# DESIGN OF PRECURSORS FOR ALD

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# Outline

How to design properties needed for ALD precursors:
Reactivity, Stability, Volatility, Melting Point

Examples: amidinates of Ni, La, Lu, Ti(III), Zr, Hf, Co

# Reactivity and Stability vs. Ligand Atoms

Weaker bonds        Stronger bonds

M-C < M-N < M-Cl ~ M-O

More reactive        Less Reactive

Less stable        More stable

Sometimes tradeoff between reactivity and thermal stability

# Reactivity and Stability vs. Crowding

| Un-crowded, loosely packed ligands | Crowded, tightly-packed ligands |
|---|---|
| More Reactive | Less Reactive |
| Less Stable | More Stable |

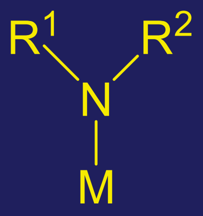
Sometimes tradeoff between reactivity and thermal stability

# Thermal Stability from Chelating Ligands

## Less stable

**alkoxide**

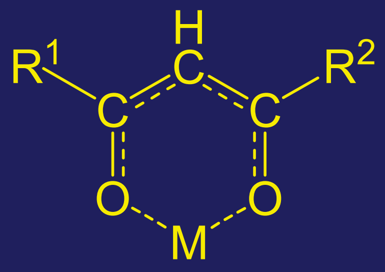
**amide**



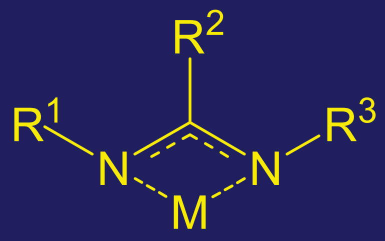
**methyl**

## More stable

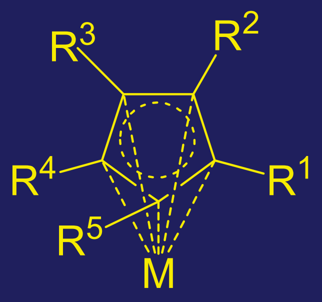
**β-diketonate**



**amidinate**

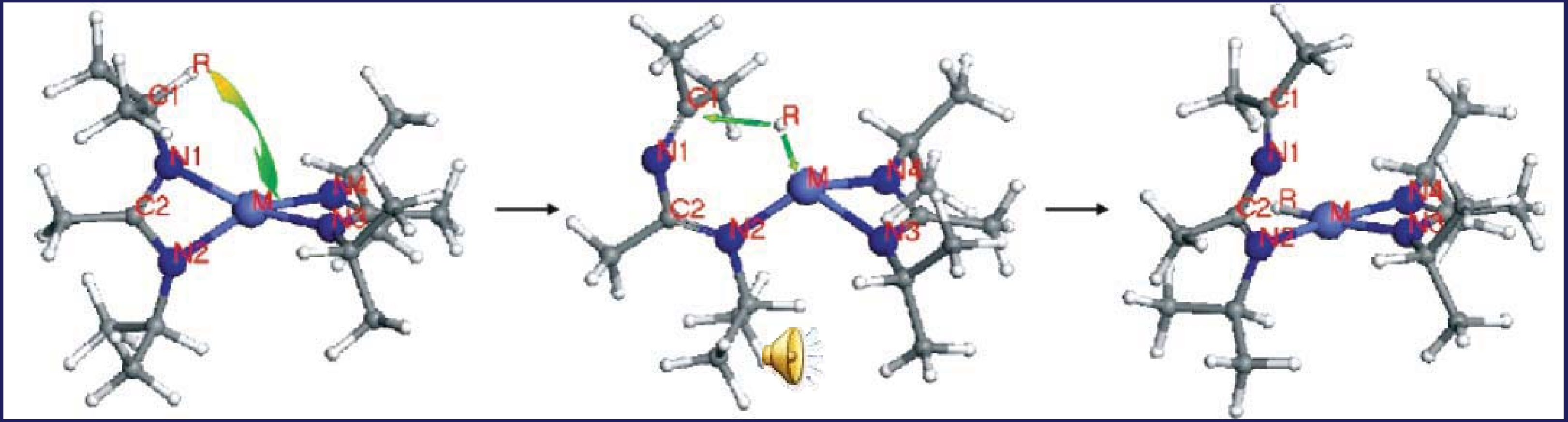


**cyclopentadienide**



# Thermal Instability from β-Hydrogen Transfer

Transfer of H from ligand to metal is a decomposition pathway



Much slower transfer when R is an alkyl group, instead of H

=> Avoid β-hydrogens to increase stability

# Volatility Trends

Smaller molecules are more volatile than larger ones

Monomers are more volatile than dimers

Polymers are usually not volatile

Bulky, crowded ligands avoid dimerization or polymerization
but bigger ligands => less volatile monomers

