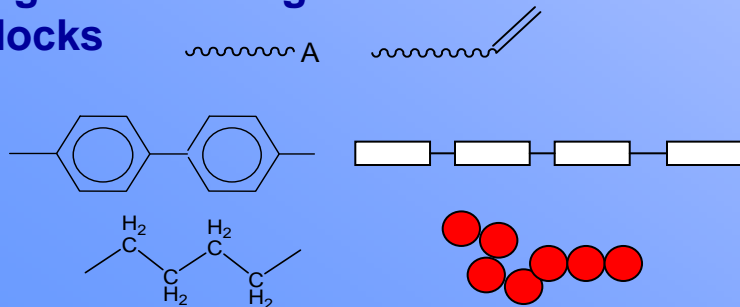
Mechanical, optical, electrical, magnetical properties

## Connecting Blocks



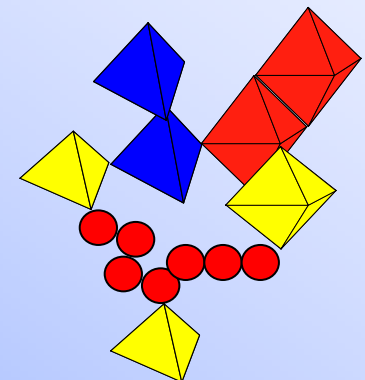
Reduction of the crosslinking density, coupling sites between inorganic / organic components

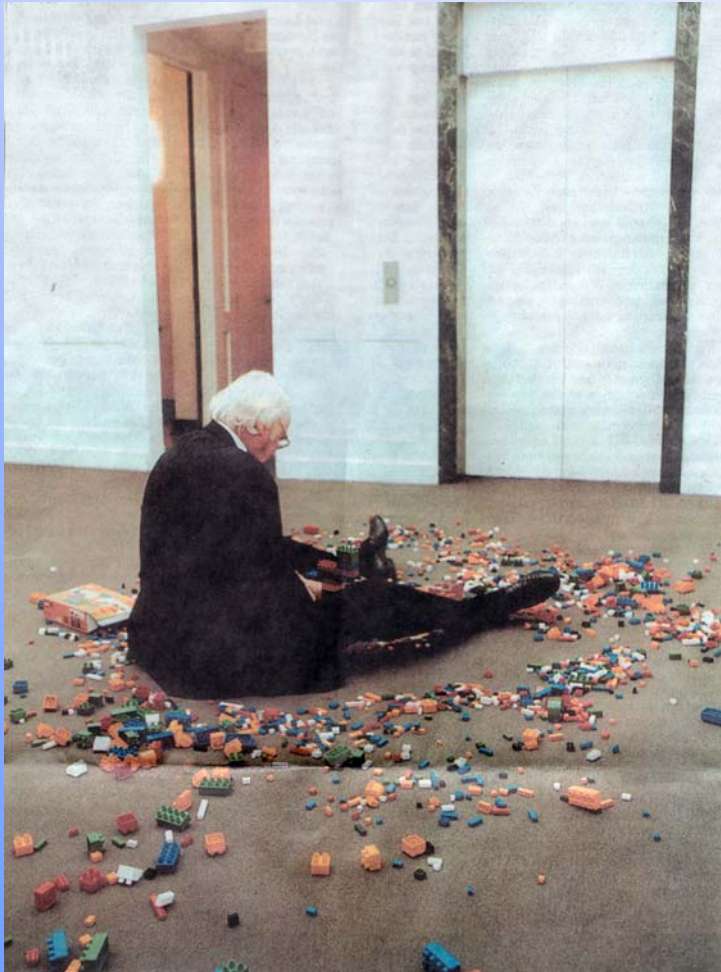
## Organic Building Blocks



Functional groups, crosslinking, polymerizability

Flexibility, elasticity, processability





## Silica Precursors

### Colloidal silica

$\text{Si(OR)}_4$  and  $\text{RSi(OR)}_3$   
preparation

## Metal Oxide Precursors

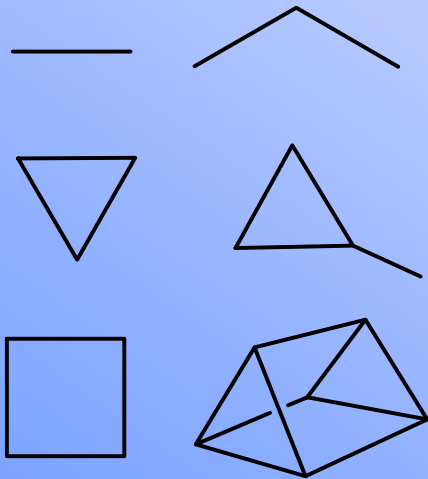
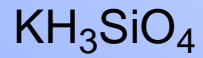
### Metal salts

aqua, hydroxo and oxo species

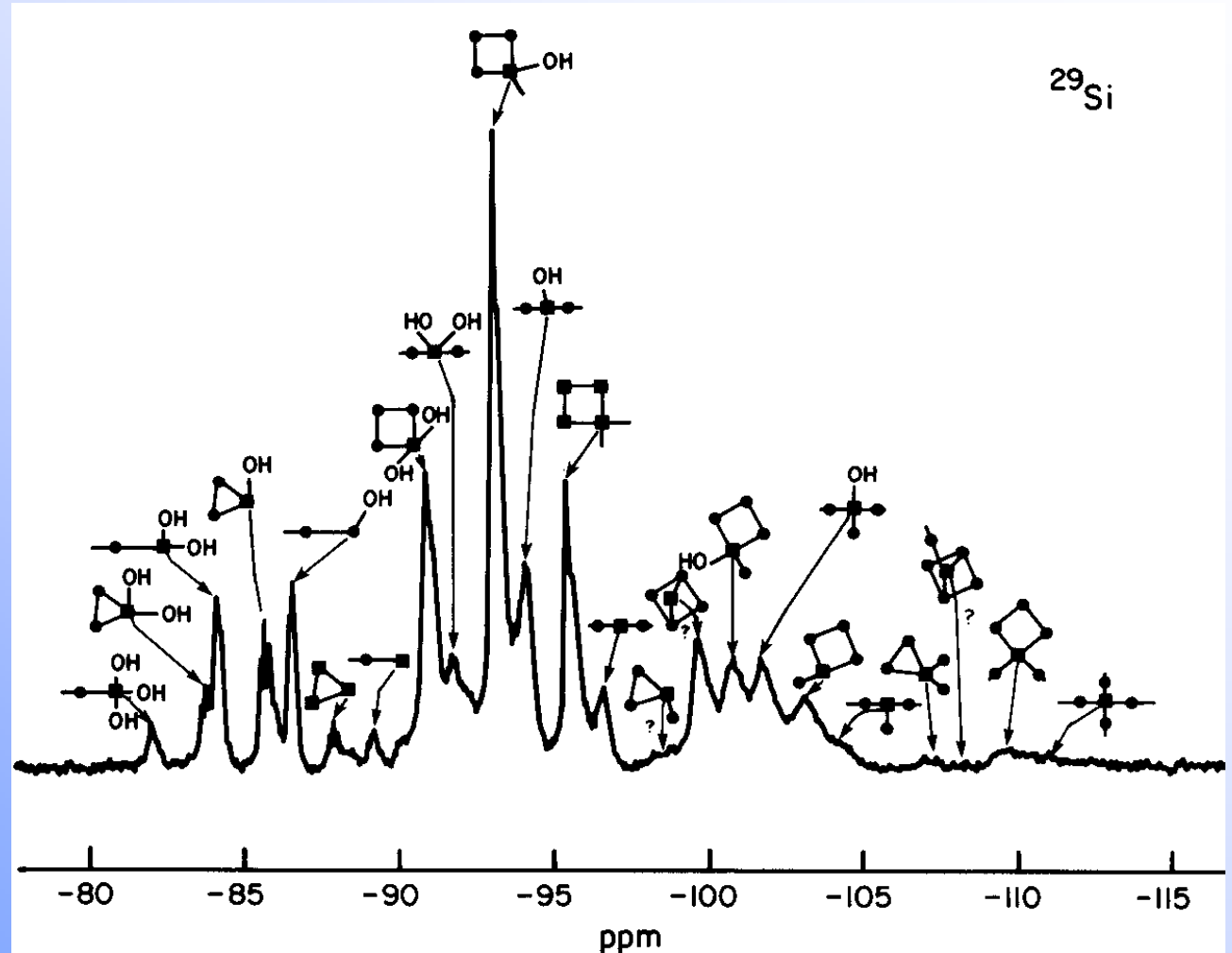
## Metal alkoxides

Lewis-acidic properties  
chemical modification

80% of particles in a 0.5 M aqueous  $K_2O \cdot SiO_2$  solution:



(— = Si-O-Si)



Generation of reactive species: hydrolysis



Network formation: condensation





Hydrolyzable  
group

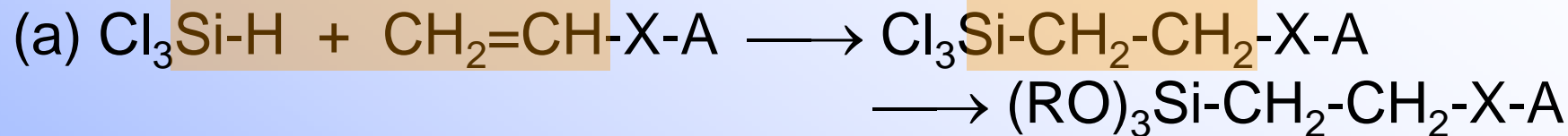
Chemically  
inert spacer

(Functional)  
Organic group

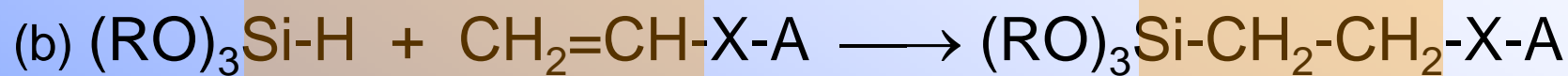
Nearly any group, except  
hydrolytically unstable  
groups

- Introduction of organic functionalities
- Polymerization and crosslinking sites

