

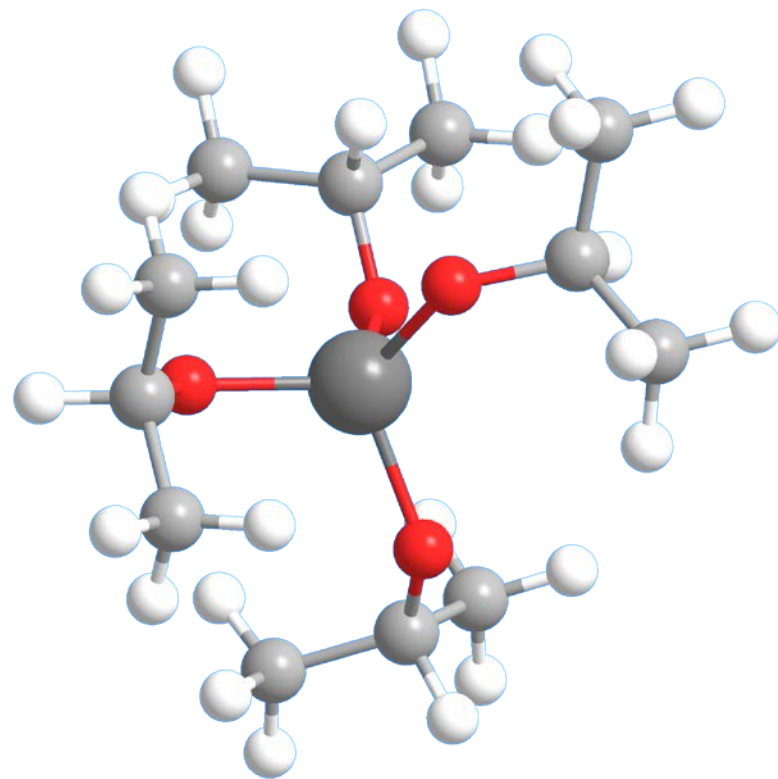
5. ALD Precursors

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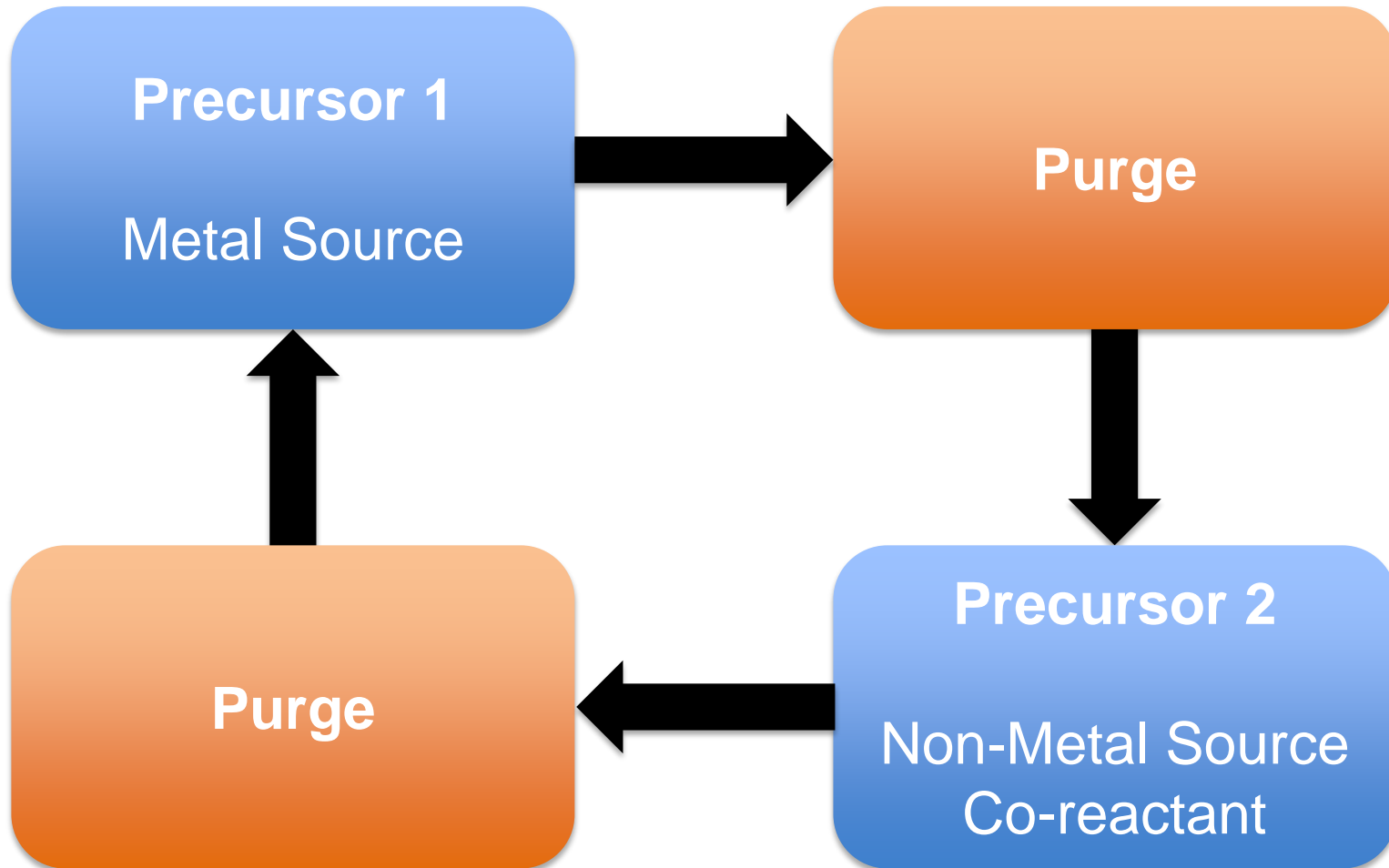
Outline

- Introduction
- The anatomy of metal precursors
- Requirements and considerations for metal precursors
 1. Oxidation state
 2. High volatility (high vapour pressure)
 3. High decomposition temperature
- Types of metal precursor
 1. General examples
 2. Metal chlorides
 3. Metal alkyls
 4. Metal carbonyls
 5. Metal cyclopentadienyls
 6. Metal alkoxides and metal amides
 7. Others
- Case Study: Al Precursors for Al_2O_3
- Summary



$[\text{Ti}(\text{O}^i\text{Pr})_4]$

A Typical ALD Cycle



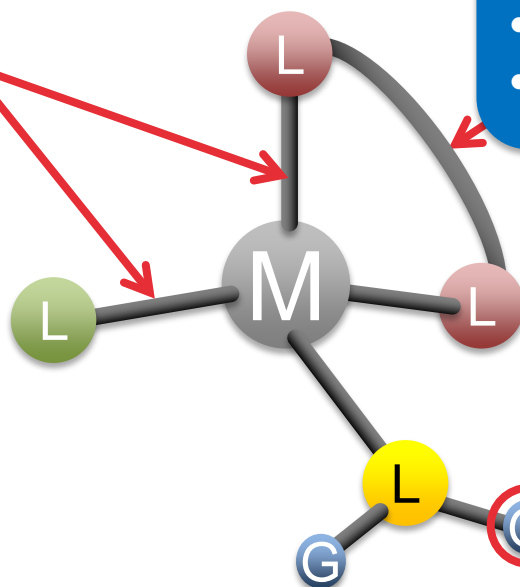
The Anatomy of Metal Precursors

Metal precursors are **coordination complexes**.

- A metal centre
- Surrounded by covalently-bonded **ligands** (atoms or small molecules/ions)
- Ligands make the complex **volatile**

High bond strengths lead to stable molecules

BUT at least one ligand needs to be reactive towards surface groups



Chelating ligands (binding through more than one site) can

- Stabilise the metal centre
- Improve volatility

Functional groups on ligands can affect the molecule's stability, *i.e.* promote decomposition.

Essential for ALD

The precursor must:

- Have high/sufficient vapour pressure (high volatility)
- Be reactive towards surface groups and leave reactive surface groups
- Have a high decomposition temperature
- Produce reaction products that
 - are volatile
 - do not adsorb to the film easily
 - do not etch the film

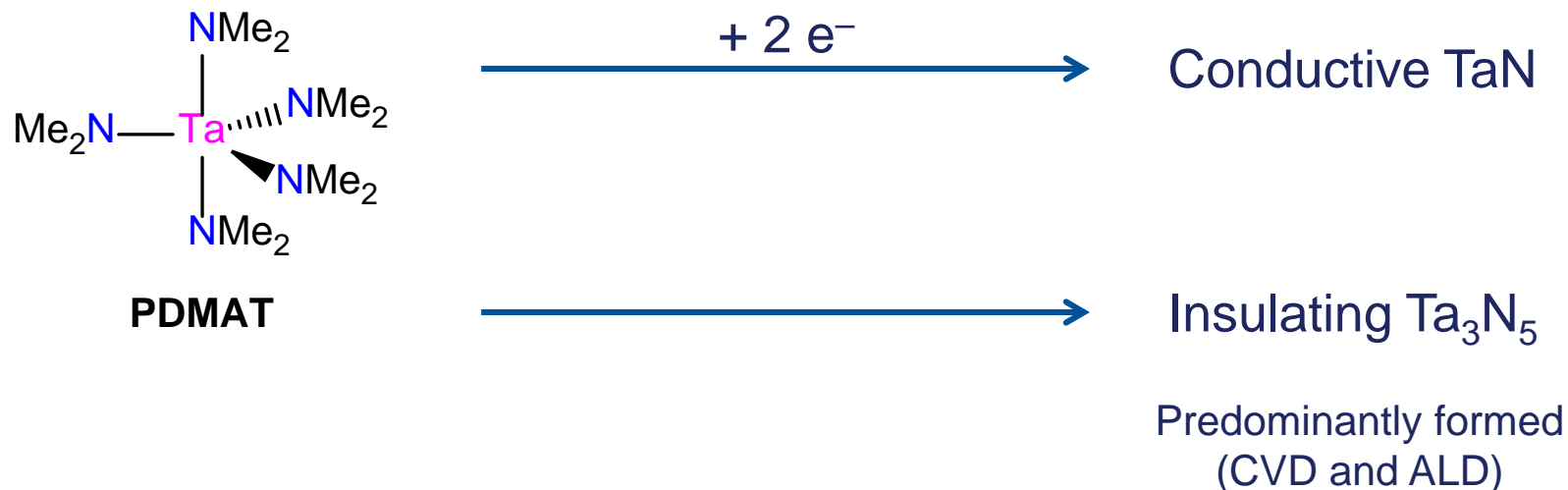
Desirable

Although not essential to the ALD mechanism, precursors should ideally:

- Be easy to synthesise and scale up
- Exhibit low toxicity
- Be easy to handle
- Be low cost