Nonpolar molecules are more volatile than polar ones

# Melting Point Trends

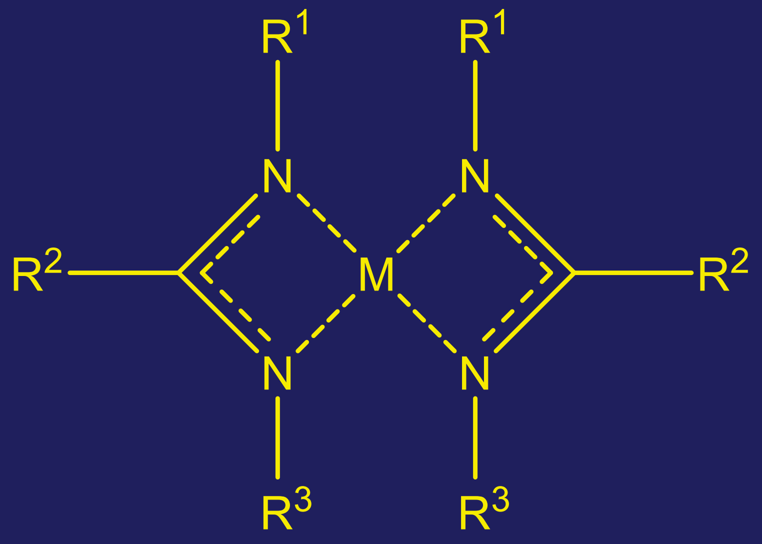
More flexible groups increase disorder, decrease melting point

e.g. rotation about C-C single bonds

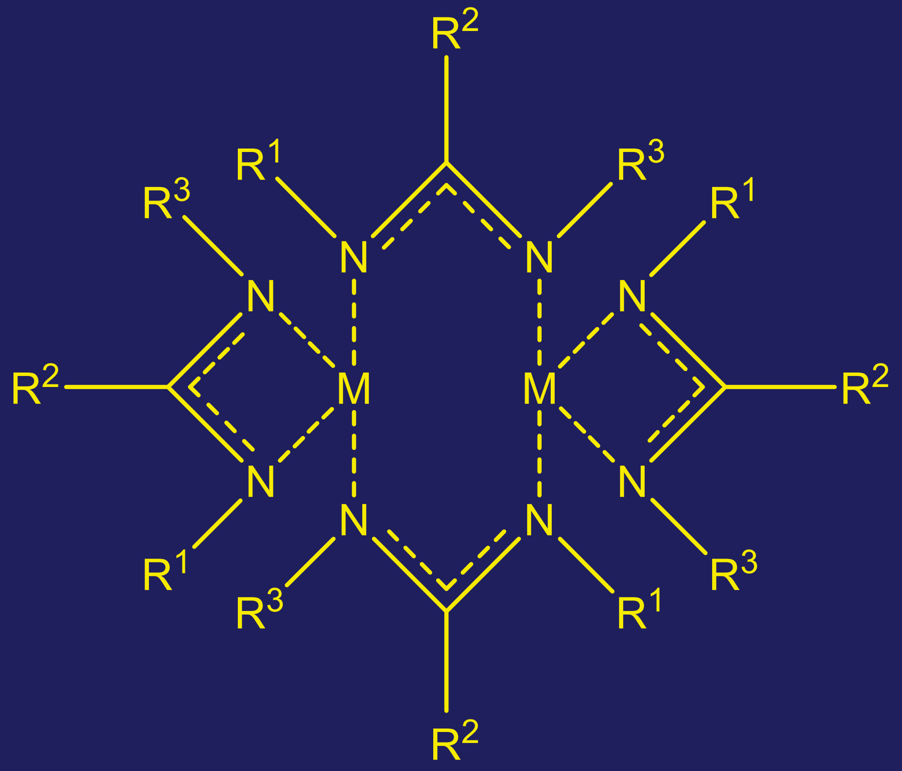
except when one end has high symmetry: $-CH_3$ or $-C(CH_3)_3$

# Metal(II) Amidinates

$R^1$, $R^2$ and $R^3$ = alkyl groups



monomer



dimer

M-N bonds => reactive to $H_2O$, $NH_3$, $H_2$, SiH, etc.