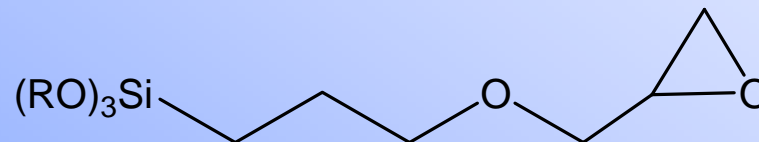
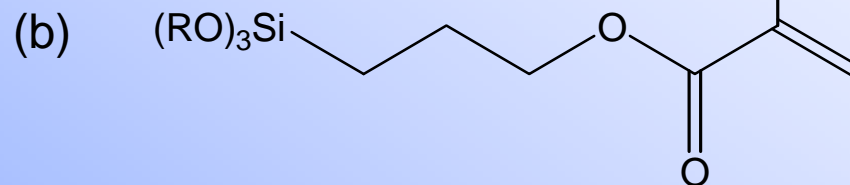
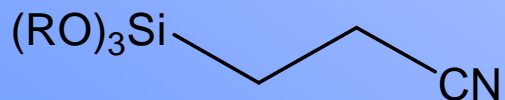
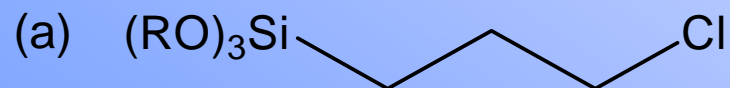


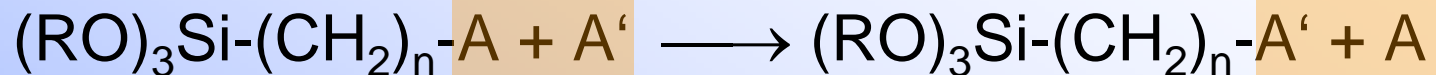


or

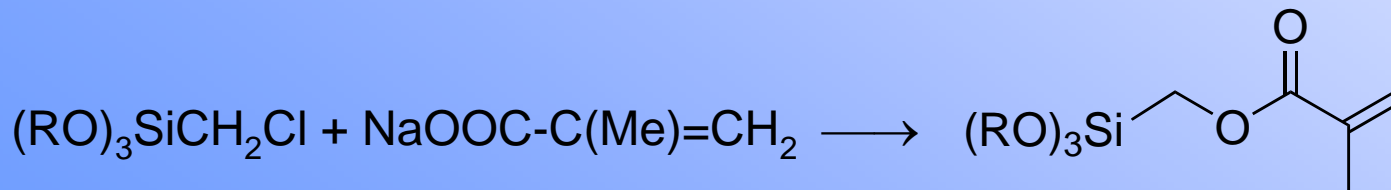
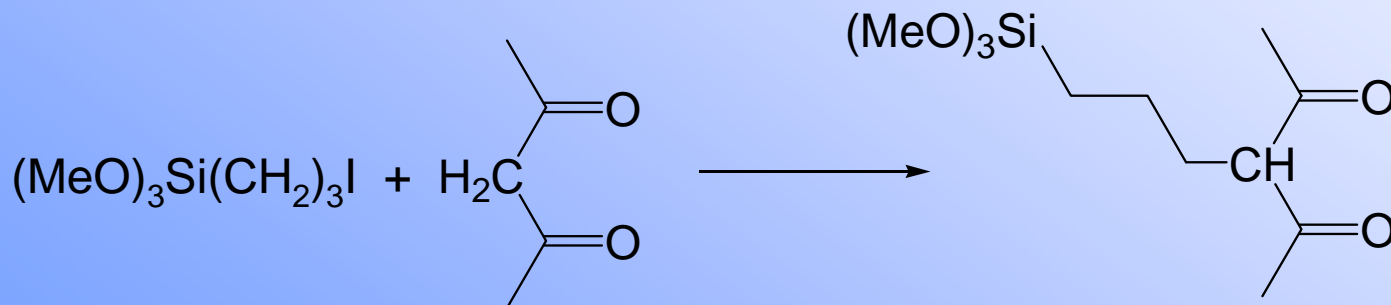


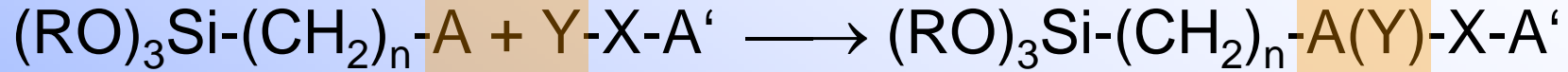
## Examples:



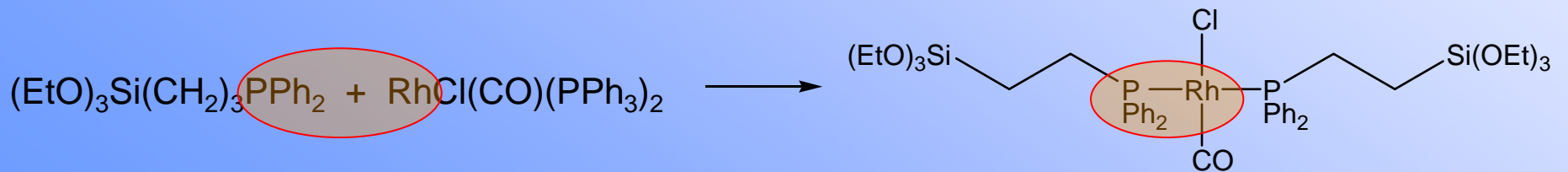
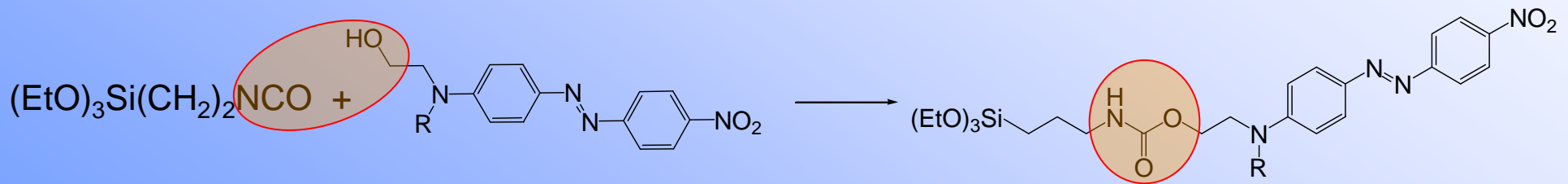
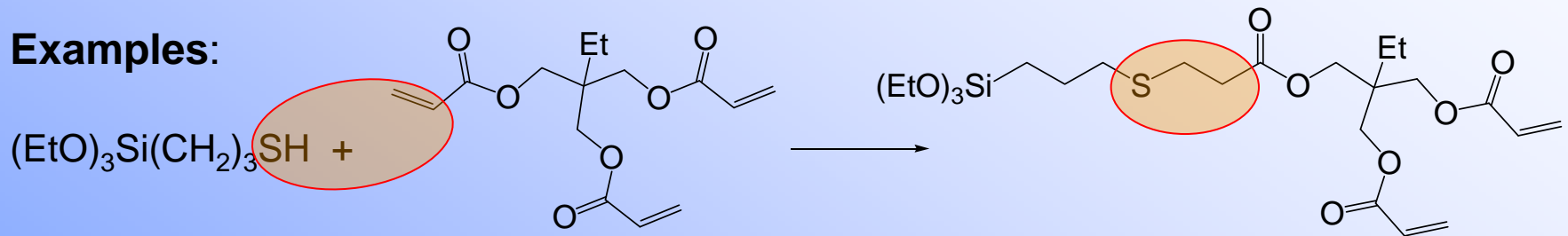


## Examples:





**Examples:**

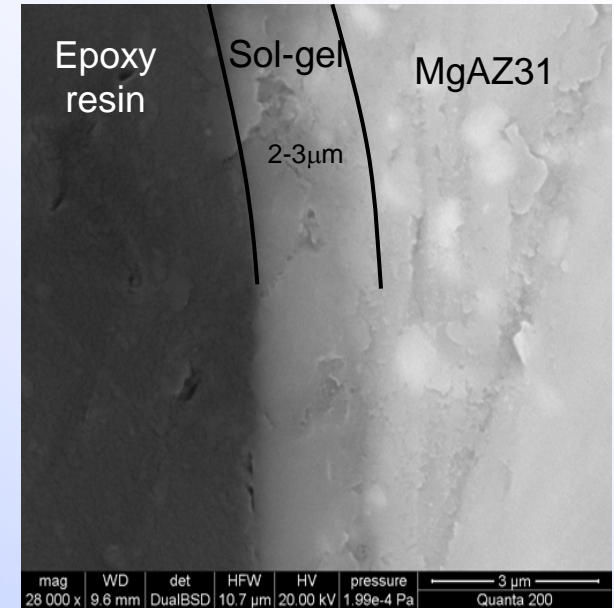


# Example: Corrosion-Protection Coating for Mg Alloys



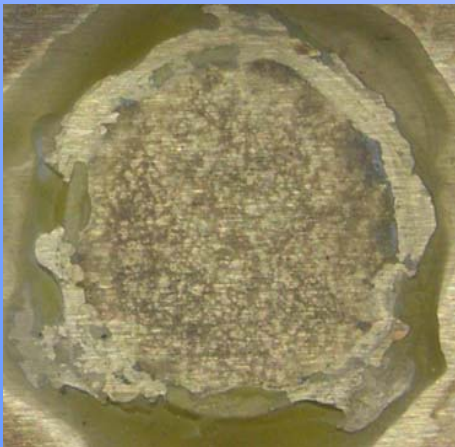
In cooperation with EADS

- (1) Cleaning of the Mg substrate by pickling with an aqueous solution of 20% acetic acid and 5%  $\text{NaNO}_3$ .
- (2) Coating sol from  $\text{MeSi}(\text{OEt})_3$ ,  $\text{Si}(\text{OEt})_4$ ,  $(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{X}$  (X = heterocyclic group with corrosion-inhibiting properties), water,  $\text{H}_3\text{PO}_4$ , alcohol and a metal-organic compound as adhesion promotor