1. Oxidation State of the Metal Centre

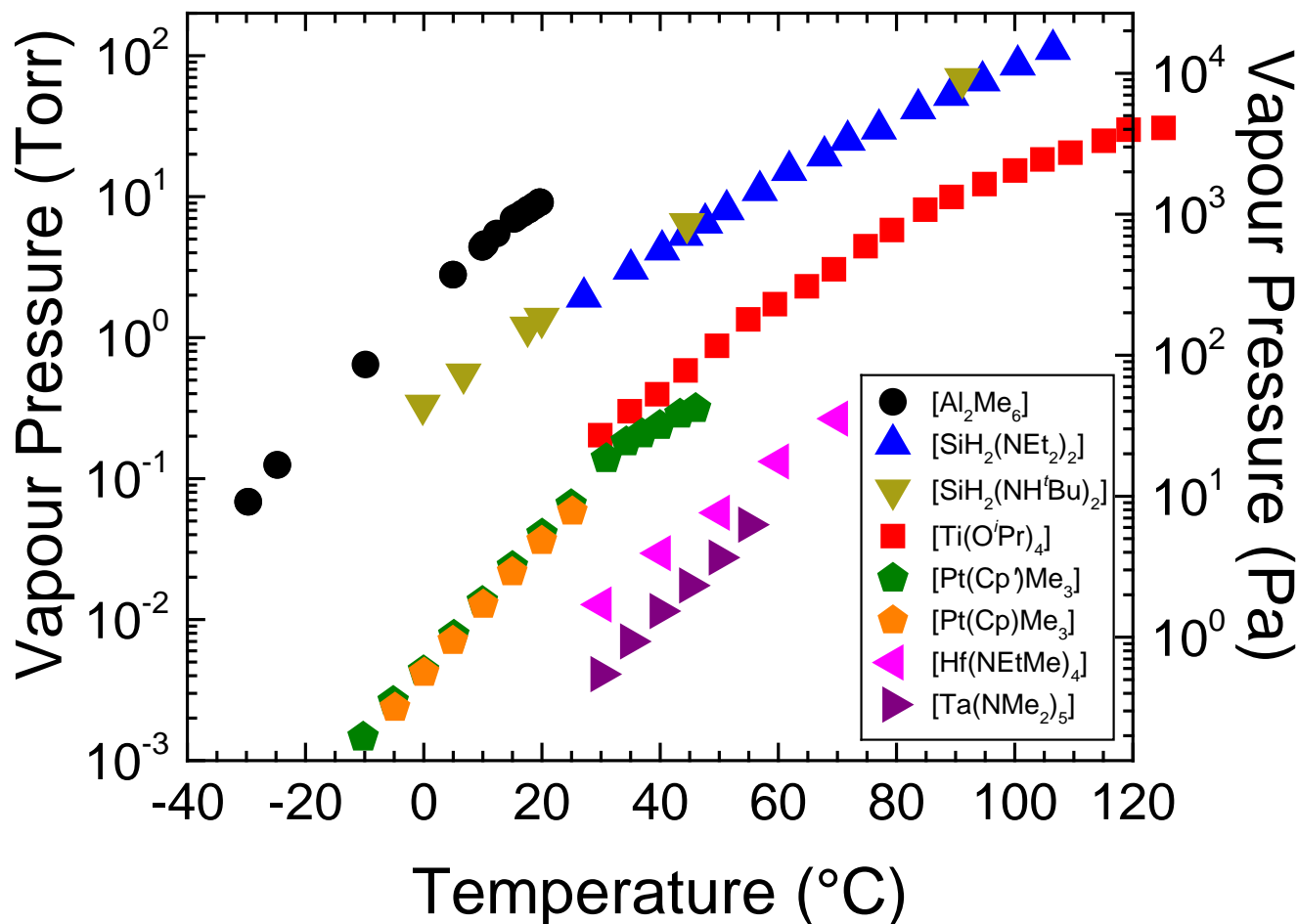
The oxidation state of the metal in the precursor can influence the oxidation state of the metal in the final film.



Ideally, the metal precursor's oxidation state and that of the metal in the final film should be the same.

2. Vapour Pressure

All compounds have a vapour pressure, which increases with increasing temperature.



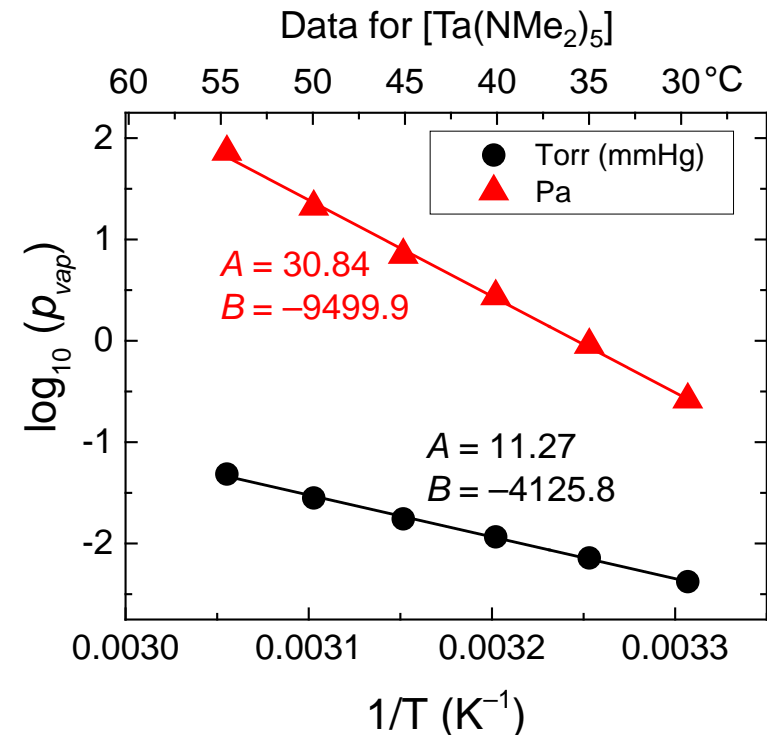
2. Vapour Pressure

- Plot vapour pressure and temperature as an Arrhenius plot
- Simplified **Antoine Equation** relates temperature to vapour pressure
- Can therefore calculate p_{vap} for precursors at various temperatures

$$\log_{10}(p_{vap}) = A - \frac{B}{T}$$

A and B = coefficients specific to the compound being tested and the units of pressure

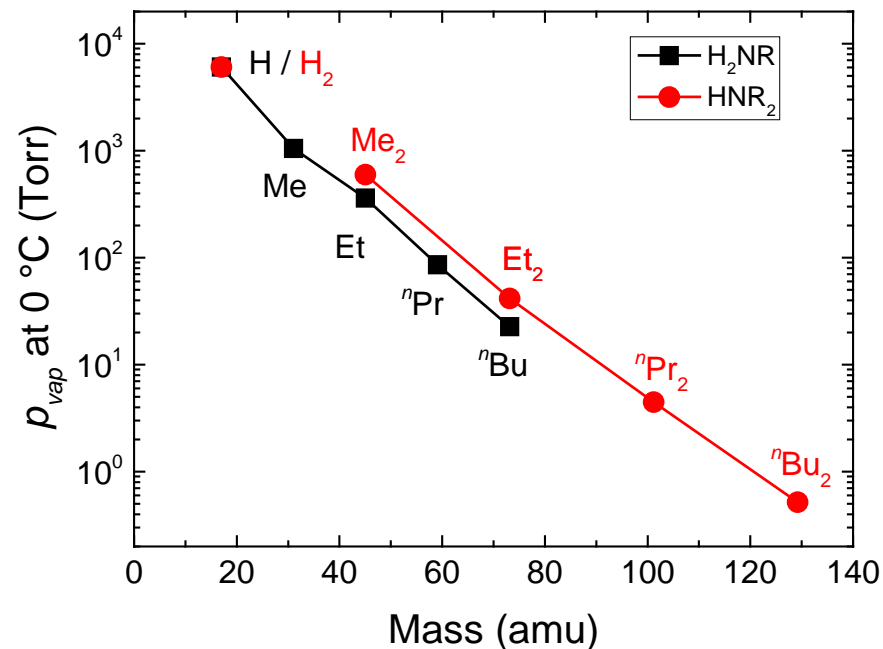
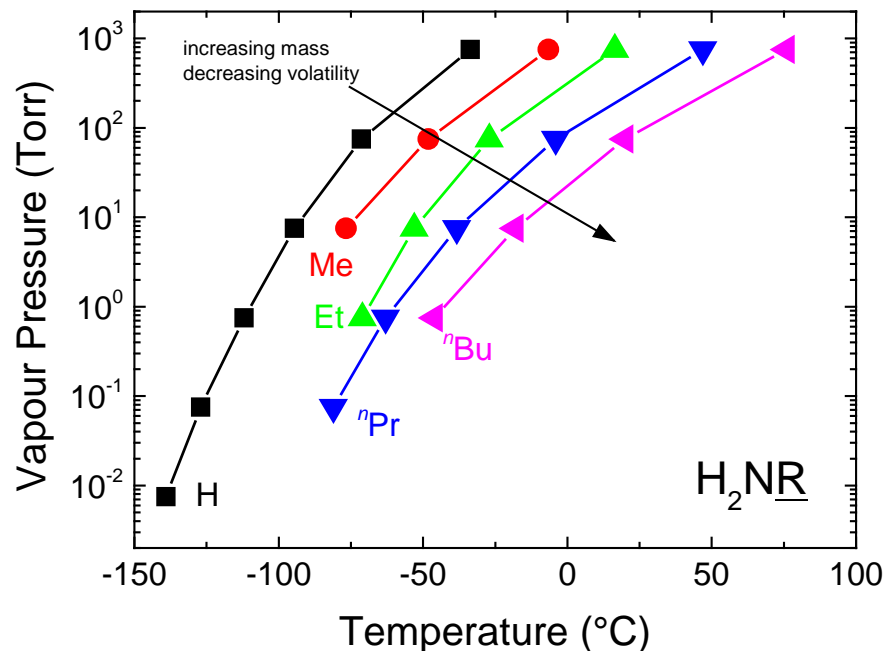
T = temperature in Kelvin



2. Vapour Pressure – Rules of Thumb

1. Vapour pressure increases with decreasing molecular mass.

Some simple amines provide good examples of this rule.