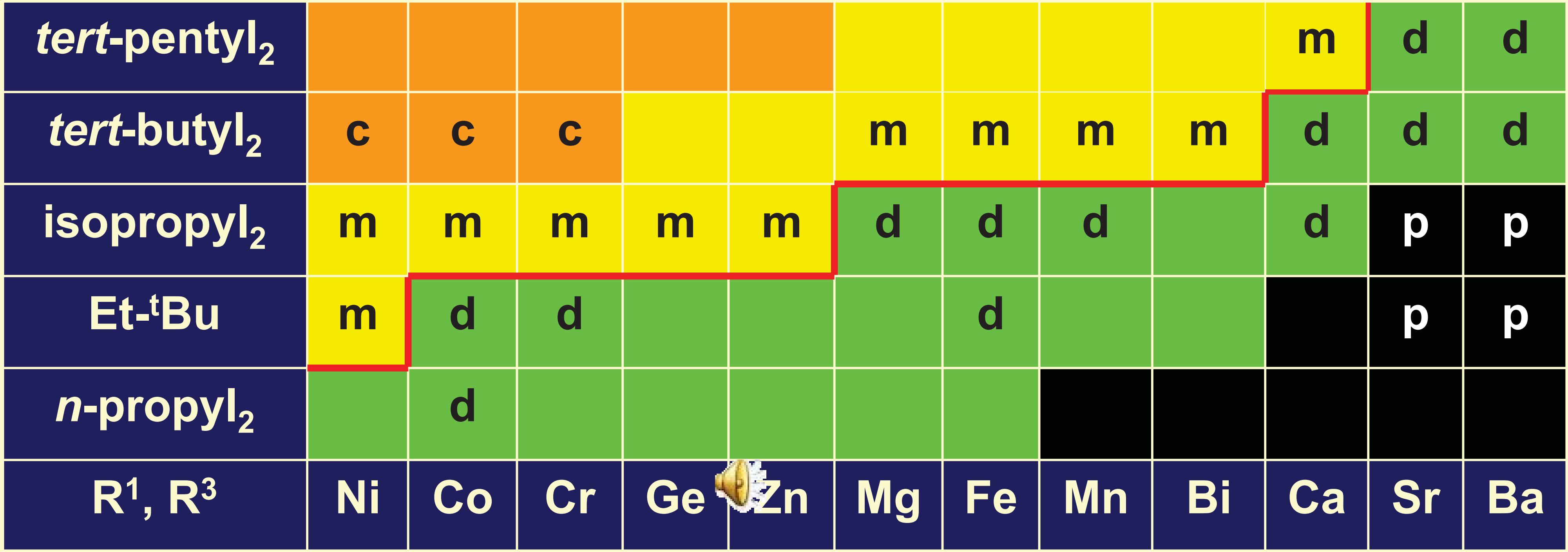
Chelate structure => thermal stability

Non-polar structure => volatility

The choices of $R^n$ affect the volatility, reactivity and stability.

# Structures of Metal Bis-Acetamidinates

Increasing ligand size ↑



| *tert*-pentyl$_2$ |  |  |  |  |  |  |  |  |  | m | d | d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *tert*-butyl$_2$ | c | c | c |  |  | m | m | m | m | d | d | d |
| isopropyl$_2$ | m | m | m | m | m | d | d | d |  | d | p | p |
| Et-$^t$Bu | m | d | d |  |  |  | d |  |  |  | p | p |
| *n*-propyl$_2$ |  | d |  |  |  |  |  |  |  |  |  |  |
| R$^1$, R$^3$ | Ni | Co | Cr | Ge | Zn | Mg | Fe | Mn | Bi | Ca | Sr | Ba |

Increasing size of metal atom ⟶

c = crowded, less reactive, more stable, volatile monomer

m = more reactive, less stable, volatile monomer

d = reactive, volatile dimer

p = non-volatile polymer

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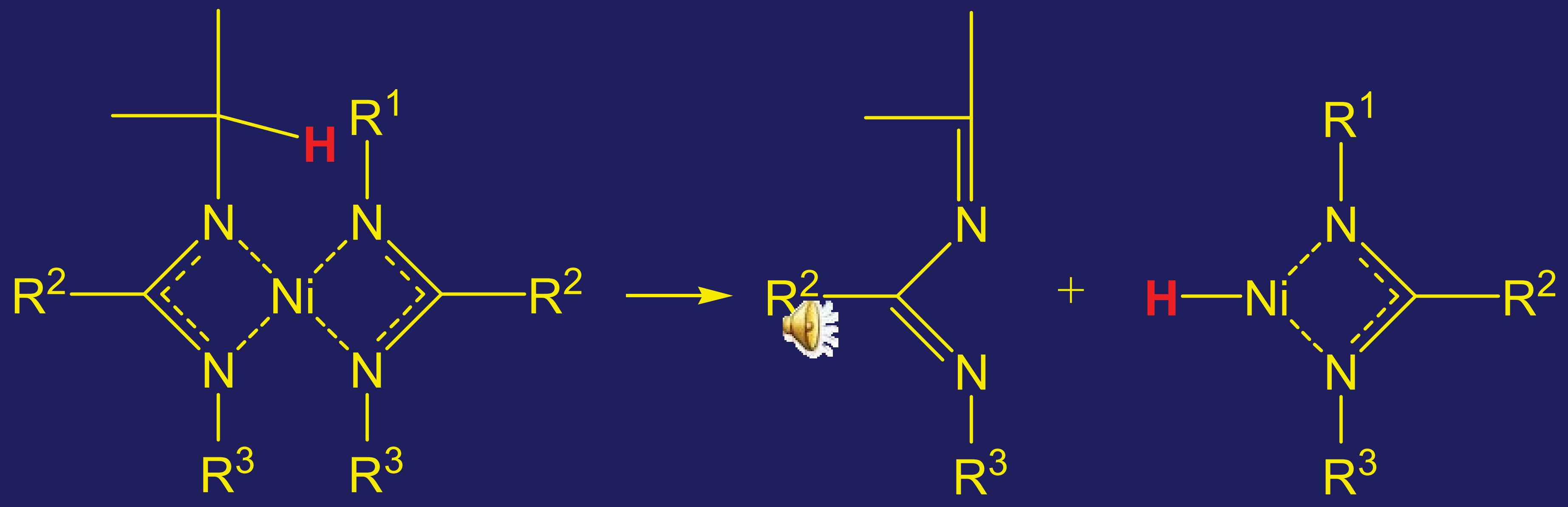
# β-hydrogen instability in Ni(II) Amidinates