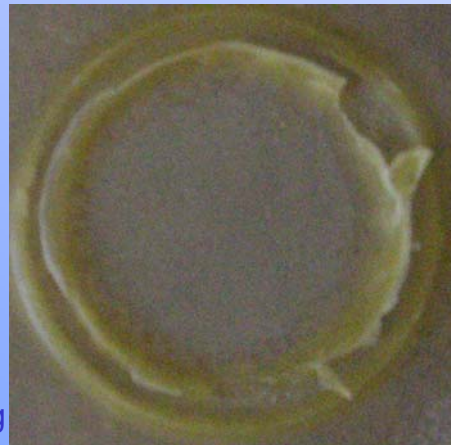


Corrosion test (WE34, 5% NaCl solution) after 24 h

untreated

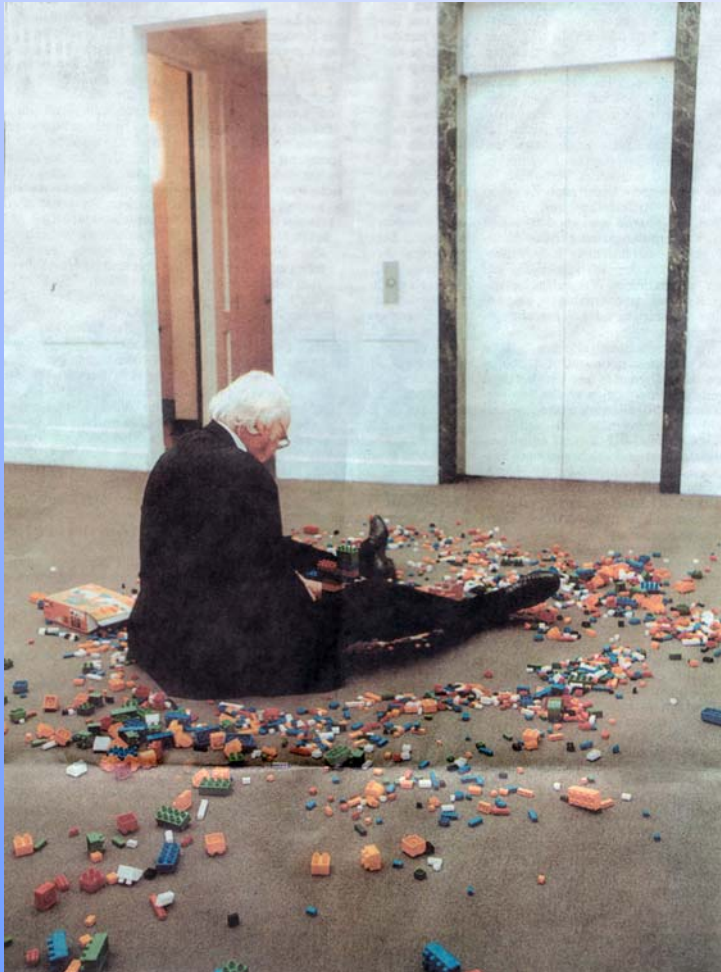


only pickling



with sol-gel coating





## Silica Precursors

Colloidal silica

$\text{Si(OR)}_4$  and  $\text{RSi(OR)}_3$   
preparation

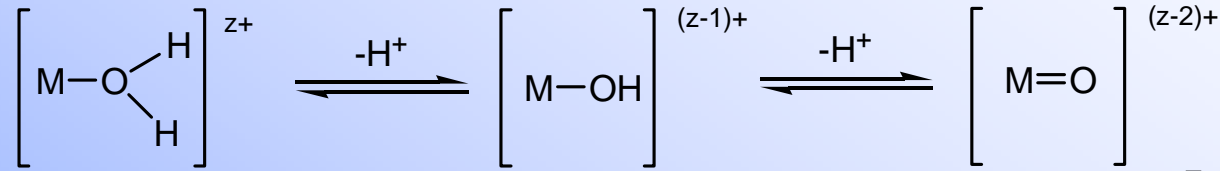
## Metal Oxide Precursors

**Metal salts**

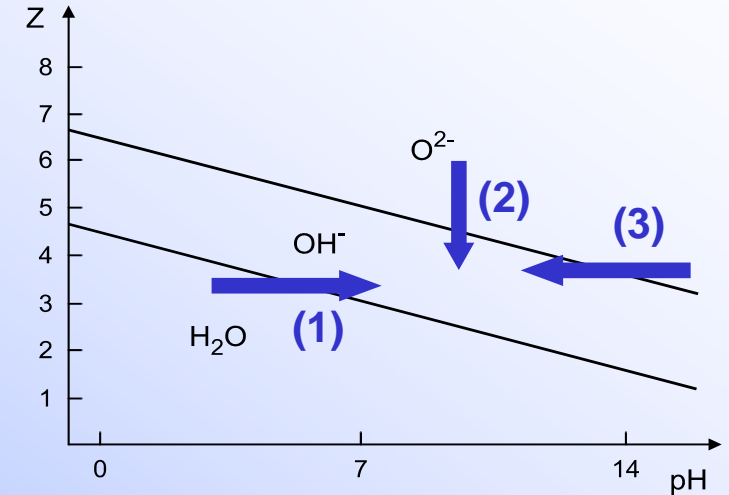
aqua, hydroxo and oxo species

**Metal alkoxides**

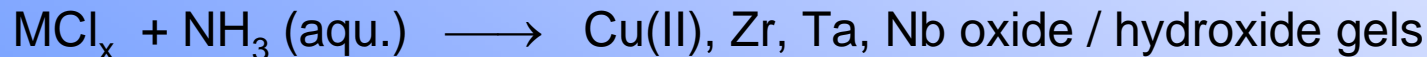
Lewis-acidic properties  
chemical modification



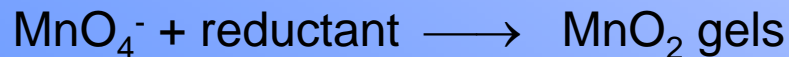
Hydroxo complexes contain both groups with good nucleophilic properties (O or OH) and good leaving groups (H<sub>2</sub>O or OH<sup>-</sup>). Therefore, it is generally necessary to be in the hydroxo domain to generate condensed species. This domain can be reached from either side by either changing the oxidation state of the metal (z) or the pH.



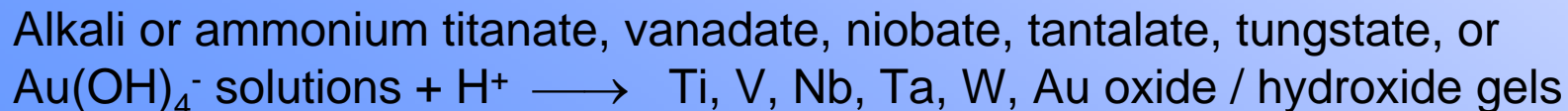
## (1) Adding a base to aquo complexes:



## (2) Reduction of metallate ions:



## (3) Acidifying solutions of metallate ions:



ZrO<sub>2</sub> / PVP

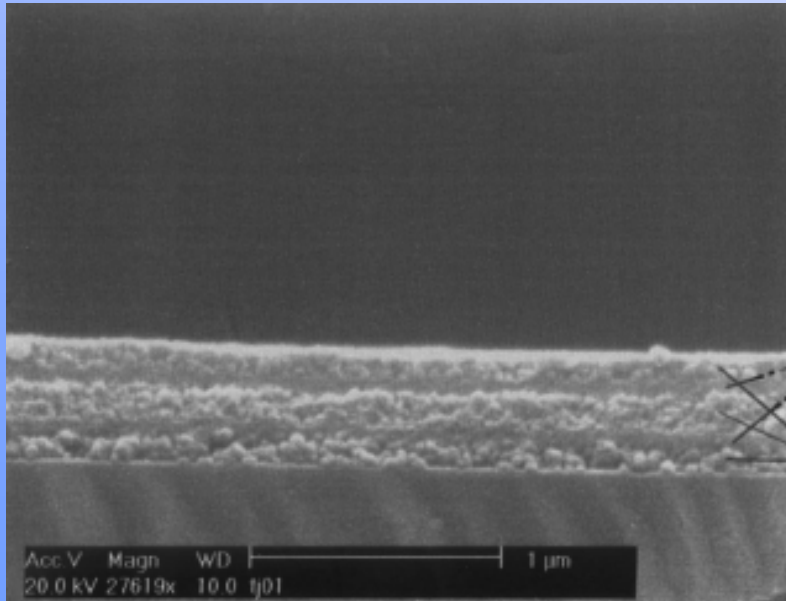


210 nm SiO<sub>2</sub>

ZrO<sub>2</sub> / PVP

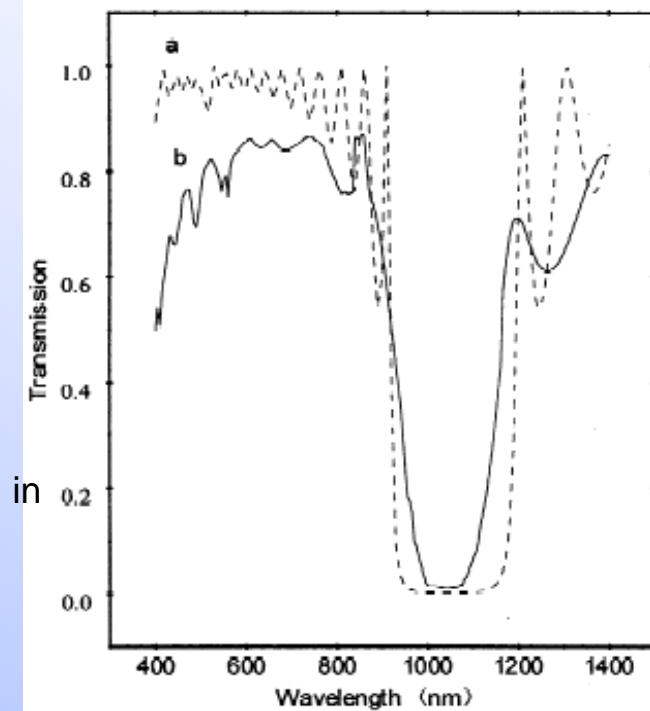
210 nm SiO<sub>2</sub>

substrate

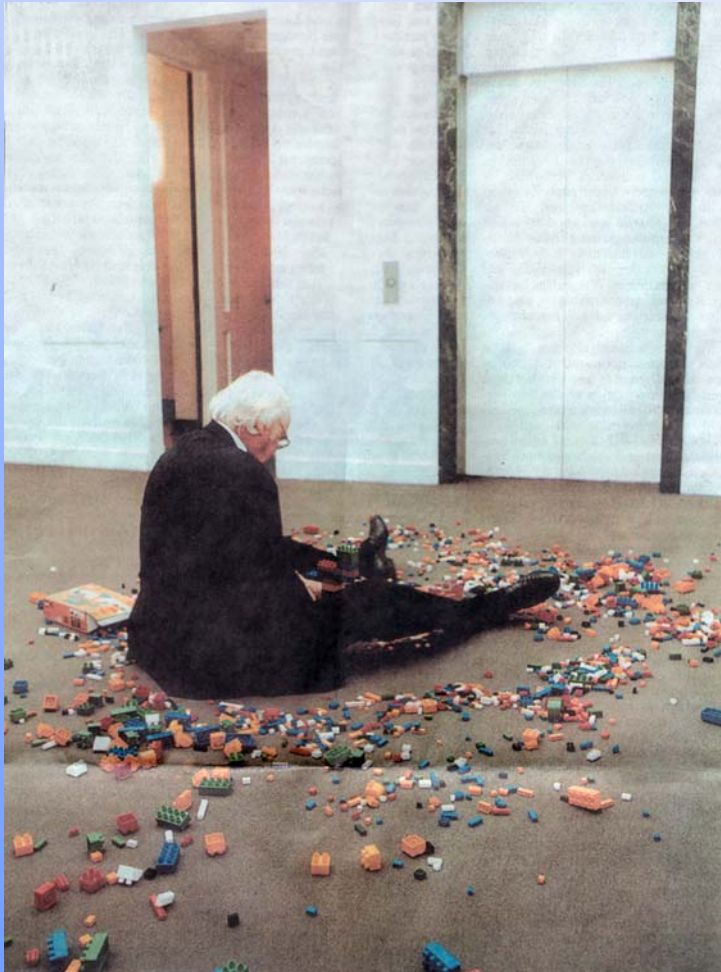


15 nm ZrO<sub>2</sub> particles (from ZrOCl<sub>2</sub>) in PVP binder (15 wt%); n<sub>D</sub> 1.70

SiO<sub>2</sub> from Si(OEt)<sub>4</sub>; n<sub>D</sub> 1.22



20 layers SiO<sub>2</sub> / ZrO<sub>2</sub>  
a: theoretical, b: experimental



## Silica Precursors

### Colloidal silica

$\text{Si(OR)}_4$  and  $\text{RSi(OR)}_3$   
preparation

## Metal Oxide Precursors

### Metal salts

aqua, hydroxo and oxo species

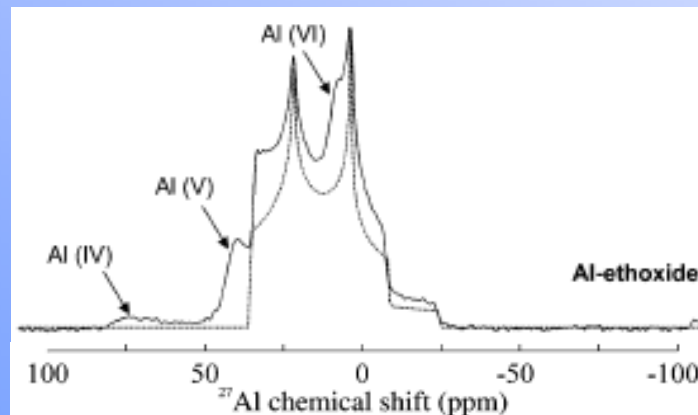
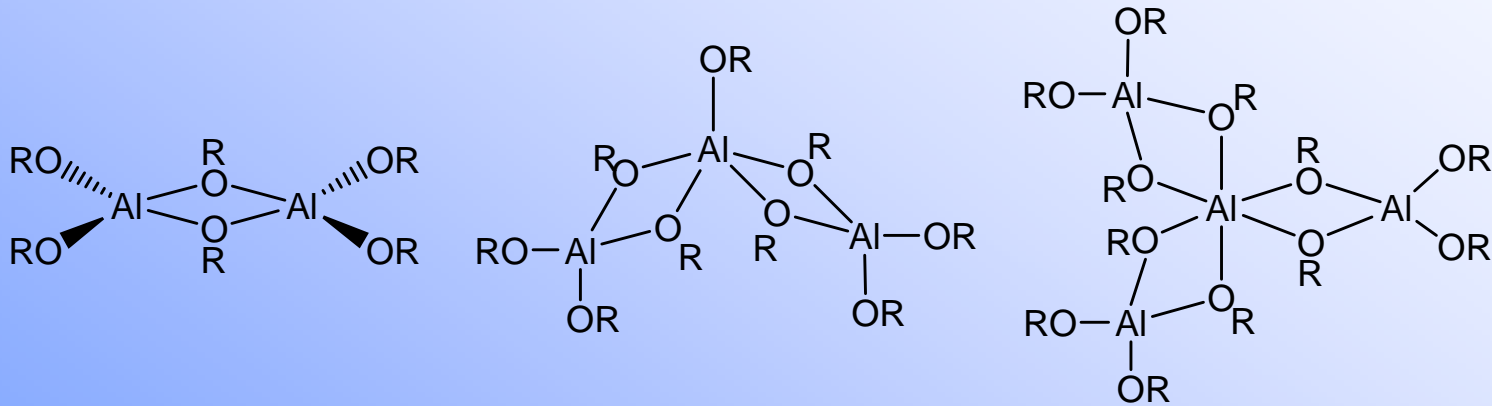
### Metal alkoxides

Lewis-acidic properties  
chemical modification

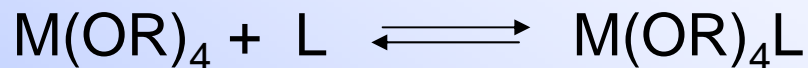
## Structures of dimeric, trimeric and tetrameric aluminum alkoxides

$Al(O^tBu)_3$  dimer

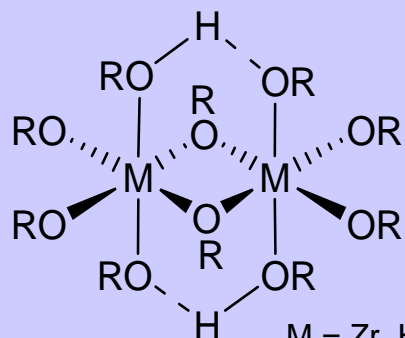
$Al(O^sBu)_3$  trimer-tetramer equilibrium (in solution)



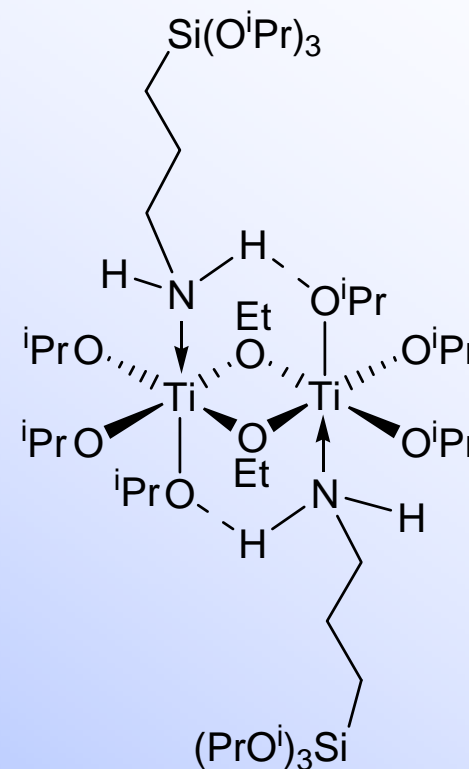
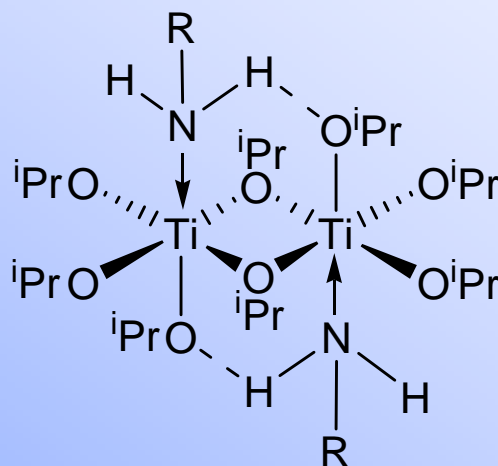
$Ti(OR)_4$  as an example



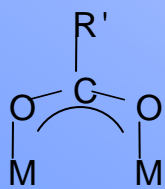
$M(OR)_4$ :



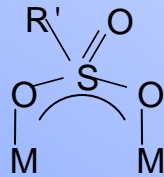
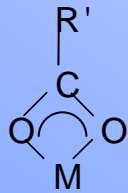
M = Zr, Hf: R = *i*Pr  
M = Ti: fluorinated R



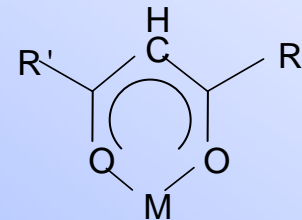
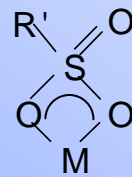
Stability of the base adducts is a balance between the strength of the M-N donor-acceptor interaction and the N-H...O hydrogen bond