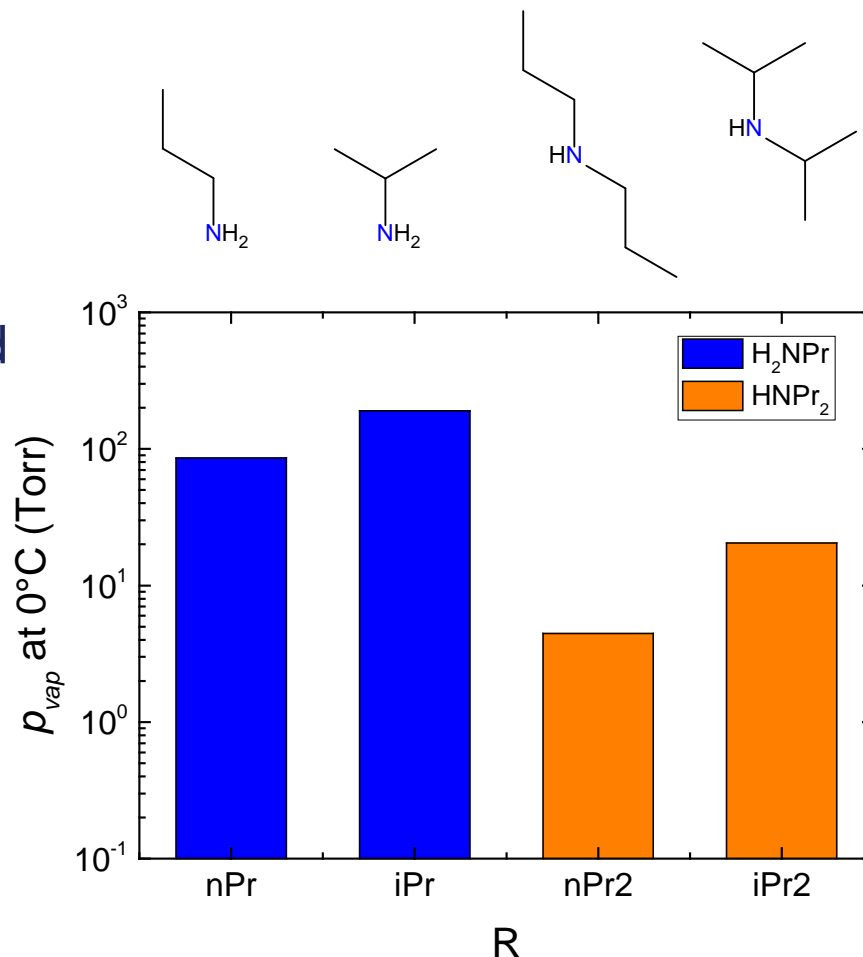
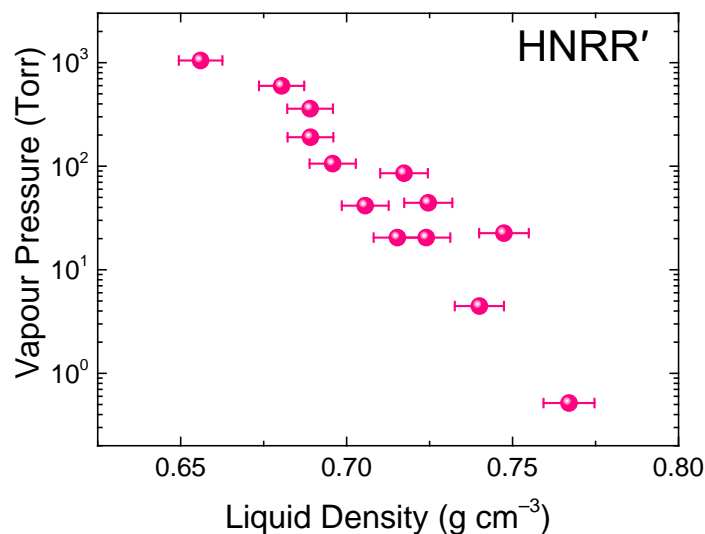


R = H or an alkyl group.

2. Vapour Pressure – Rules of Thumb

2. Vapour pressure **increases** with **increased alkyl branching**.

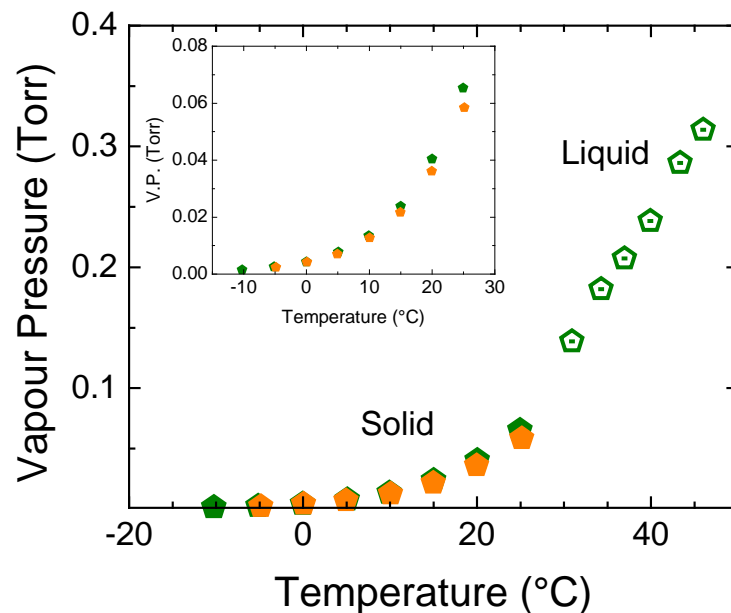
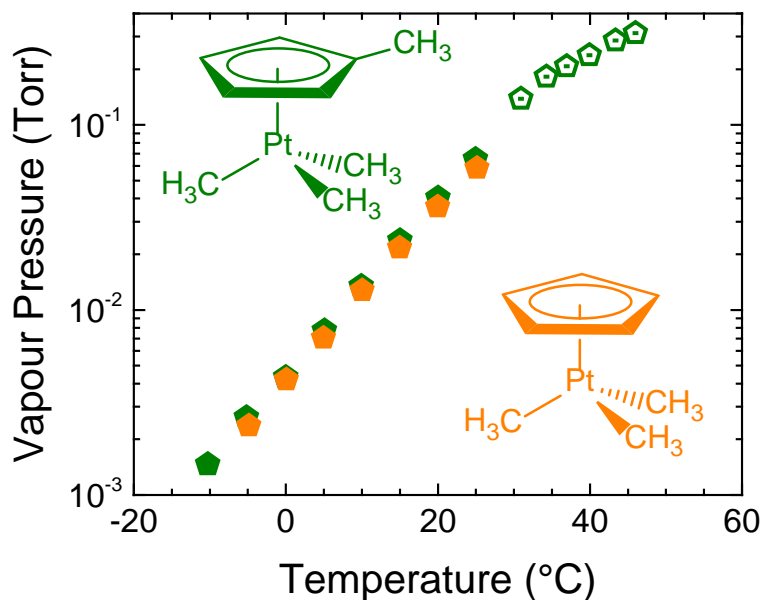
- The harder a structure is to pack together, the higher the vapour pressure
- Due to decrease in Van der Waal's force
- Compare vapour pressure with liquid density:



2. Vapour Pressure Example 1

Example of Platinum Precursors: $[\text{Pt}(\text{Cp}^{\text{R}})\text{Me}_3]$

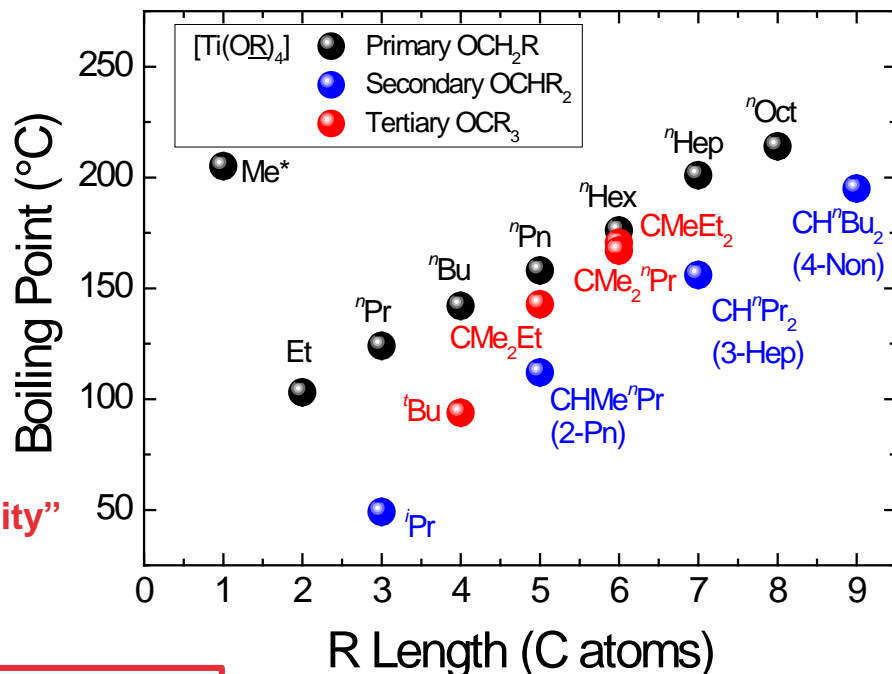
- Change in molecular mass vs. branching.
- Adding an Me group to the Cp enhances the vapour pressure slightly, despite increasing the overall mass



2. Vapour Pressure Example 2

Example of Titanium Alkoxide Precursors: $[\text{Ti}(\text{OR})_4]$

The nature of alkyl (R) groups on metals or ligands affects volatility



- Primary C – 1 R group
- Secondary C – 2 R groups
- Tertiary C – 3 R groups

In general (reminder)

- Heavier compounds are less volatile.
- Compounds with more asymmetric R groups are more volatile.

$$p_{\text{vap}} \propto \frac{1}{T_{\text{boil}}}$$

“Mass” →

2. Effect of Oligomerisation on Volatility

Example of Titanium Alkoxide Precursors: $[\text{Ti}(\text{OR})_4]$

- Titanium(IV) alkoxides are not coordinatively saturated.
- This allows them to oligomerise (form dimers, trimers...)