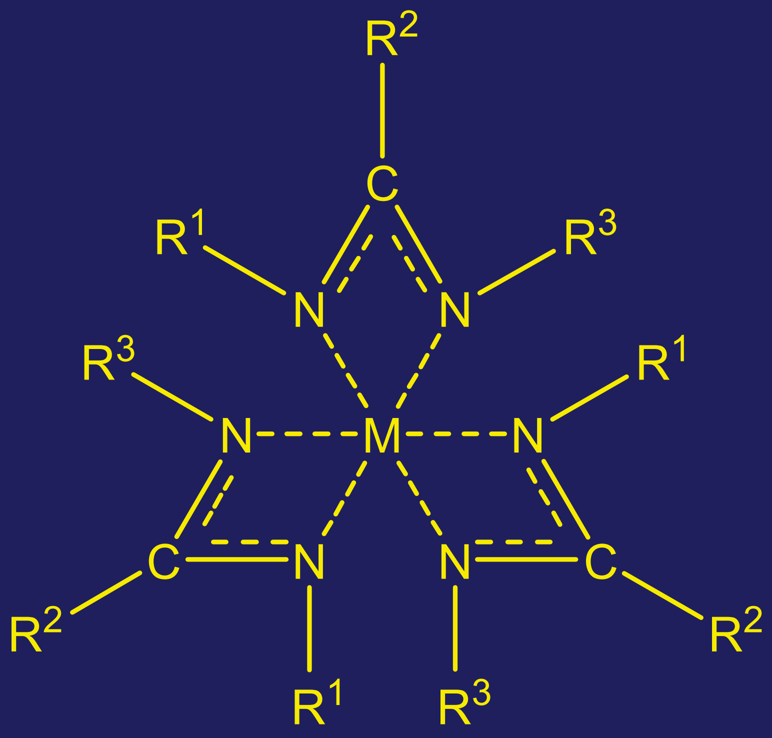
**For $R^1$ = isopropyl, decomposition is rapid**



**If the labile H is replaced by $CH_3$ ($R^1$ = *tert*-butyl) the compound is much more stable**

J. Wu, J. Li, C. Zhou, X. Lei, T. Gaffney, J. A. T. Norman, Z. Li, R. G. Gordon and H. Cheng, *Organometallics* 26, 2803 (2007)