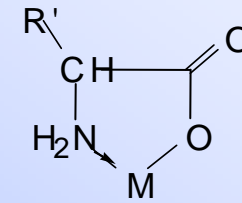
Carboxylate



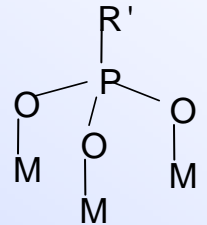
Sulfonate



$\beta$ -Diketonate

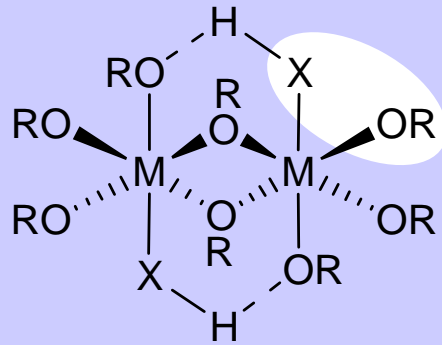


$\alpha$ -Amino-  
carboxylate

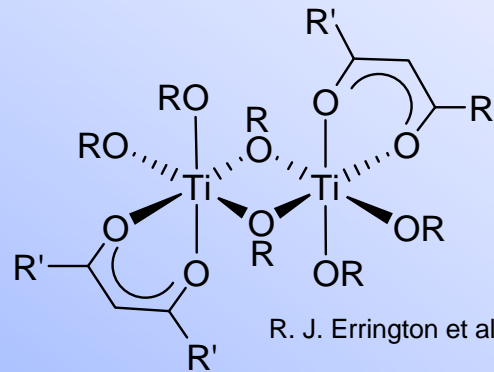


Phosphonate

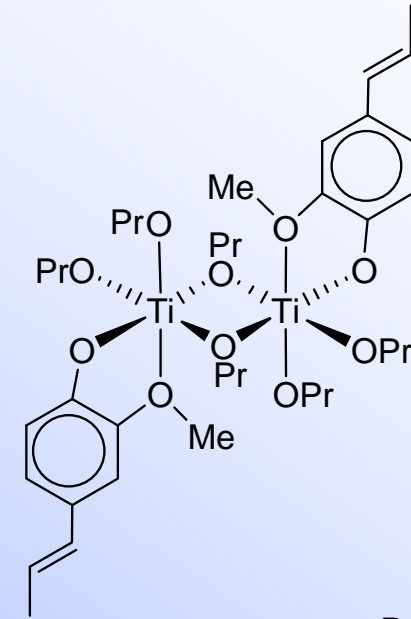
# Organic Modification of $Ti(OR)_4$ by Bidentate Ligands (BL)



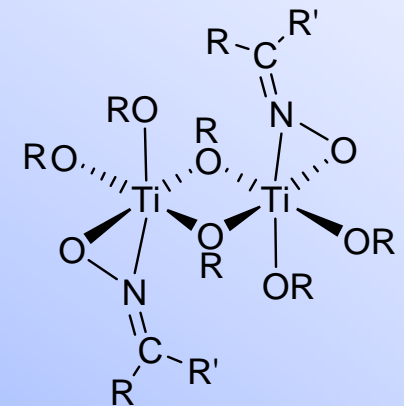
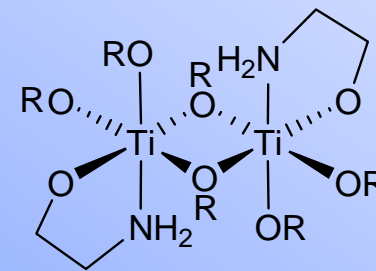
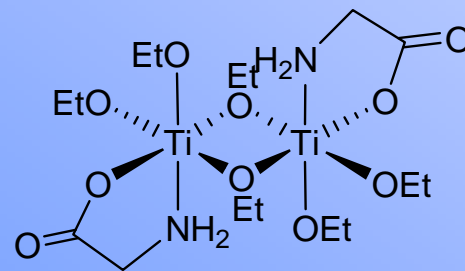
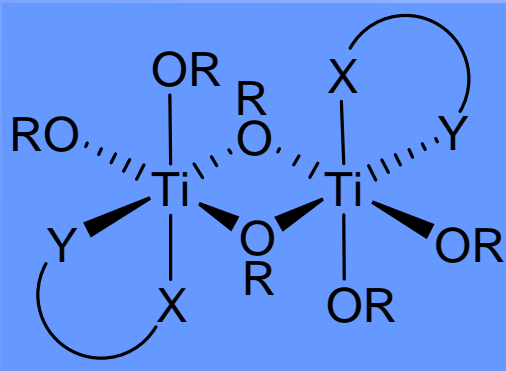
$X = OR \text{ or } NHR$

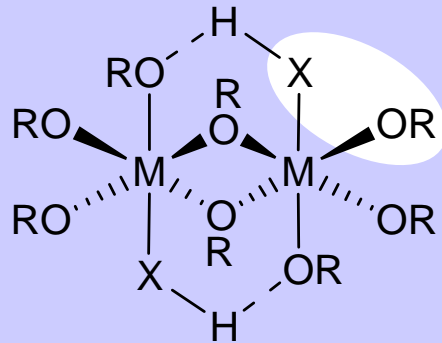


R. J. Errington et al., 1998



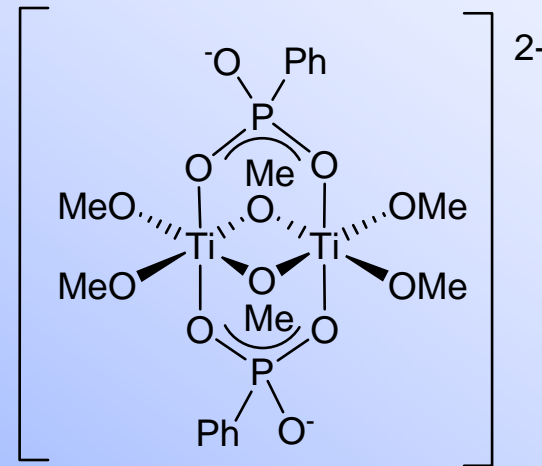
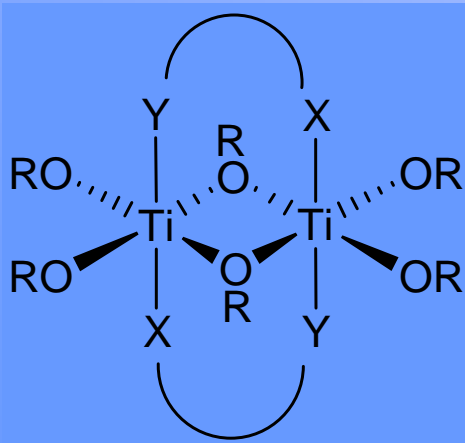
Chelating ligands:





$X = OR \text{ or } NHR$

Bridging ligands:



# Example: Preparation of Lead Zirconate Titanate (PZT)

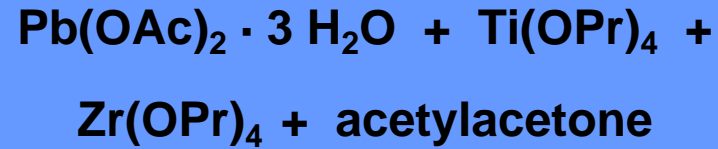
## Solid State Reaction



750 - 1100 °C  
several h

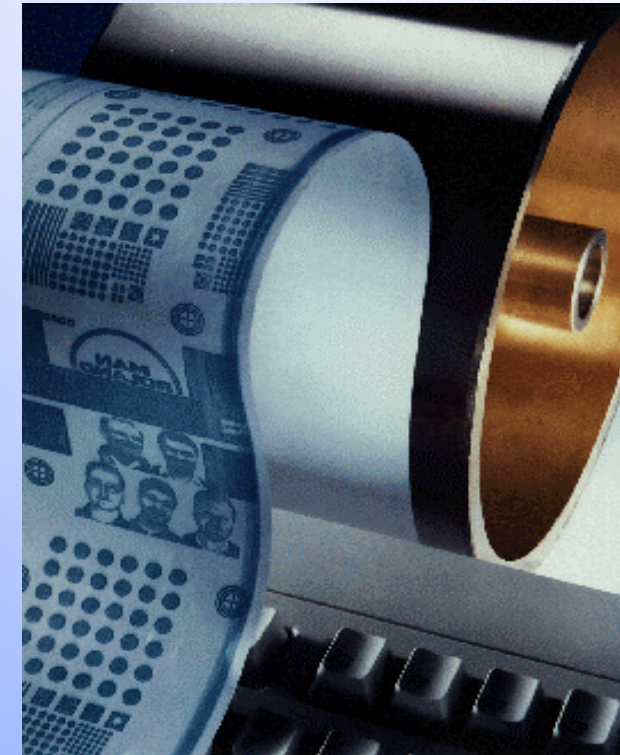


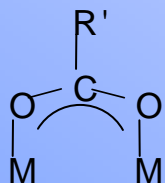
## Sol-Gel Processing



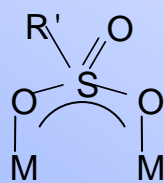
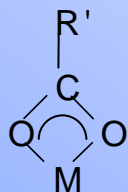
PZT Sol

700 °C / 2 min

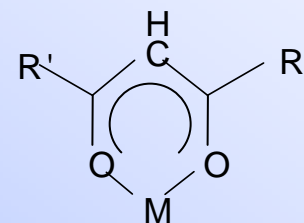
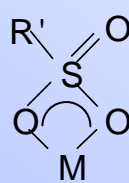