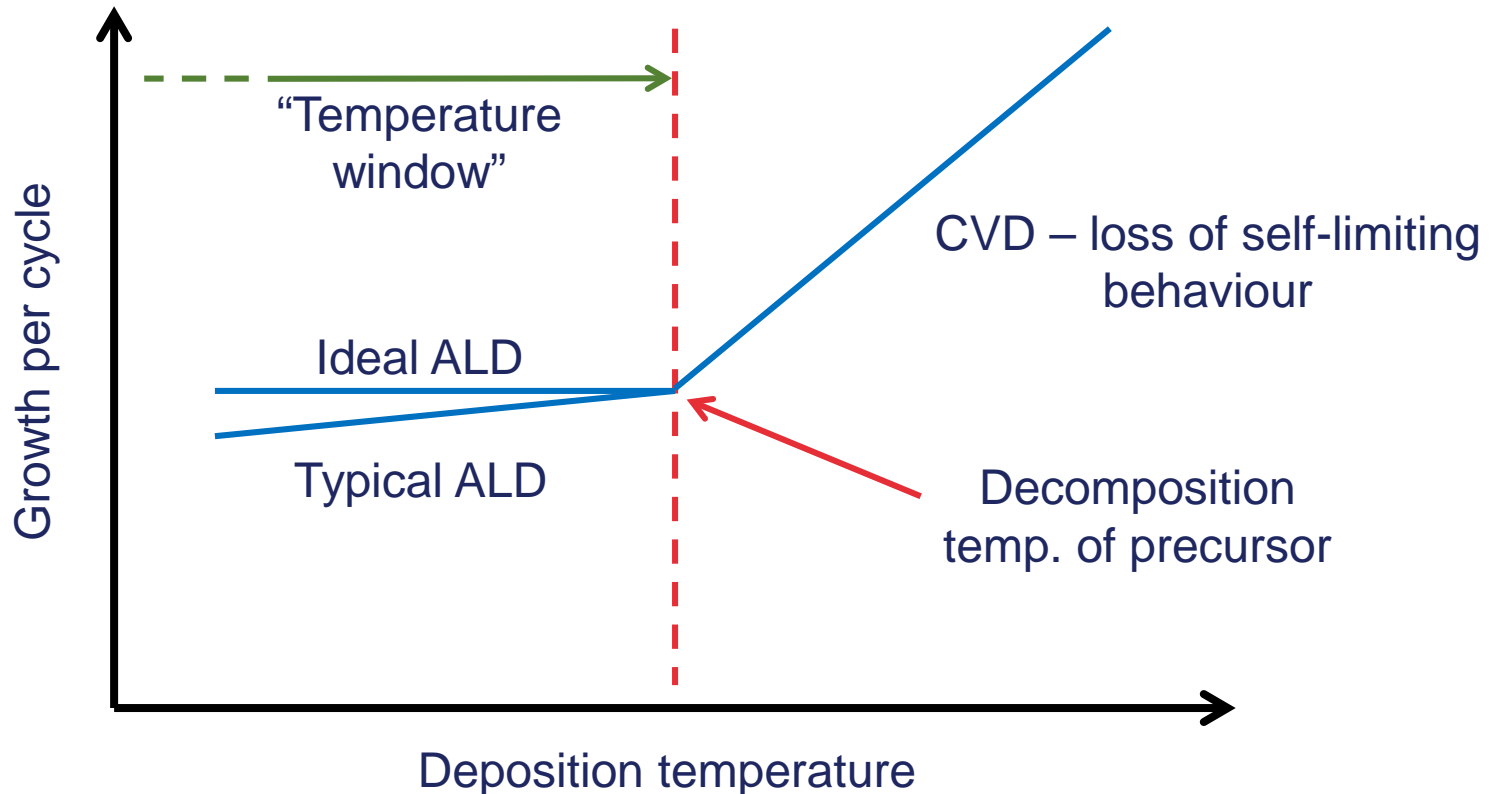
Alkyl Group	Compound	Carbon Atoms in Alkyl (R) Group	Number-Average Degree of Polymerisation, n	Closest Oligomer
Linear	$[\text{Ti}(\text{OMe})_4]$	1	<i>Not studied here</i>	4 (tetramer)
	$[\text{Ti}(\text{OEt})_4]$	2	2.96	
	$[\text{Ti}(\text{O}^n\text{Pr})_4]$	3	2.95	3 (trimer)
	$[\text{Ti}(\text{O}^n\text{Bu})_4]$	4	2.97	
Branched	$[\text{Ti}(\text{O}^i\text{Pr})_4]$	3	1.01	1 (monomer)
	$[\text{Ti}(\text{O}^i\text{Bu})_4]$	4	1.77–2.68	2 (dimer)
	$[\text{Ti}(\text{O}^t\text{Bu})_4]$	4	0.98	1 (monomer)

Oligomerisation effectively leads to a **higher molecular mass and hence a higher vapour pressure.**

3. Precursor Decomposition

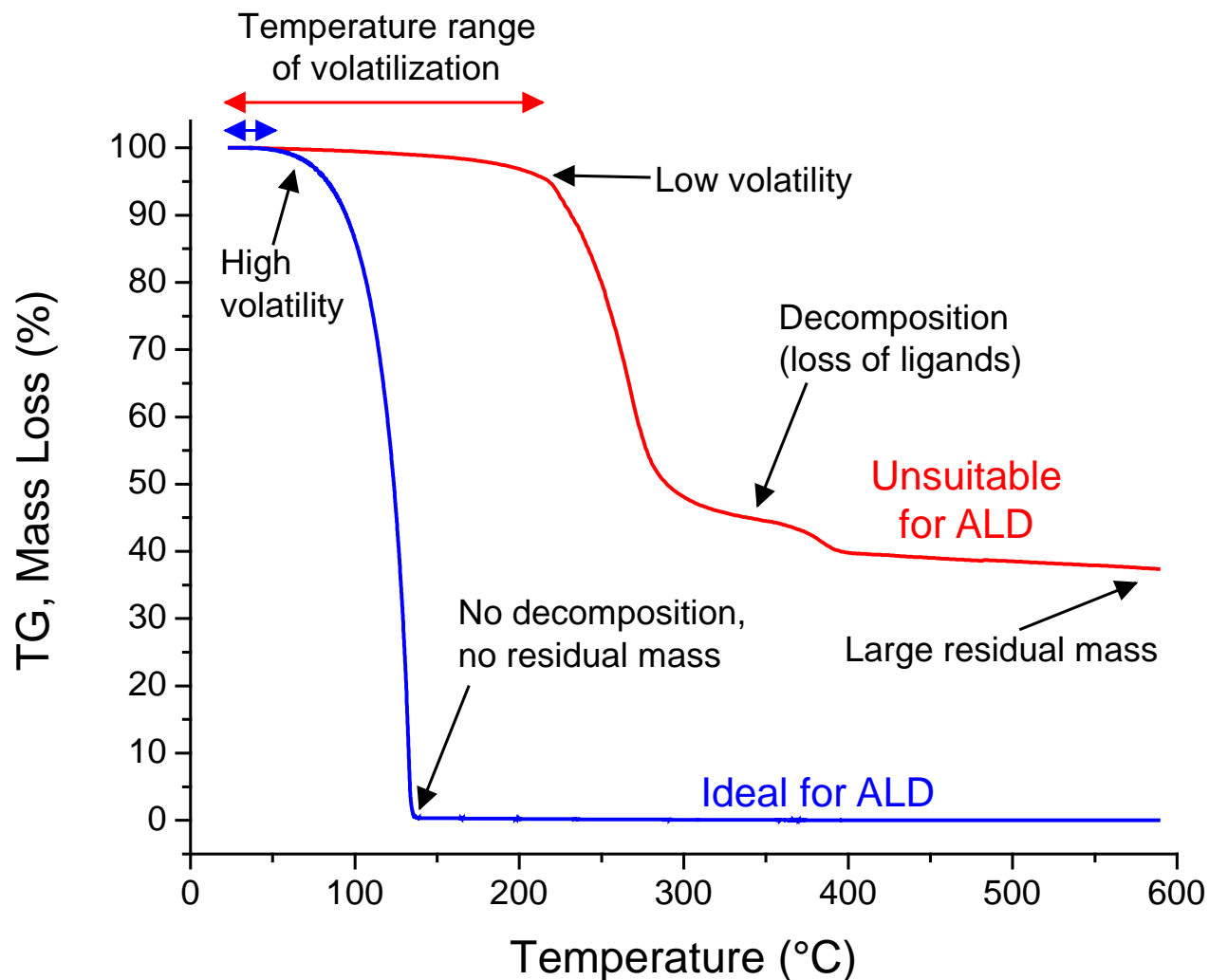
Decomposition temperature should be **as high as possible** (opposite to CVD precursors).

- Typical range (ALD) = **room temp. to ~400 °C.**



3. Thermogravimetric Analysis (TGA)

- Constant heating rate (typically $10\text{ }^{\circ}\text{C min}^{-1}$)
- Under air, inert gas or vacuum.
- Can also heat at a constant temperature as a function of time to check volatility.
- Weighing cups can be open or closed.

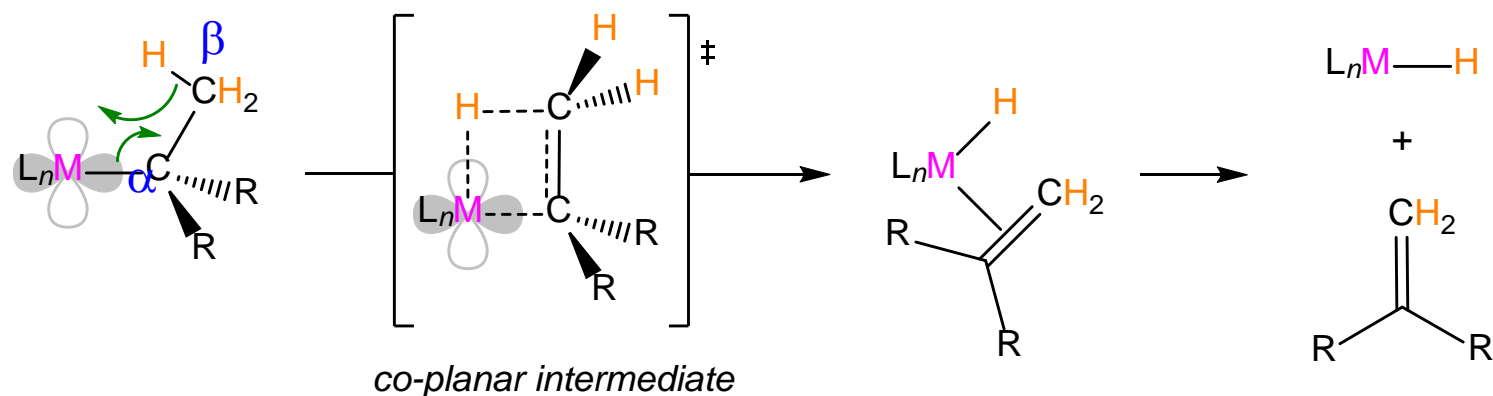


3. β -Elimination

Unoccupied orbitals on metal or heteroatoms (e.g. O, N) on ligands provide a **pathway for decomposition**.

β -elimination involves **hydride** transfer.

Example: an alkyl ligand on a metal.