# Metal(III) Amidinates



monomer

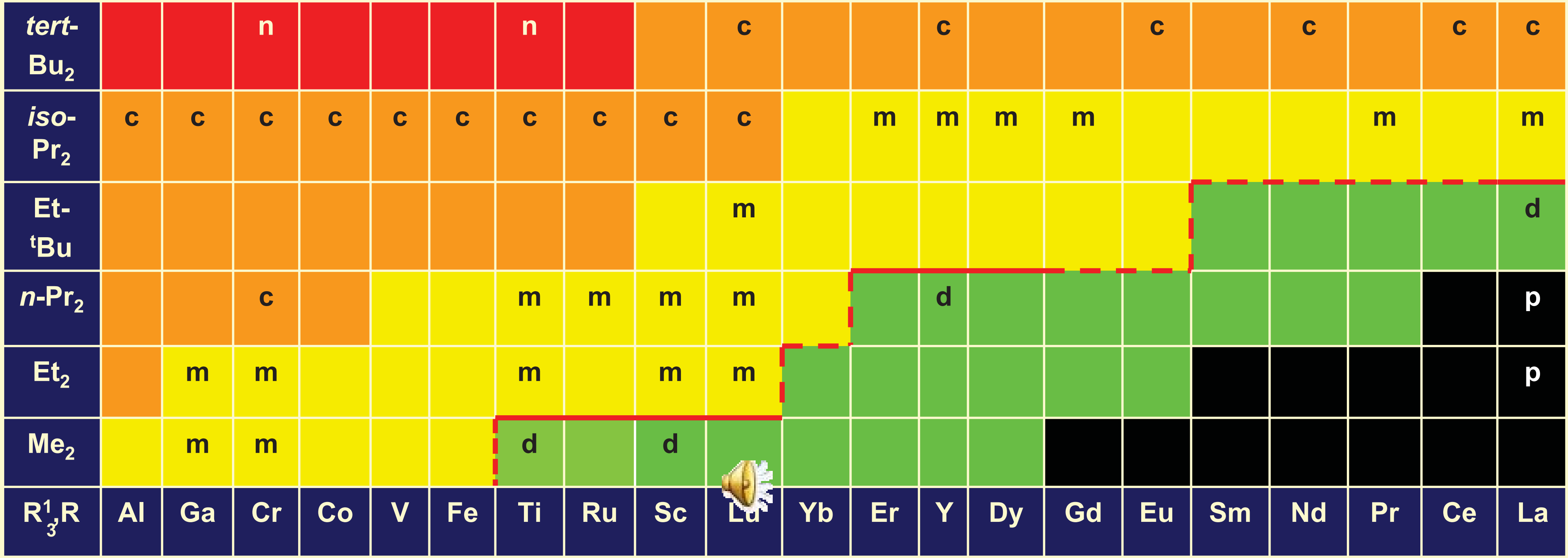
Formamidinates: $R^2 = H$

Acetamidinates: $R^2 = CH_3$

$R^1$ and $R^3$ = alkyl groups

Structures of dimers are unknown, probably bridged

# Structures of Metal(III) Tris-Amidinates



Increasing ligand size ↑

| | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *tert*-Bu$_2$ | 🟥 | 🟥 | n | 🟥 | 🟥 | 🟥 | n | 🟥 | 🟧 | c | 🟧 | 🟧 | c | 🟧 | 🟧 | c | 🟧 | c | 🟧 | c | c |
| *iso*-Pr$_2$ | c | c | c | c | c | c | c | c | c | c | 🟨 | m | m | m | m | 🟨 | 🟨 | 🟨 | m | 🟨 | m |
| Et-$^t$Bu | 🟧 | 🟧 | 🟧 | 🟧 | 🟧 | 🟧 | 🟧 | 🟧 | 🟨 | m | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | 🟨 | 🟩 | 🟩 | 🟩 | 🟩 | d |
| *n*-Pr$_2$ | 🟧 | 🟧 | c | 🟧 | 🟨 | 🟨 | m | m | m | m | 🟨 | 🟩 | d | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | ⬛ | p |
| Et$_2$ | 🟧 | m | m | 🟨 | 🟨 | 🟨 | m | 🟨 | m | m | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | ⬛ | ⬛ | ⬛ | ⬛ | p |
| Me$_2$ | 🟨 | m | m | 🟨 | 🟨 | 🟨 | d | 🟩 | d | 🟩 | 🟩 | 🟩 | 🟩 | 🟩 | ⬛ | ⬛ | ⬛ | ⬛ | ⬛ | ⬛ | ⬛ |
| $R^1,R^3$ | Al | Ga | Cr | Co | V | Fe | Ti | Ru | Sc | Lu | Yb | Er | Y | Dy | Gd | Eu | Sm | Nd | Pr | Ce | La |

Increasing size of metal atom →

n = non-existent

c = crowded, less reactive monomer

m = more reactive monomer

d = low-volatility dimer

p = non-volatile polymer

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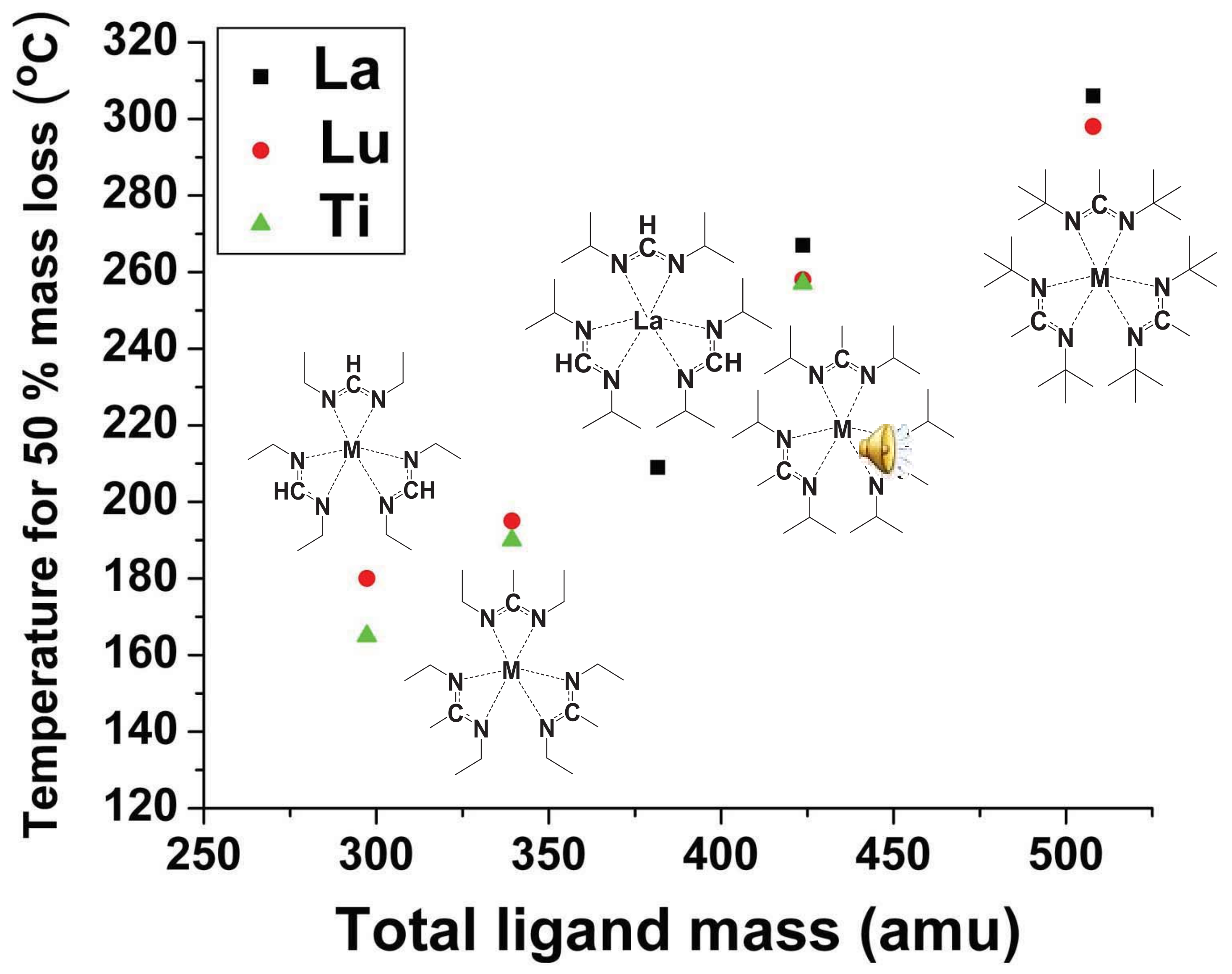
# Volatility Trends