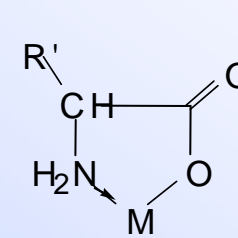
Carboxylate



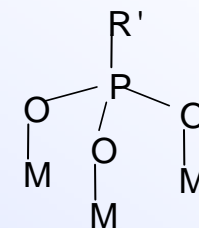
Sulfonate



$\beta$ -Diketonate



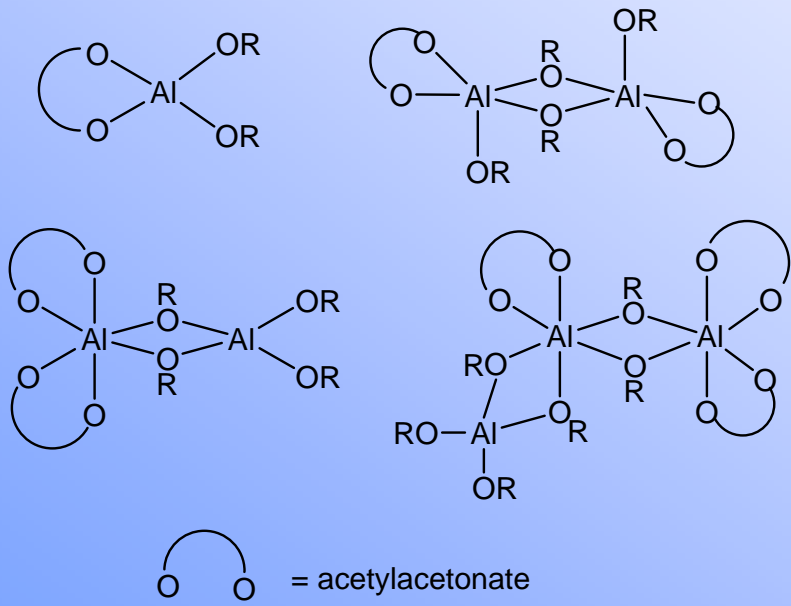
$\alpha$ -Amino-carboxylate



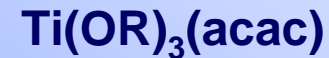
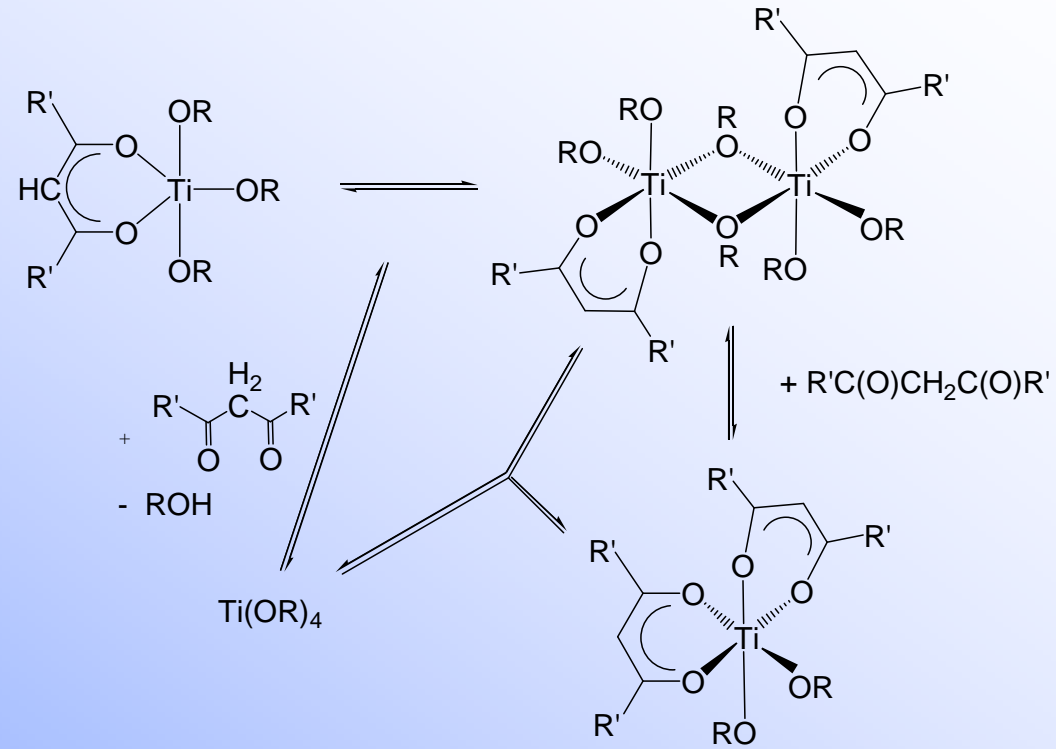
Phosphonate

## Chemical issues:

- Coordination equilibria
- Degree of substitution ( $y$ )
- Introduction of functional organic groups
- Organic side reactions
- Structural developments during hydrolysis



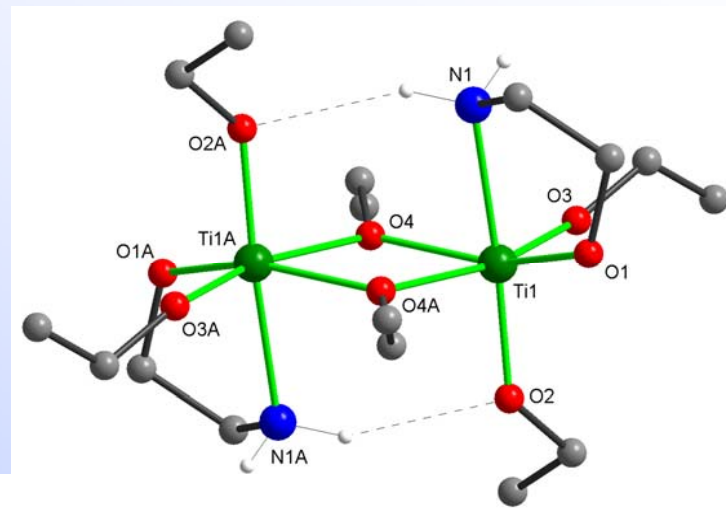
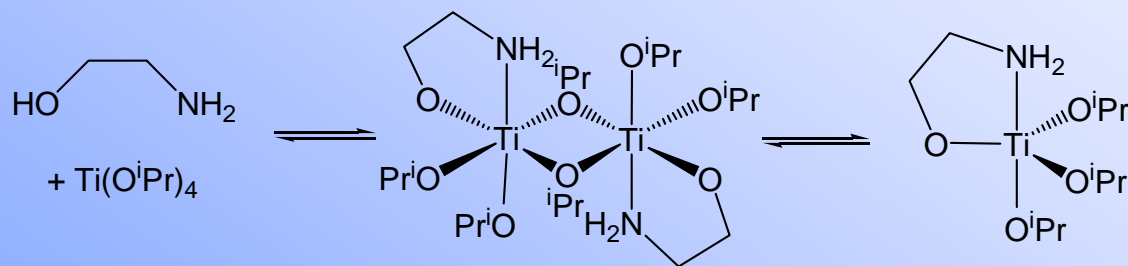
Proposed structures (from NMR)



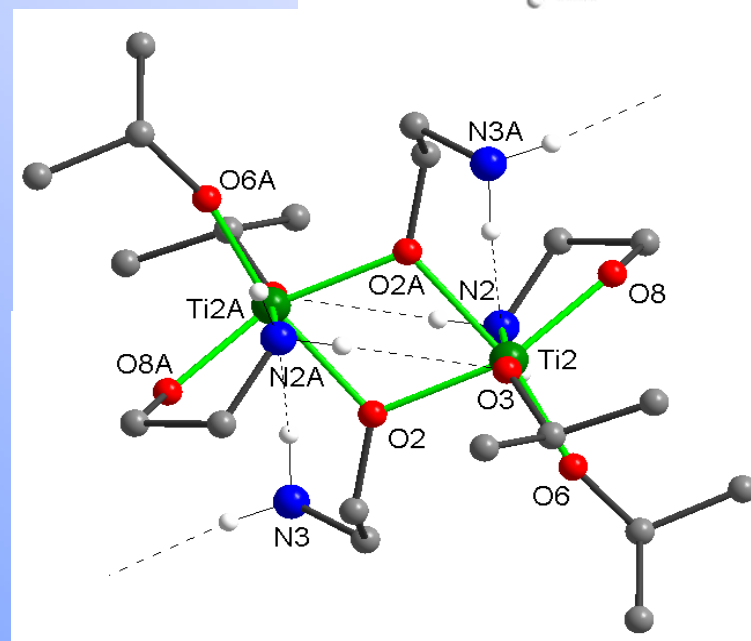
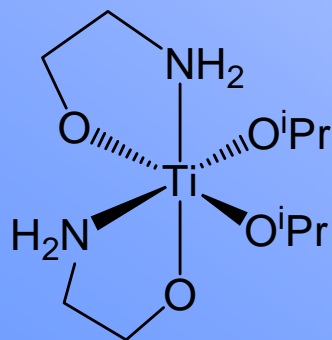
$\Rightarrow$  The metal : ligand ratio tells nothing about the molecular structures