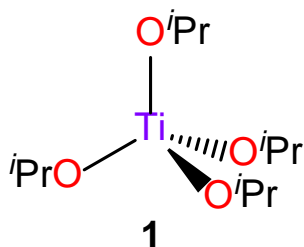
Therefore, the following can lead to facile decomposition of the precursor:

- Ligands containing β -hydrogens
- Coordinatively unsaturated precursors

3. Increasing the Decomposition Temperature

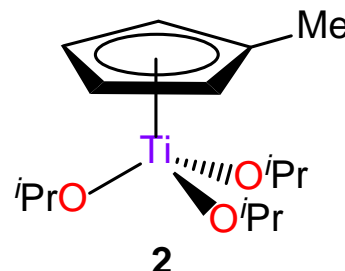
Example: Titanium Precursors

1. Standard reference compound.



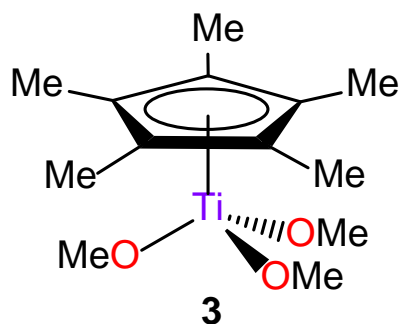
VP = ~0.91 Torr
 $T_{\text{dec}} > 210\text{ }^{\circ}\text{C}$

2. Addition of Cp' ligand to achieve coordinative saturation.



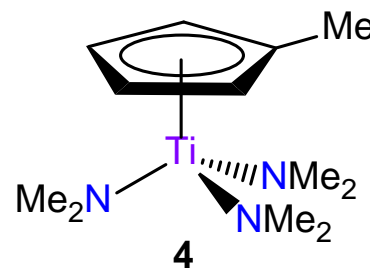
VP = ~0.23 Torr
 $T_{\text{dec}} > 250\text{ }^{\circ}\text{C}$

3. In addition to Cp*, use of ligands with no β -hydrogens.



VP = ~0.07 Torr
 $T_{\text{dec}} > 300\text{ }^{\circ}\text{C}$

4. For comparison, weaker-bonded alkylamido ligands

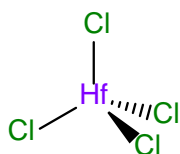


VP = ~0.27 Torr
 $T_{\text{dec}} > 200\text{ }^{\circ}\text{C}$

Me = CH₃, iPr = CH(CH₃)₂

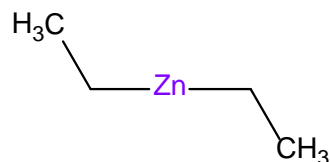
Examples of ALD Precursors

Halide



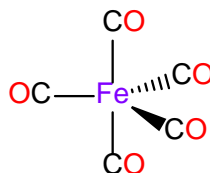
Tetrachlorohafnium(IV)

Alkyl



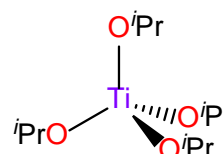
Diethylzinc
DEZ

Carbonyl



Pentacarbonyliron(0)

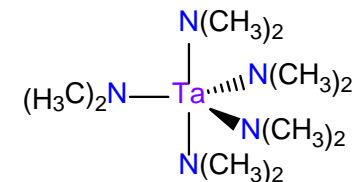
Alkoxide



Tetrakispropoxytitanium(IV)
TTIP

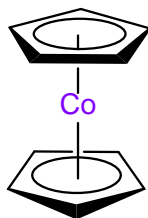
*i*Pr = CH(CH₃)₂

Alkylamide



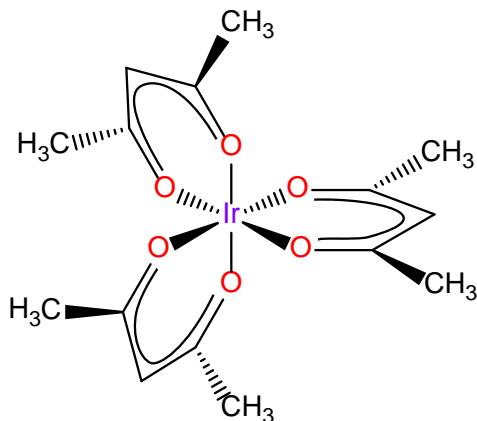
Pentakis(dimethylamino)tantalum(V)
PDMAT

Cyclopentadienyl



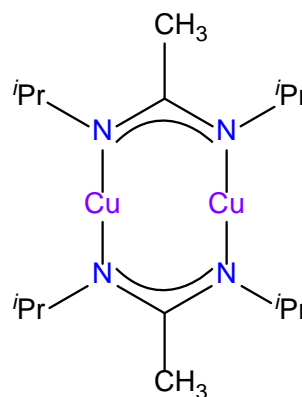
Bis(cyclopentadienyl)cobalt(II)
Cobaltocene

β -Diketonate



Trisacetylacetonatoiridium(III)

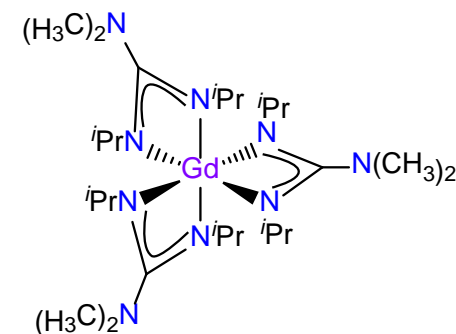
Amidinate



Bis(*N,N'*-diisopropylacetamidinato)dicopper(I)

*i*Pr = CH(CH₃)₂

Guanidinate



Tris(1,3-diisopropyl-2-dimethylamino)guanidinato)gadolinium(III)

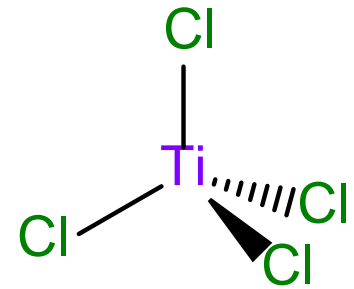
1. Metal Halides

Advantages

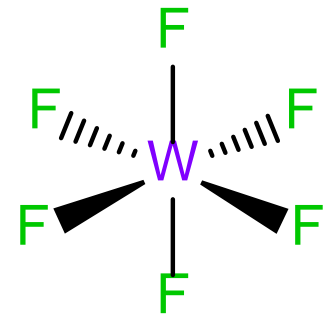
- Highly reactive
- Easy to handle
 - Most are solids, TiCl_4 is a liquid
- Thermally stable
- Inexpensive

Known Issues

- Tendency to contaminate films with halide ions
- HX reaction product is corrosive and can etch the growing film and ALD reactor

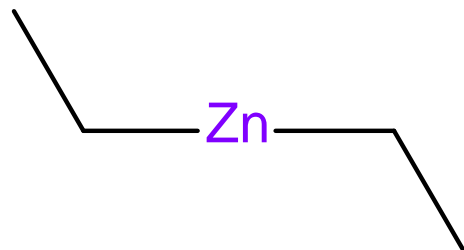


Tetrachlorotitanium(IV)
Titanium tetrachloride

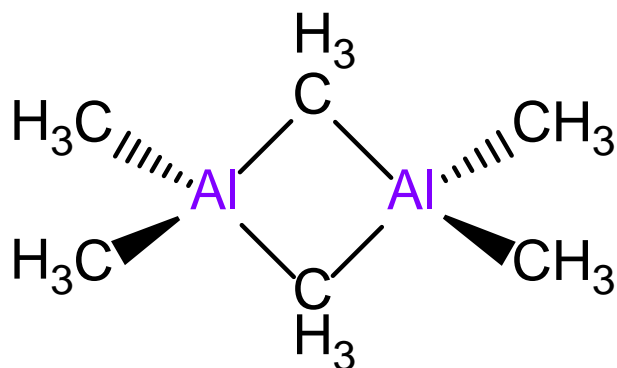


Hexafluorotungsten(VI)
Tungsten hexafluoride

2. Organometallics: Metal Alkyls



Diethylzinc



Trimethylaluminum

Key Feature

- M–C σ -bonds
 - High thermodynamic stability
 - Low kinetic stability

Advantages

- Highly reactive with surface groups, even at room temperature
- Relatively little film contamination
- Very high vapour pressures

Known Issues

- Difficult to handle – **pyrophoric**
- Low thermal stability, which can affect shelf-life

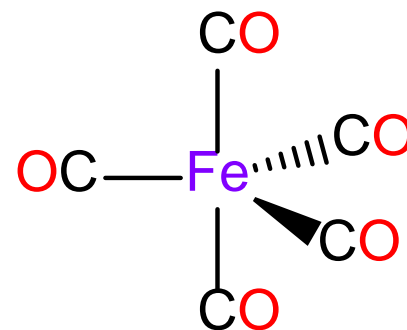
3. Organometallics: Metal Carbonyls

Advantages

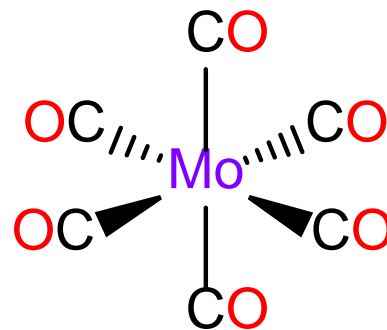
- Highly volatile
- Stabilises metals in low(er) oxidation states

Known Issues

- Extremely toxic
- Prone to decomposition at relatively low temperatures
- Not clear how they would interact with surface groups in a classical ligand exchange mechanism (condensation/hydrolysis)

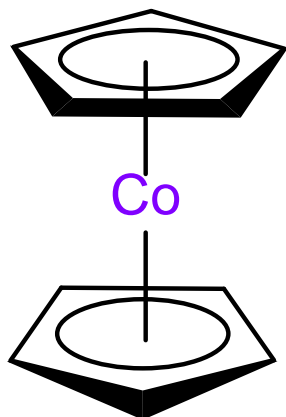


Pentacarbonyliron(0)
Iron pentacarbonyl

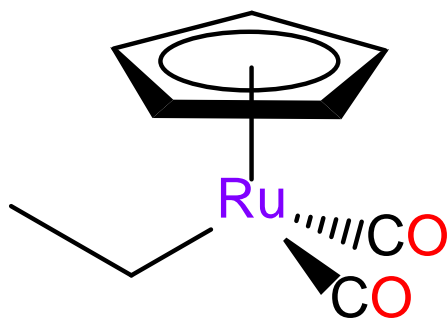


Hexacarbonylmolybdenum(0)
Molybdenum hexacarbonyl

4. Organometallics: Metal Cyclopentadienyls (Cp)



Bis(cyclopentadienyl)cobalt(II)
Cobaltocene



Dicarboxylcyclopentadienylethyl-
ruthenium(II)

Key Features

- Strongly bound to metal via σ - and π -bonding interactions
- Cp occupies up to three coordination sites
 - Electronic and coordinative saturation

Advantages

- Stable compounds with relatively long shelf-lives

Known Issues

- Low volatility (relative)
- For some metals, hydrolysis is difficult (requires energy-enhanced techniques)

5. Metal Alkoxides & Alkylamides

Key Features

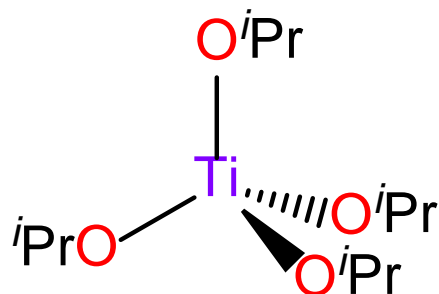
- Highly reactive in ALD terms
- More thermally stable than alkyl compounds and not generally pyrophoric

Advantages

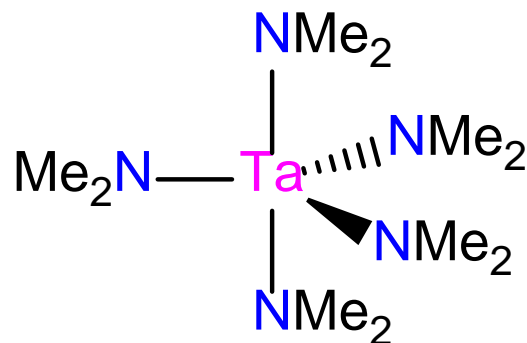
- Alkoxides are thermally stable liquids
- Alkyl amides provide a halide-free route to nitride thin films

Known Issues

- Oligomerisation can reduce volatility
- Amido compounds are less thermally stable than alkoxides, so have a shorter shelf-life



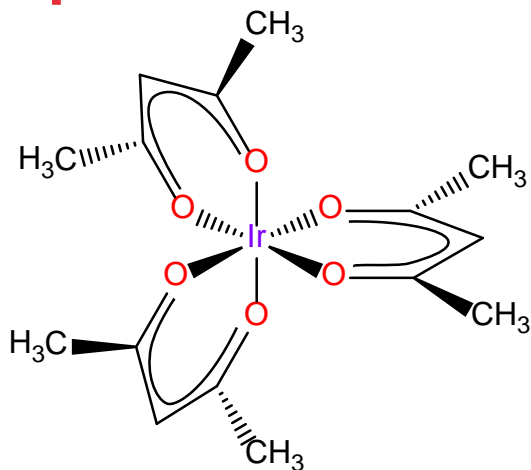
Tetraisopropoxytitanium(IV)
Titanium tetraisopropoxide, TTIP



Pentakisdimethylamidotantalum(V)
PDMAT

6. Other Metal Precursors

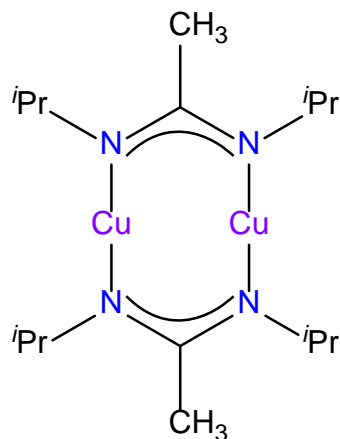
β -Diketonates



Trisacetylacetonatoiridium(III)

- Very high thermal stability
- Low volatility
- Reaction with surface groups?