## Vaporization temperature increases with ligand mass



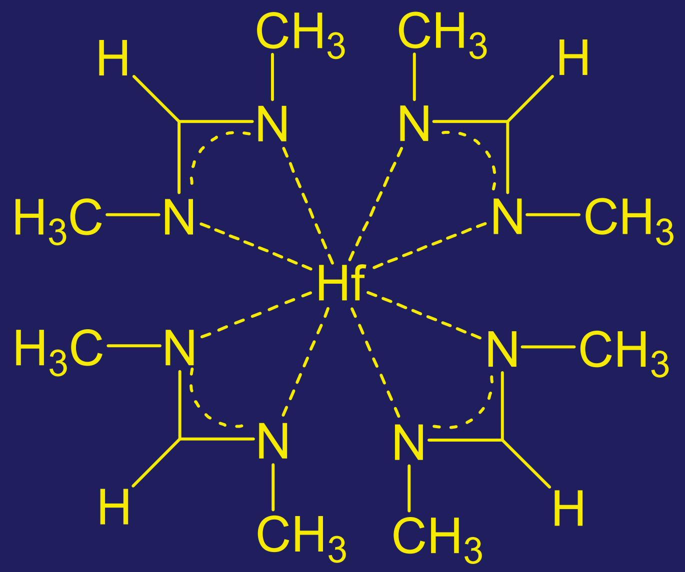
ALD of $LaLuO_3$
see poster P-27

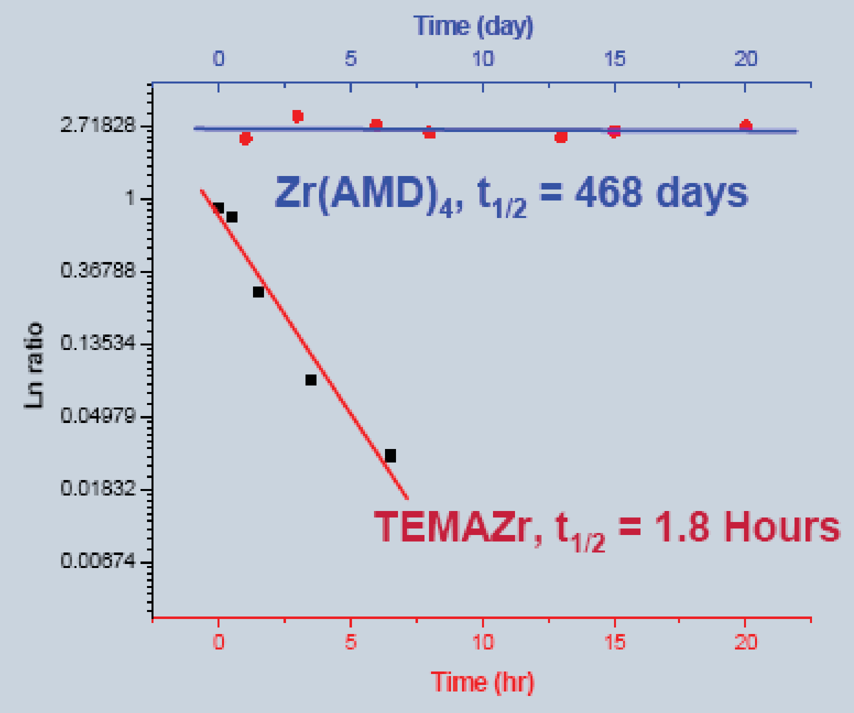
ALD of TiN see
paper WedA2a-5
17:00 Wed

# Chelate Effect in Metal(IV) Tetra-Amidinates

$Zr(amd)_4$ and $Hf(amd)_4$

Require small $R^n$ groups such as H and $CH_3$



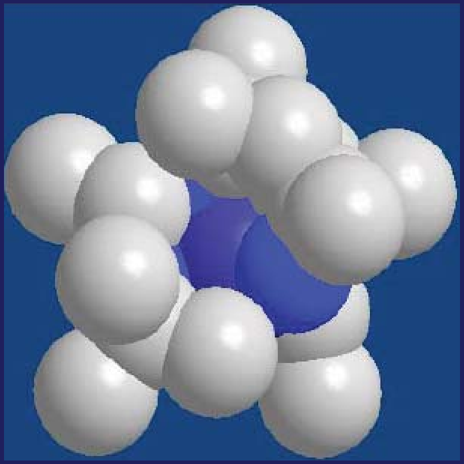


Thermal decomposition at 200 °C

Zr amidinate is much more stable than Zr amide, $Zr(NEtMe)_4$

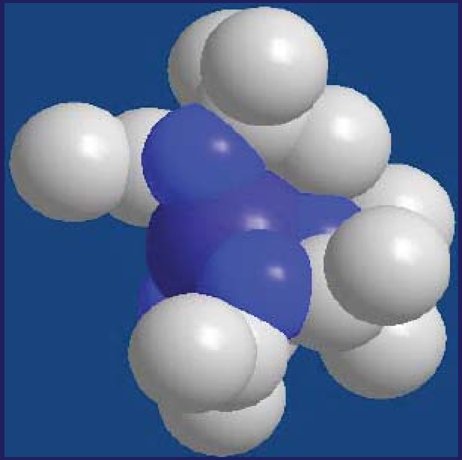
Greater stability of amidinates is due to chelate structure (2 metal-nitrogen bonds instead of one)