## Solid state structures

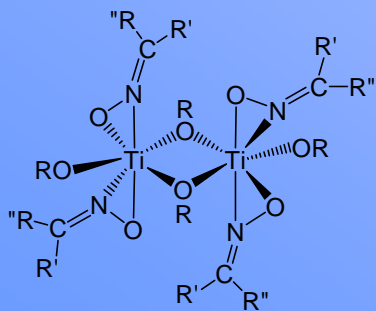
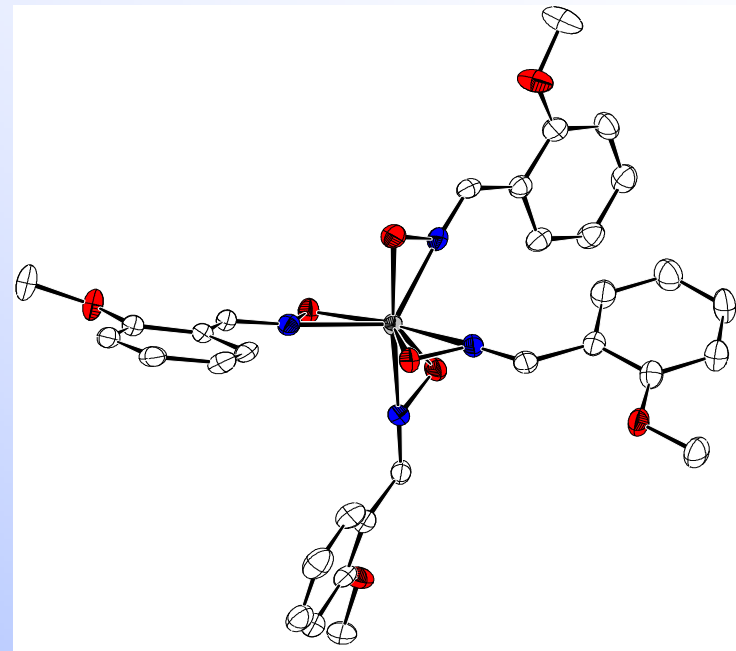
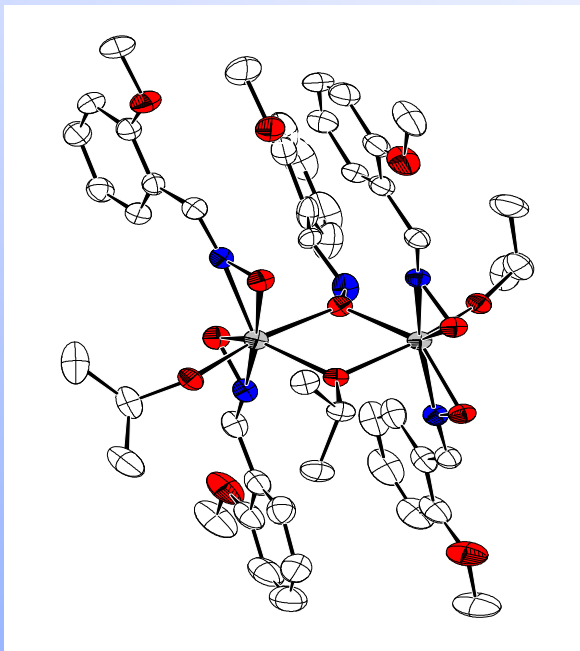
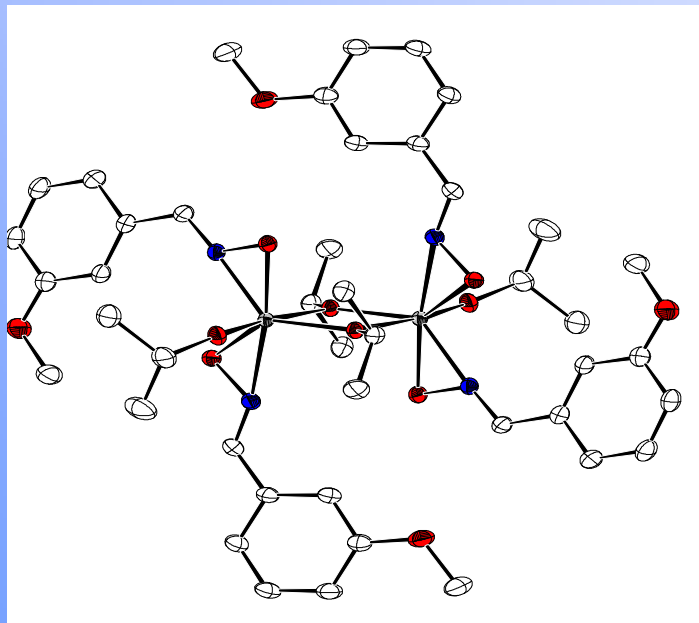
Mono-substitution product in benzene solution



Di-substitution product in gas phase



# Degree of Substitution: Oximate Derivatives

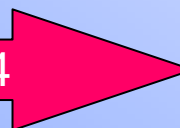


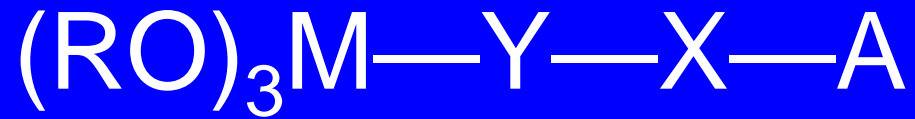
degree of substitution

2

2.5

4





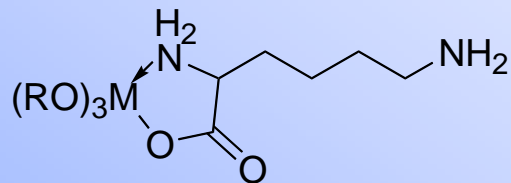
Hydrolyzable  
group

Bidentate  
group

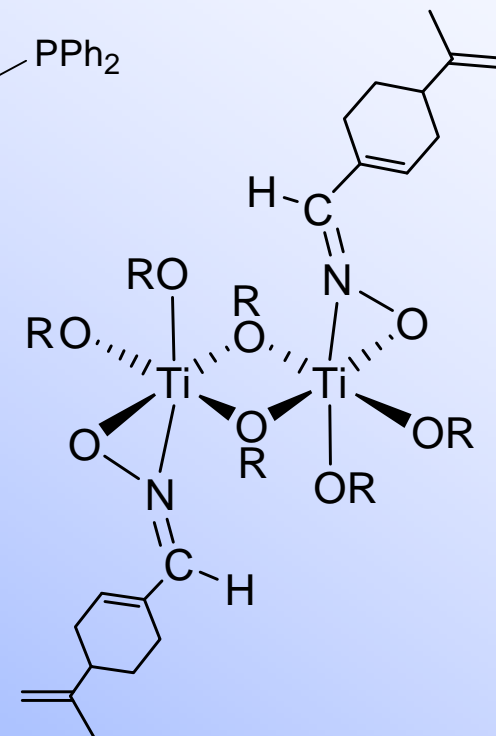
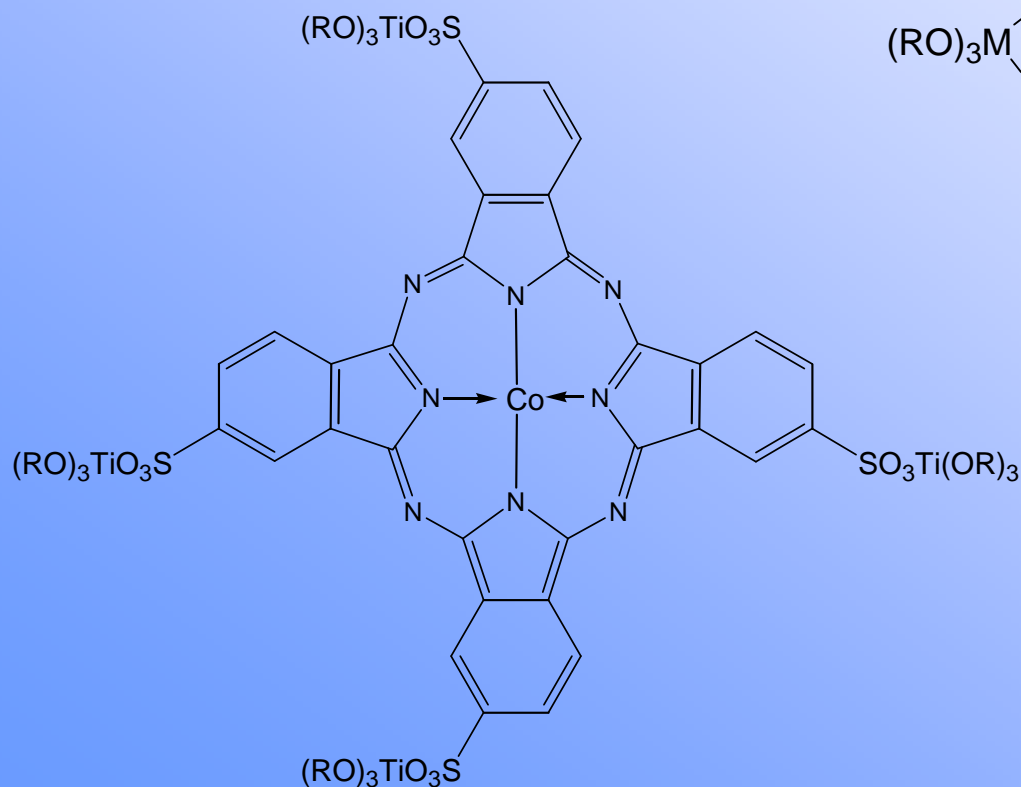
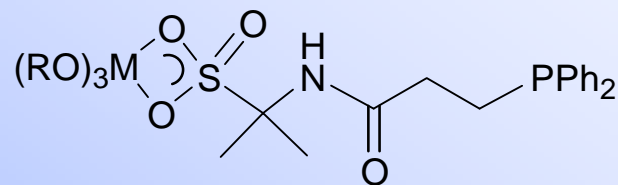
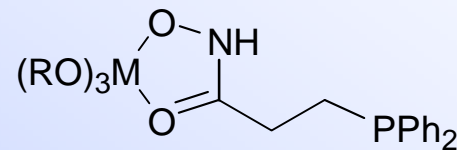
Chemically  
inert spacer

(Functional)  
Organic group

# Metal Alkoxides with Functional Organic Ligands: Examples



M = Ti, Zr

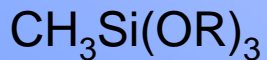


## Silicon precursors:

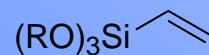
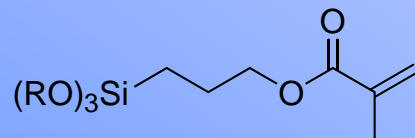
$\text{Si}(\text{OR})_4$ , water glass

## Organically modified alkoxysilanes:

Examples:



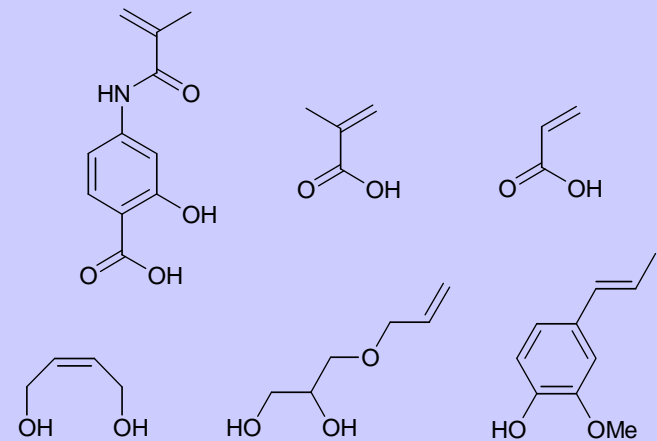
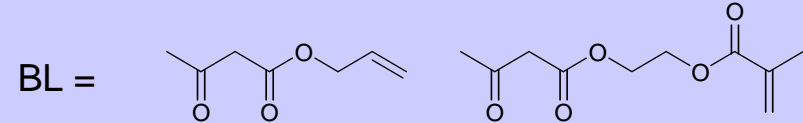
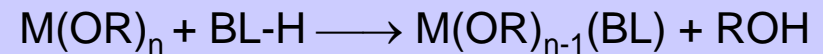
X = functional group