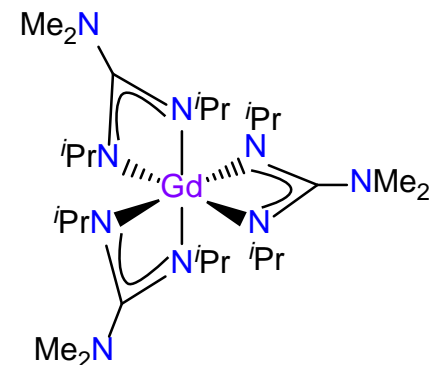
Amidines



Bis(*N,N'*-diisopropylacetamidinato)-dicopper(I)

- High thermal stability but more reactive than β -diketonates
- Can form volatile compounds of late transition metals (e.g., Cu).
- Can form volatile compounds of lanthanoid metals (e.g., Gd).

Guanidines



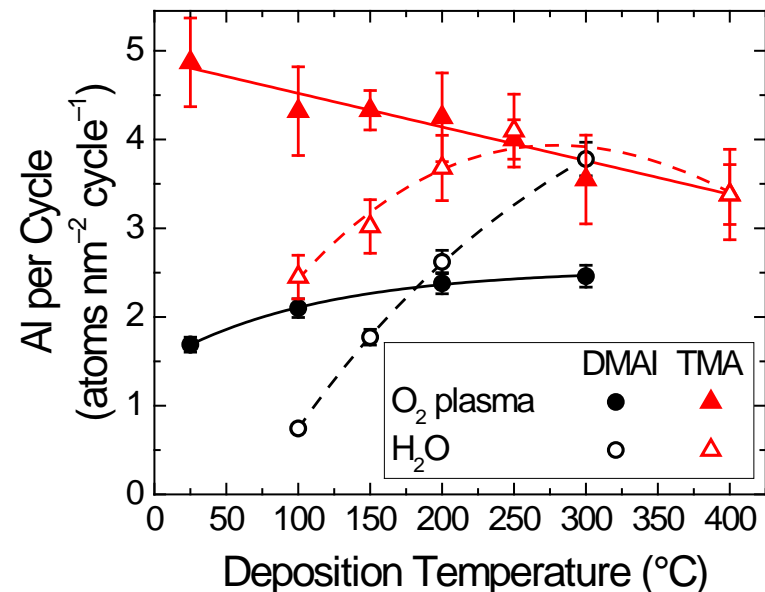
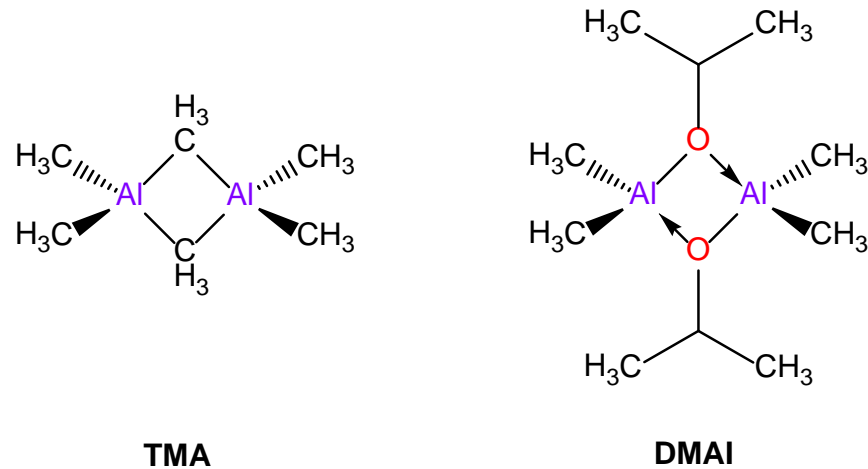
Tris(1,3-diisopropyl-2-dimethylaminoguanidinato)-gadolinium(III)

Case Study: TMA vs. DMAI as Al Precursors for Al₂O₃

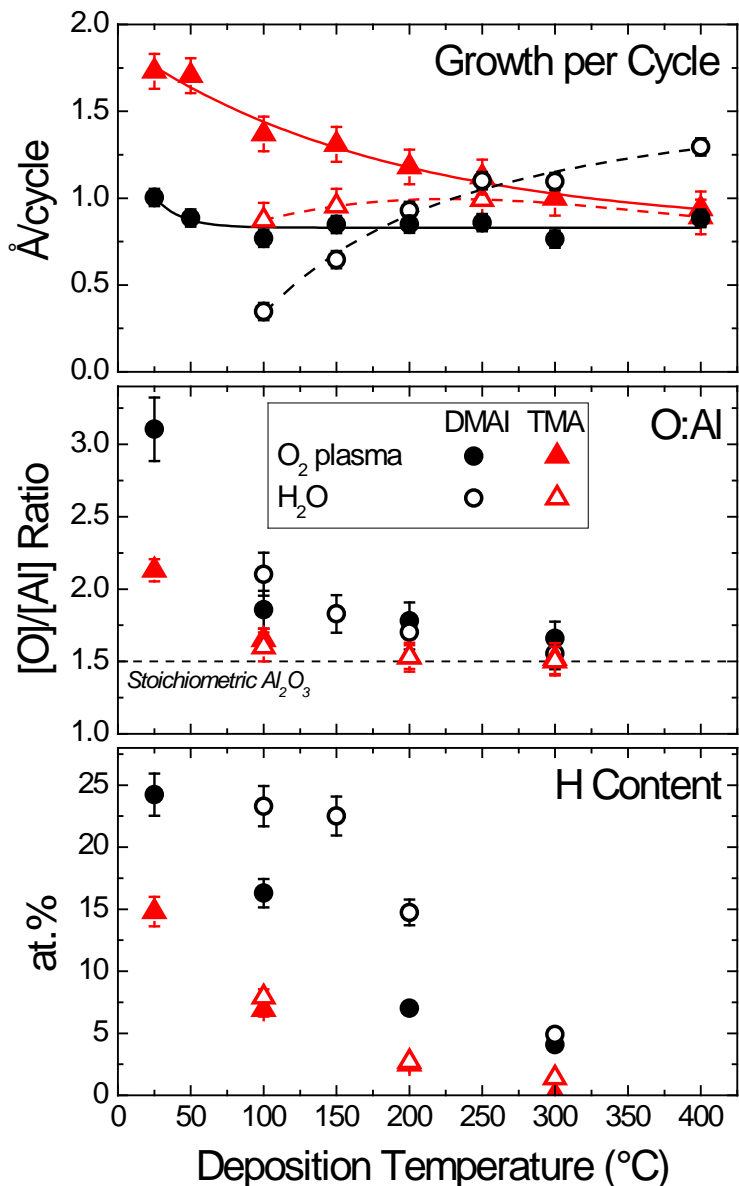
ALD growth can be affected by the **size** of the precursors (steric hindrance).

The precursor with larger ligands gives a lower growth per cycle.

- Bond dissociation energy Al-C \ll Al-O
- Larger OⁱPr ligand covers reactive surface sites



Case Study: TMA vs. DMAI as Al Precursors for Al₂O₃

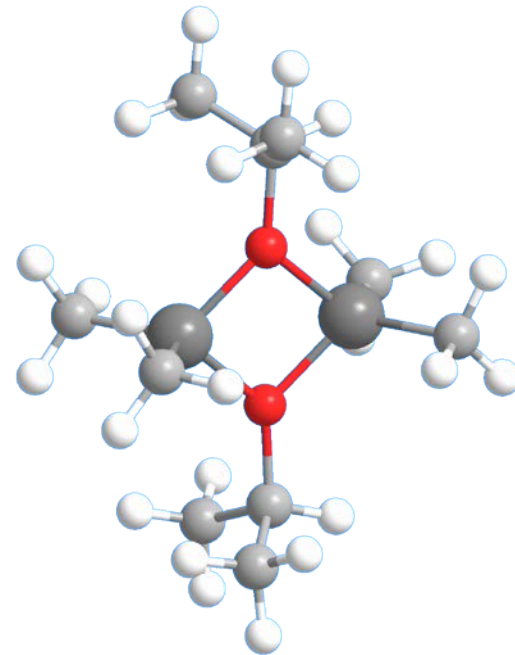
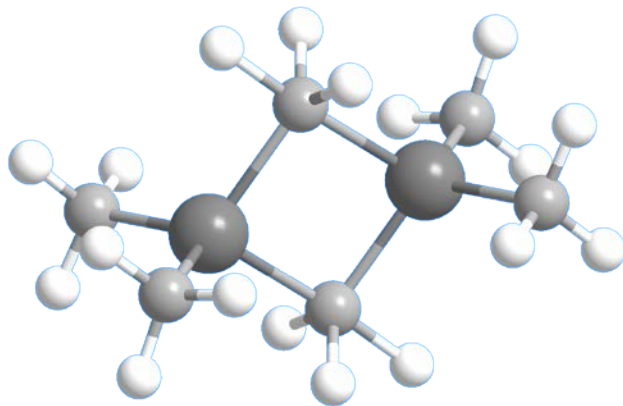