# Reactivity of cobalt precursors with hydrogen



Bulky groups (*tert*-butyl)
on each N of amidinate

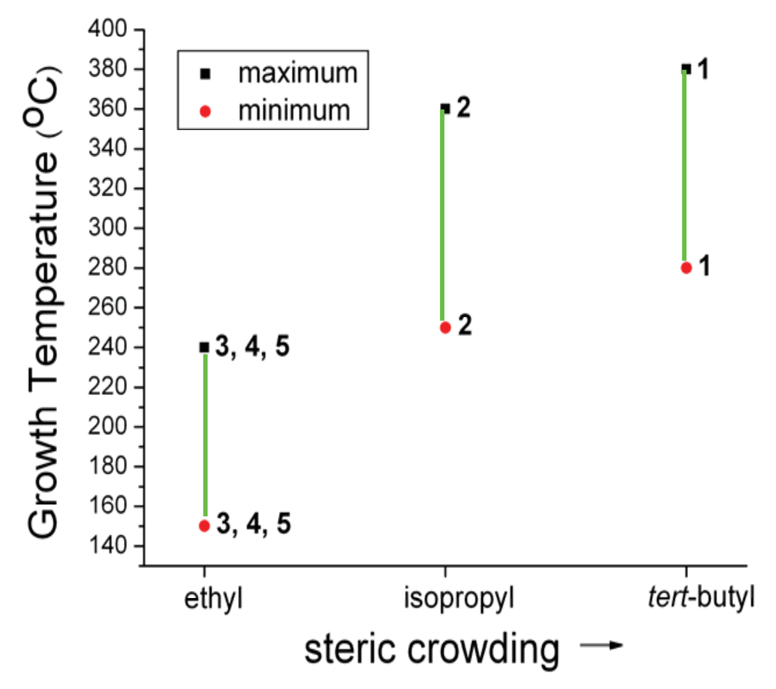
=> low reactivity

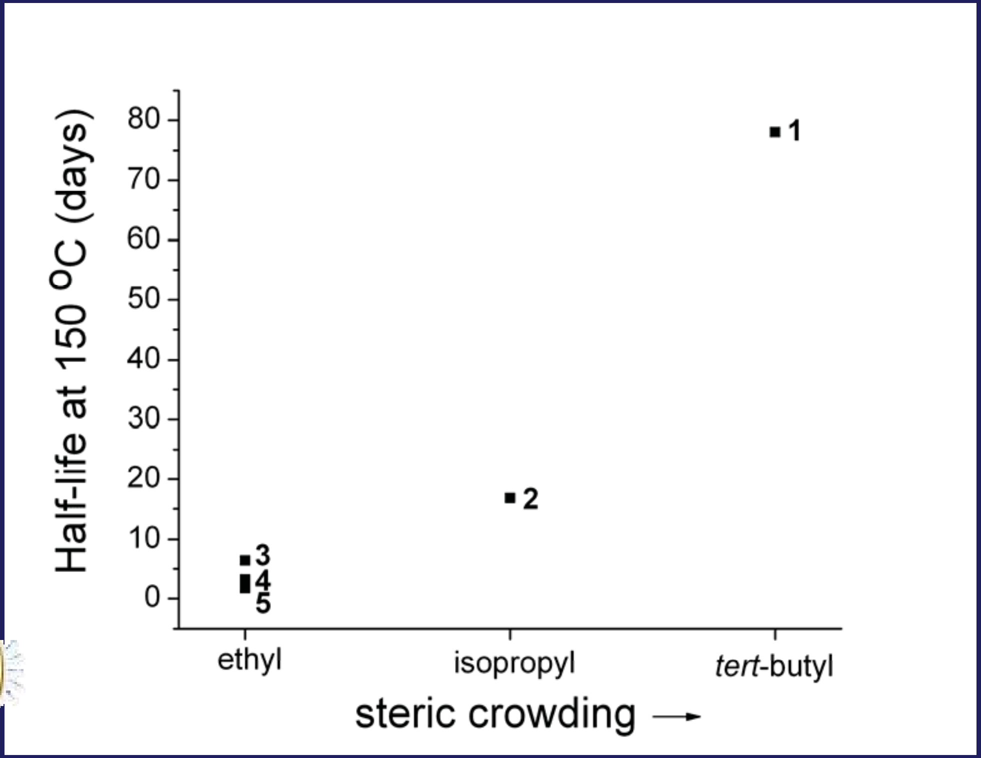


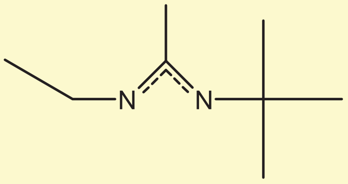
Less bulky groups (ethyl)
on half the N’s of amidinate

=> higher reactivity

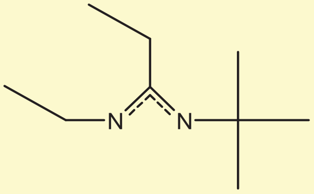
# ALD Reactivity of Cobalt(II) amidinate precursors