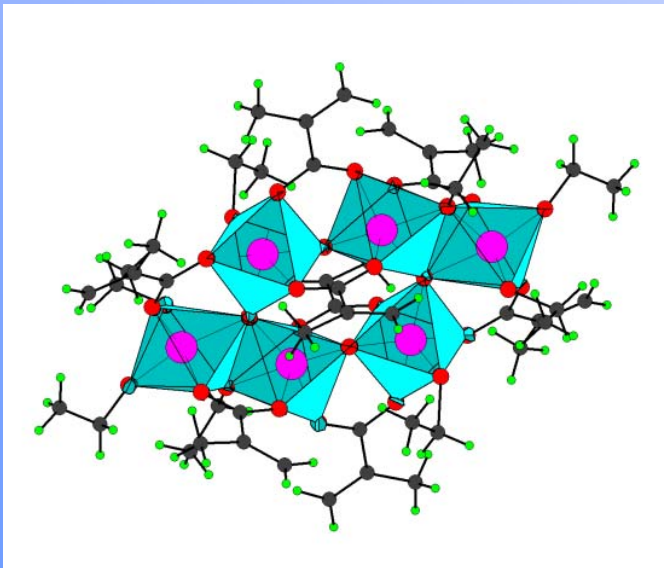
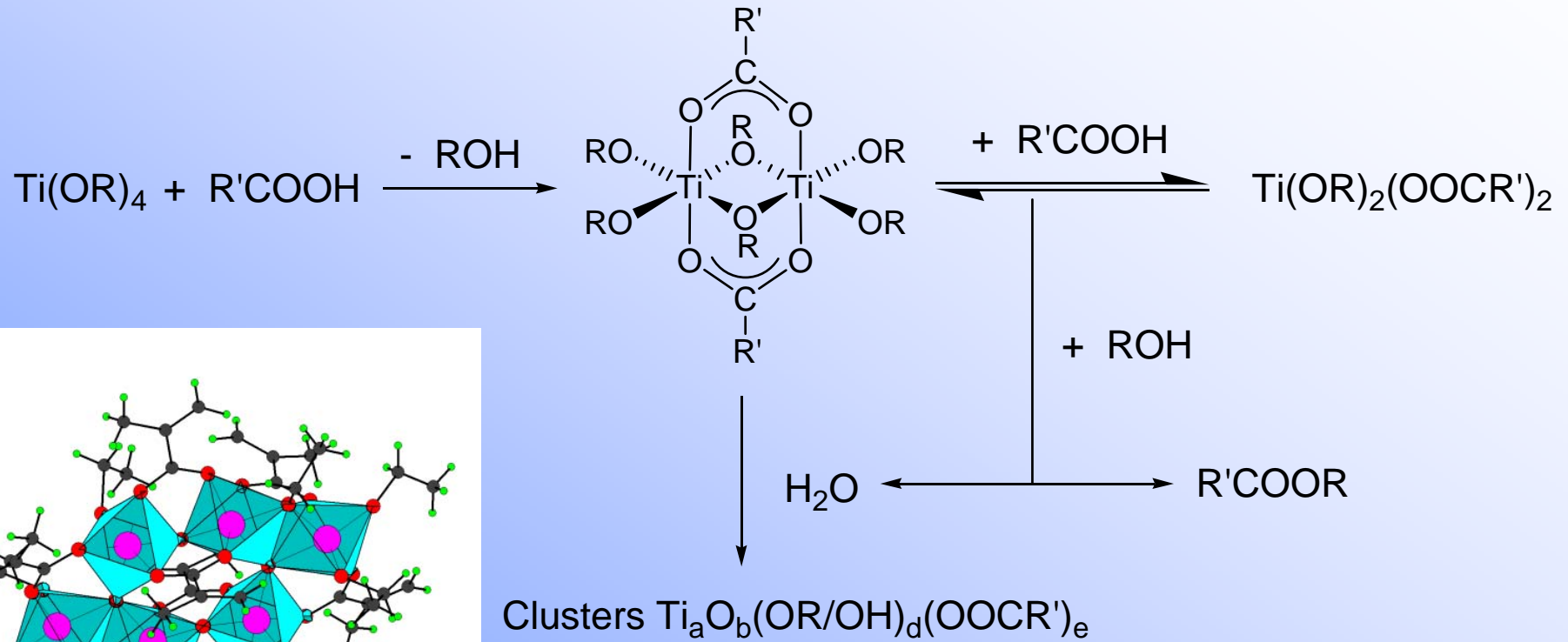
## Metal precursors:

$\text{M}(\text{OR})_n$ , hydrolysable metal salts, e.g. acetates, nitrates

## Organically modified metal alkoxides:

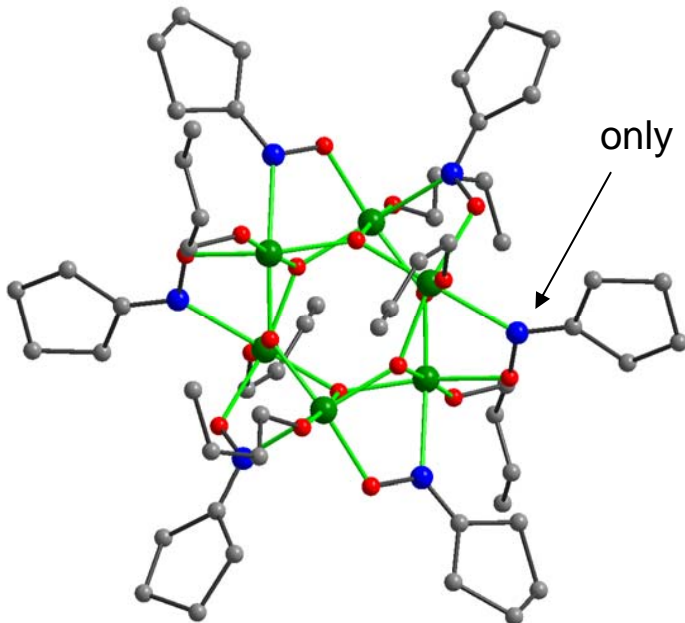
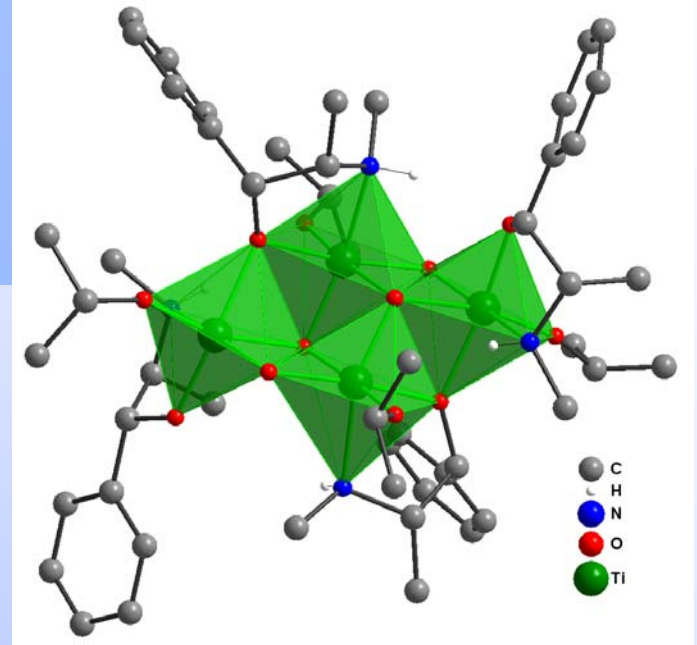
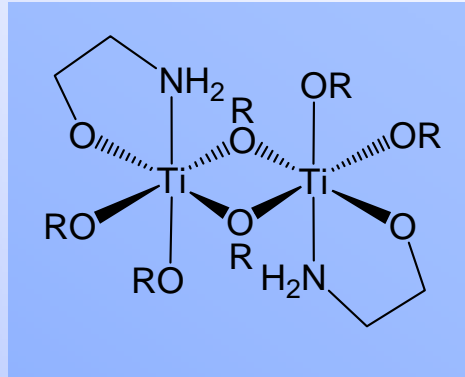
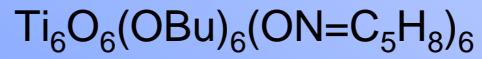
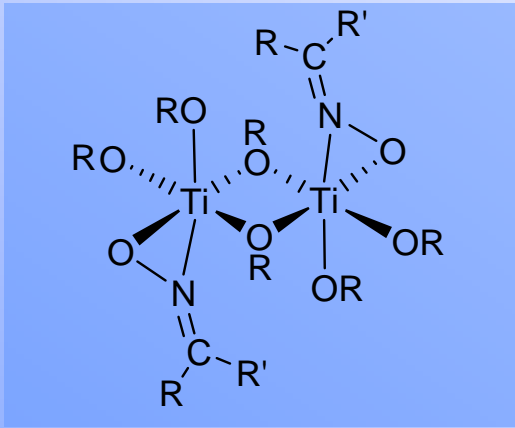


# Reaction Metal Alkoxides with Carboxylic Acids

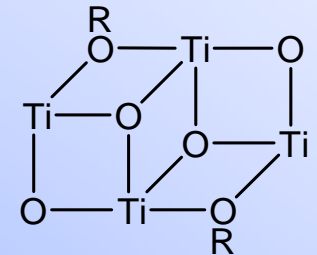
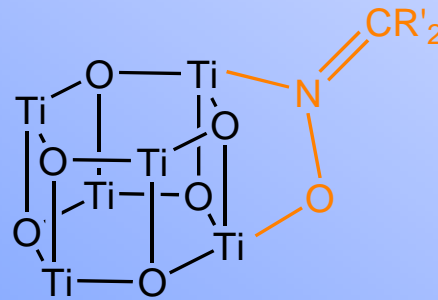


$\text{Ti}_6\text{O}_4(\text{OEt})_8(\text{methacrylate})_8$

# Partial Hydrolysis Products



only bridging oximate ligands!



Same structure as  $\text{Ti}_6\text{O}_6(\text{OR})_6(\text{OOC-R}')_6$   
with bridging carboxylate ligands

# „Library“ of Partially Hydrolyzed Derivatives

BL/Ti (degree of substitution, BL = bidentate ligand)