Al₂O₃ Film Composition

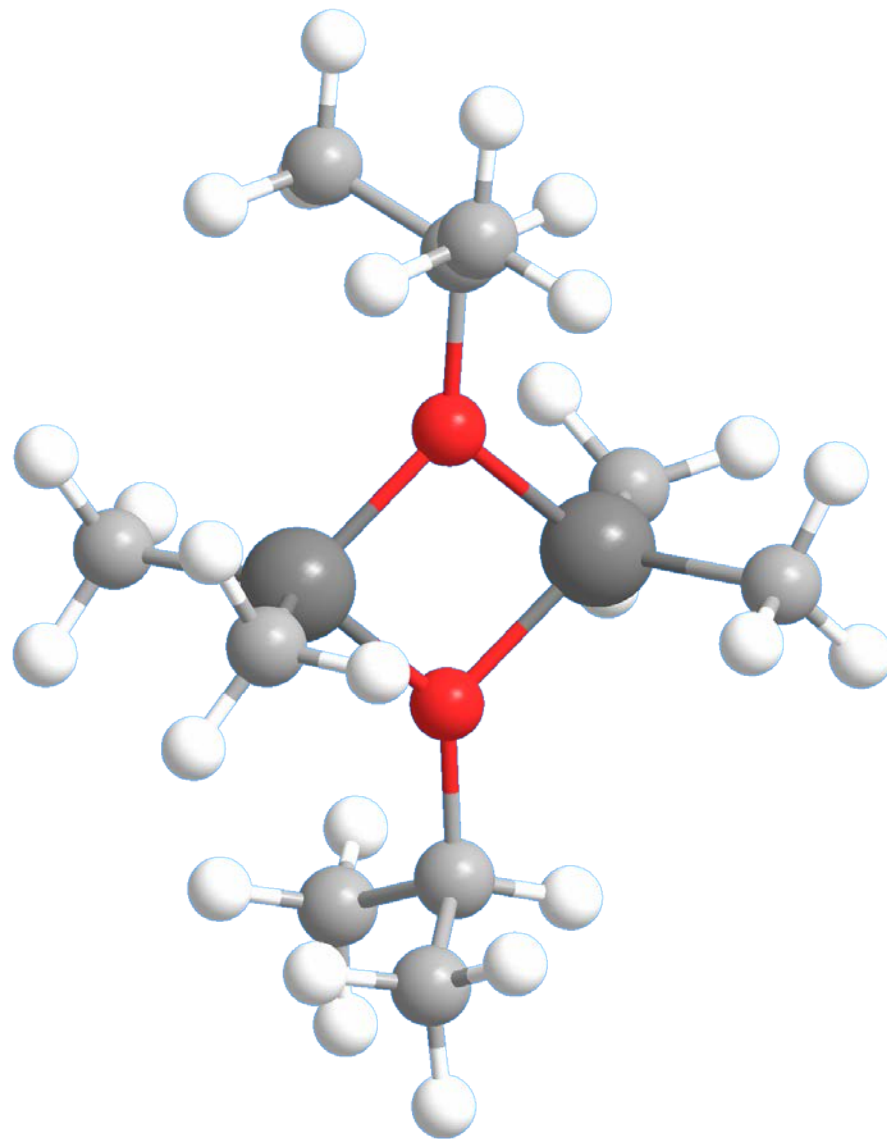
- General trend: more H and O at lower temperatures
- Typically due to OH in the films
- Films from DMAI contain more O and H than those from TMA
- At 25 °C,
 - O/Al for DMAI > TMA
 - O/Al > 3 (DMAI), suggests carbonate or formate incorporation
 - Most likely a result of O'Pr

(Further) Key Points

- Al–OⁱPr requires more thermal energy for reaction
- Lower growth per cycle than TMA due to size of precursor and
- ≥150 °C – **equivalent** to those from TMA
- <150 °C – higher [OH], inclusion of carbonates at 25 °C (EEALD)



- Metal sources for ALD are inorganic coordination complexes.
 - Metal centre surrounded by ligands
- When using/selecting a compound, you should be aware of:
 - Its reactivity with the surface and the surface it leaves
 - Its volatility (vapour pressure)
 - Its decomposition temperature
 - The size of the molecule
 - The metal's oxidation state
- Different ligands can tune the precursor's properties
 - As above
 - Thermal stability/shelf life
 - Reactivity
 - Growth per cycle due to size/thermodynamics/kinetics



Self-Test Questions (1/2)

1. Which of the pairs of the following precursors would you expect to give the highest growth per cycle?
 - a. Al_2Cl_6 or $[\text{Al}(\text{O}^i\text{Pr})_3]_4$
 - b. $[\text{Ti}(\text{O}^i\text{Pr})_4]$ or $[\text{Zr}(\text{O}^i\text{Pr})_4]_3$
2. Why does $[\text{Zr}(\text{O}^i\text{Pr})_4]_3$ form a trimer/tetramer whereas $[\text{Ti}(\text{O}^i\text{Pr})_4]$ is monomeric?
3. Which of the following pairs of precursors would you expect to have the highest decomposition temperature?
 - a. $[\text{Ta}(\text{NMe}_2)_5]$ or $[\text{Ta}(\text{NEt}_2)_5]$
 - b. $[\text{Hf}(\text{OEt})_4]$ or $[\text{Hf}(\text{NEt}_2)_4]$
 - c. ZrCl_4 or $[\text{ZrCp}_2\text{Cl}_2]$
4. $[\text{Ti}(\text{O}^i\text{Pr})_4]$ is a commonly-used precursor to TiO_2 thin films.
 - a. Use the simplified Antoine equation to estimate its vapour pressure at $75\text{ }^\circ\text{C}$, given $A = 9.837$ and $B = 3194\text{ K}$, where the units of pressure are Torr.*
 - b. Some more volatile precursors exhibit vapour pressures of 10 Torr at room temperature. To which temperature ($^\circ\text{C}$) would you need to heat the $[\text{Ti}(\text{O}^i\text{Pr})_4]$ to achieve this vapour pressure?
 - c. Why might it not be advisable to heat a precursor to such a temperature for prolonged periods?

Self-Test Questions (2/2)

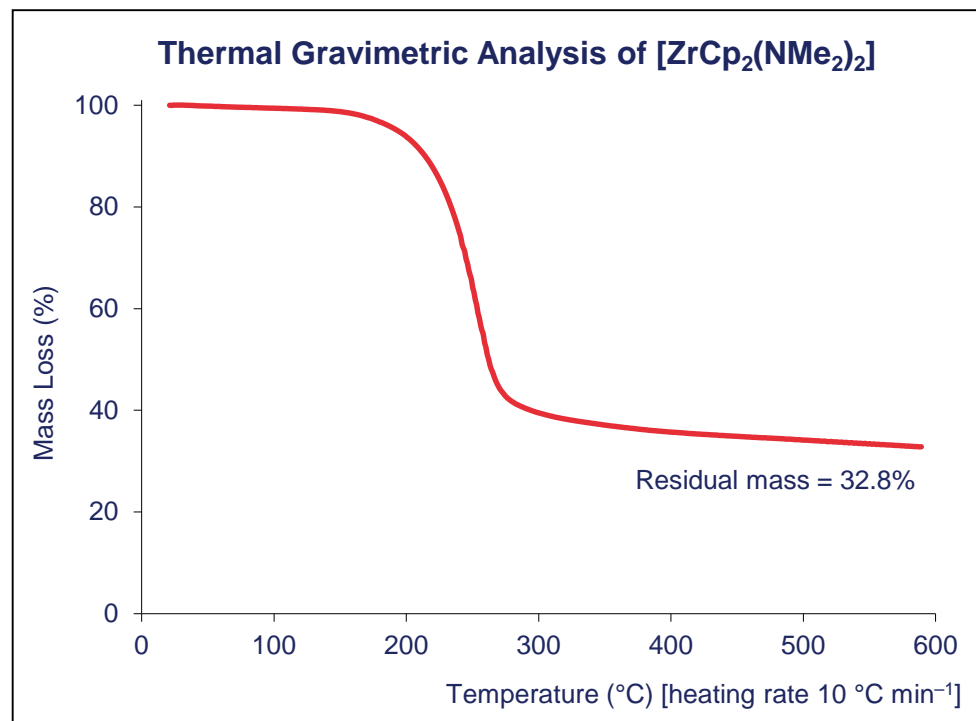
5. $[\text{ZrCp}_2(\text{NMe}_2)_2]$ (RMM = $309.56 \text{ g mol}^{-1}$) was tested as a possible precursor for ZrN thin films.* The thermal gravimetric analysis, carried out under vacuum, is shown below.

a. Describe what is happening to the compound over the following temperature ranges:

- i. 25-150 °C,
- ii. 150-270 °C.

b. Show that the residual mass is, in principle, consistent with the formation of stoichiometric ZrN. Account for any potential discrepancy.

c. Comment on the suitability of $[\text{ZrCp}_2(\text{NMe}_2)_2]$ as a precursor for the ALD of ZrN.

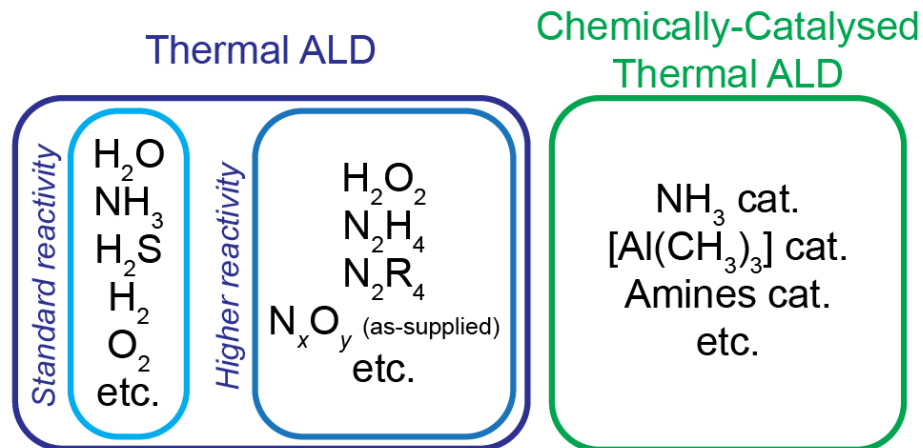


6. Why does industry currently generally prefer to use metal halide precursors?

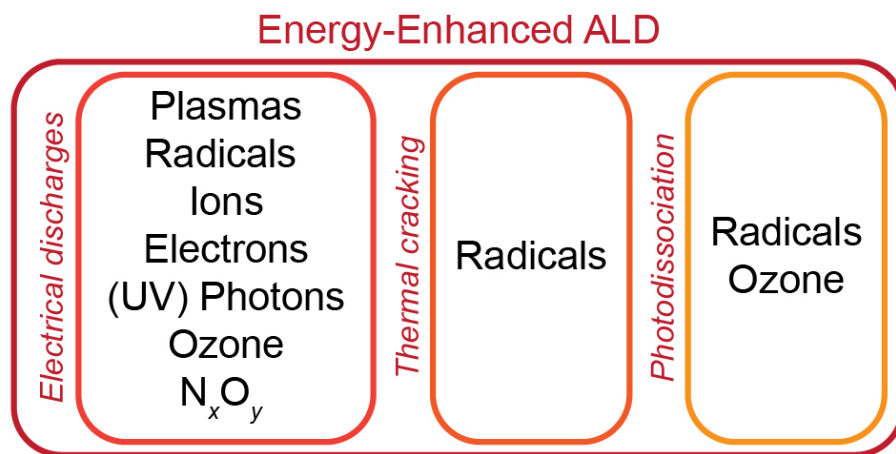
Co-Reactants (Briefly)

- Co-reactants are sometimes referred to as precursors.
- The main focus of this tutorial is the metal-source.