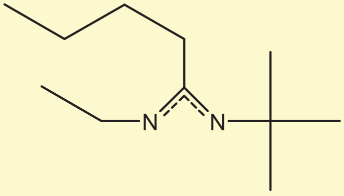




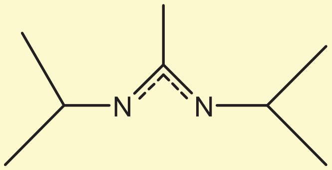
**5**
R’=Et
R’’=$^t$Bu
R = Me



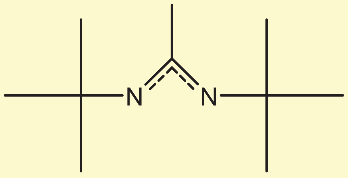
**4**
R’=Et
R’’=$^t$Bu
R = Et



**3**
R’=Et
R’’=$^t$Bu
R = n-Bu



**2**
R’=R’’=$^i$Pr
R = Me



**1**
R’=R’’=$^t$Bu
R = Me

less crowded ligands,
more reactive at low T

↔

more crowded ligands,
reactive only at higher T

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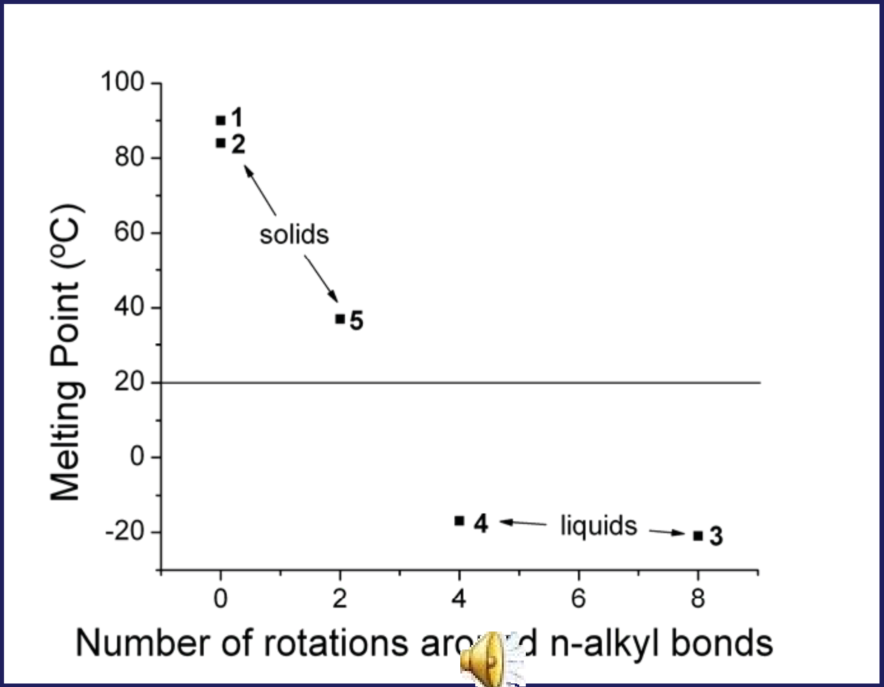
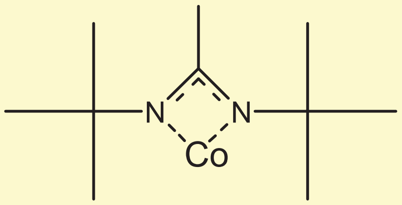
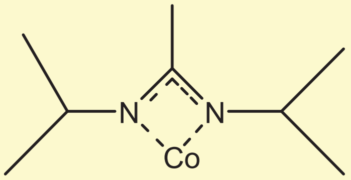
# Melting Points of Co(II) amidinate precursors

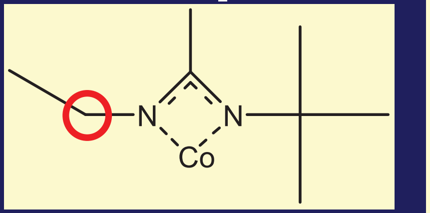




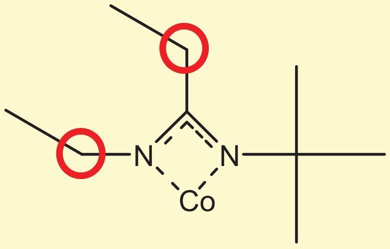
**1**
R'=R''=$^t$Bu
R = Me



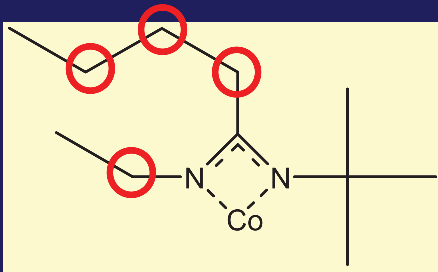
**2**
R'=R''=$^i$Pr
R = Me



**5**
R'=Et
R''=$^t$Bu
R = Me



**4**
R'=Et
R''=$^t$Bu
R = Et



**3**
R'=Et
R''=$^t$Bu
R = n-Bu

**Increasing number of rotations around n-alkyl bonds ➔**

**0 0 2 4 8**

# Summary

CVD requires volatile and reactive precursors

ALD requires volatile precursors with self-limited reactivity and high thermal stability

Amidinates of many metals can meet these requirements by suitable choices of their alk[illegible]l substituents

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