(a) Substrate heating only



(b) Additional energy to convert **gaseous** species



Measurement of Vapour Pressure

- Under reduced pressure
 - Removes process gases
 - Thorough leak-testing required
 - Wait period to ensure no further out-gassing occurs
- Calibrated with known compound (e.g. naphthalene)
- Selection of temperatures
 - Stepwise increase in temperature
 - Time to ensure accurate measurement
 - Avoid decomposition!
- Experiment conducted in reverse
 - Ensures repeatability

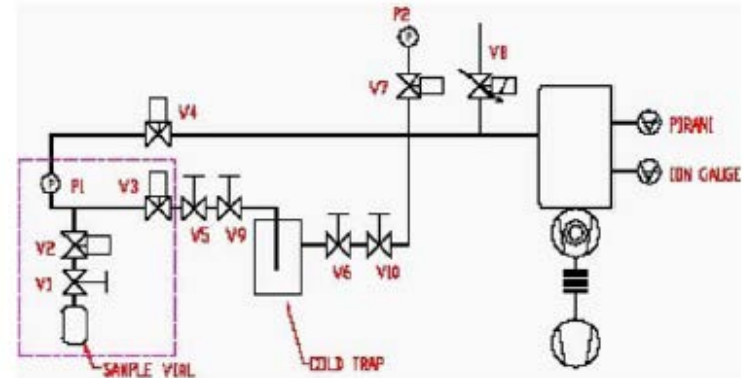


Fig. 1. Schematic of vapour pressure equipment. Grey line defines the oven enclosure.



Fig. 2. Picture of vapour pressure system.

Vapour Pressure

Example

$$\log_{10}(p_{\text{vap}}) = A - \frac{B}{T}$$

What is the vapour pressure of $[\text{Ta}(\text{NMe}_2)_5]$ (PDMAT), in Torr, at 50 °C?

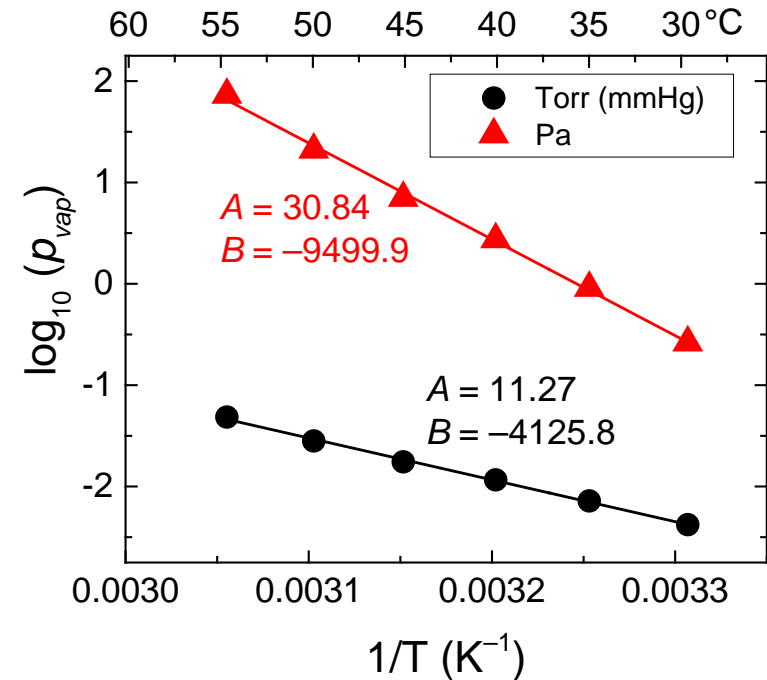
$A = 11.3$, $B = 4125$ (graph's gradient is $-B$)

$$\log_{10}(p_{\text{vap}}) = 11.3 - (4125/\{50+273.16\})$$

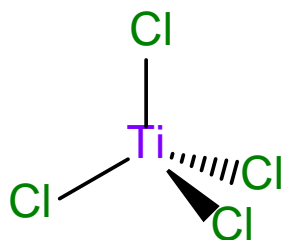
$$\log_{10}(p_{\text{vap}}) = -1.46$$

$$p_{\text{vap}} = 10^{-1.46}$$

$$p_{\text{vap}} = \underline{0.0343 \text{ Torr}} \quad (34.3 \text{ mTorr})$$

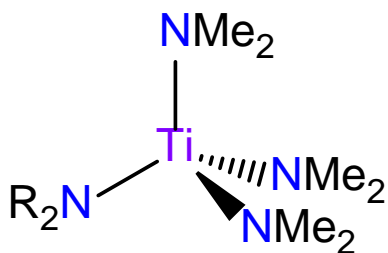


Ti Precursors: Plasma ALD Case Study



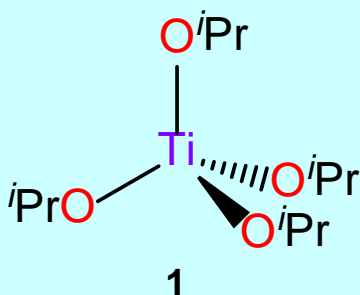
Halides

- Film contamination
- Corrosive by-products (HX)

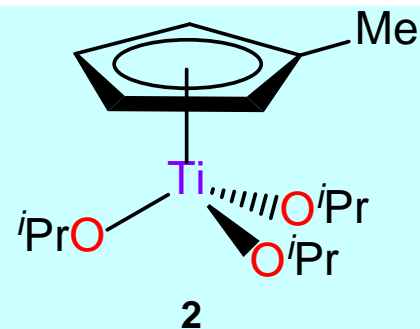
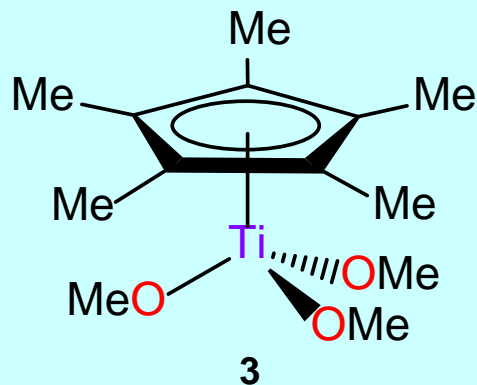


Homoleptic Amides

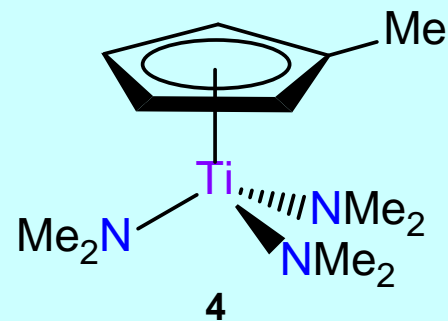
- Low stability



Homoleptic Alkoxides

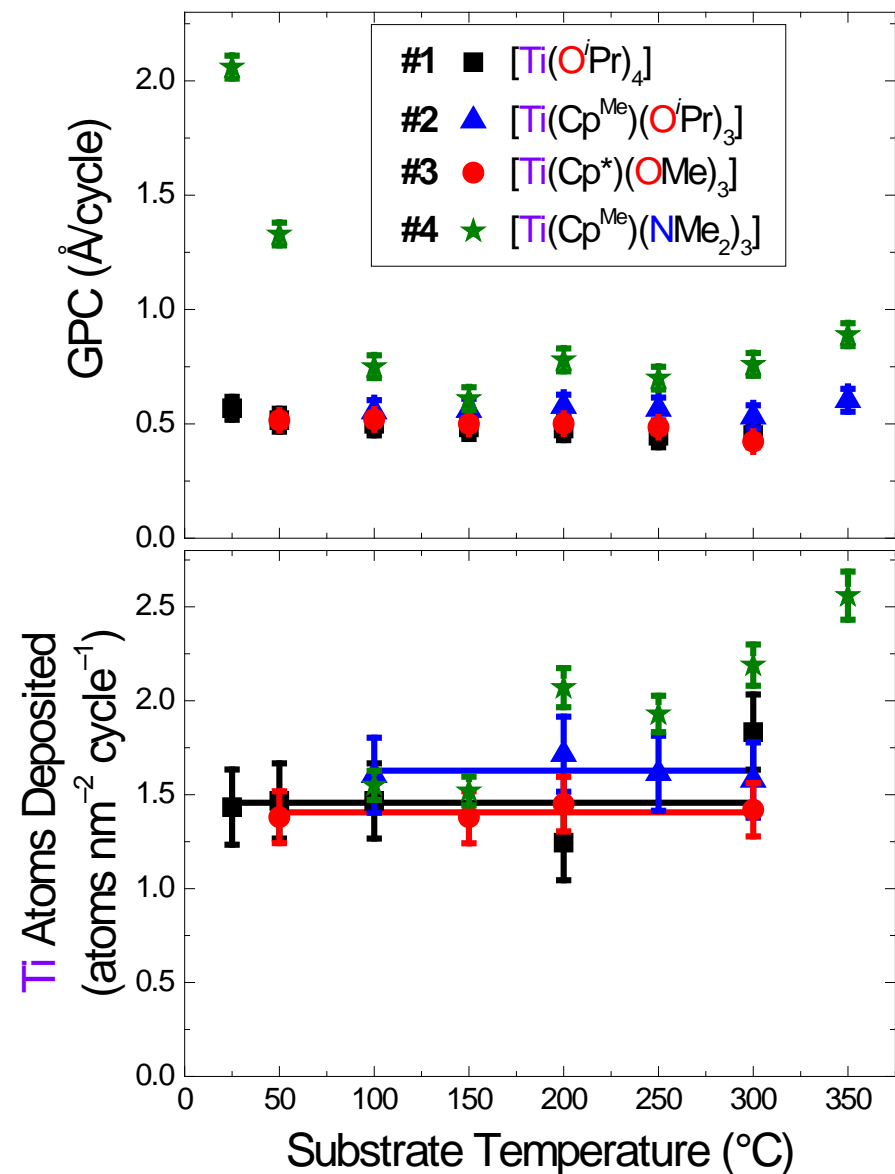


Heteroleptic Cp-Compounds (2-4)



For more on ligand possibilities, see: N. Blasco *et al.*, *Sr and Ti Precursors Development for Next Generation Thin Film Application*, 216th ECS Meeting, Vienna (2009).

Ti Precursors: Plasma ALD Case Study



- **O/Ti ratio = 2.0 ± 0.1**
- **H present**
 - Generally <4 at.%.
 - #4 at 100 °C, ~7 at.%
- **Ti/cycle**
 - Not affected by film density
 - #2 and #3 (Cp/OR) – consistent
 - #4 – increases with temperature
- **OR + Cp^{Me}**
 - most consistent GPCs and Ti/cycles
- **NR₂ (+ Cp^{Me})**
 - higher reactivity, increasing with temperature. **Decomposition?**