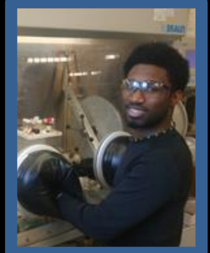
ALD Precursors, Precursor Design, Chemistry and Mechanisms

D. J. H. Emslie

ALD/ALE Tutorial, Denver, Colorado

July 15, 2017

Emslie Group in June 2017, McMaster Univ., Hamilton, ON, Canada



OUTLINE

- ALD versus CVD from Chemistry and Film-Deposition Perspectives
- Overview – H_2O, H_2S, NH_3, O_2/O_3, H_2, H_2/NH_3 etc.
- Precursor design – stability, volatility, m.p., reactivity, evaluation
- Unique Examples of Element ALD:
  - Introduction to Cu ALD
  - Cu ALD using $ZnEt_2$ as the co-reactant (inc. solution studies)
  - Early Transition Metal ALD
    - WF_6 + Si_2H_6 (vs TaF_5)
    - $TiCl_4$ + 1,4-disilyl-substituted 2,5-cyclohexadiene or 1,4-dihydropyrazine co-reagents
    - ML_2 + $BH_3(NHMe_2)$ [M = Cr, and possibly Mn]
    - MnR_2 + H_2 (organometallic precursors)
- Summary / Conclusions

CVD vs ALD from different perspectives

Chemistry Perspective:

Basic CVD is distinct in that it involves *just 1 precursor*

p-CVD and ALD are similar since they *utilize a precursor and a co-reactant* – this offers more reactivity possibilities

CVD

pulsed-CVD

ALD

Thin Film Deposition Perspective:

CVD and p-CVD are similar in that they *do not allow for self-limiting growth or highly conformal and uniform deposition (not to the extent possible with ALD)*

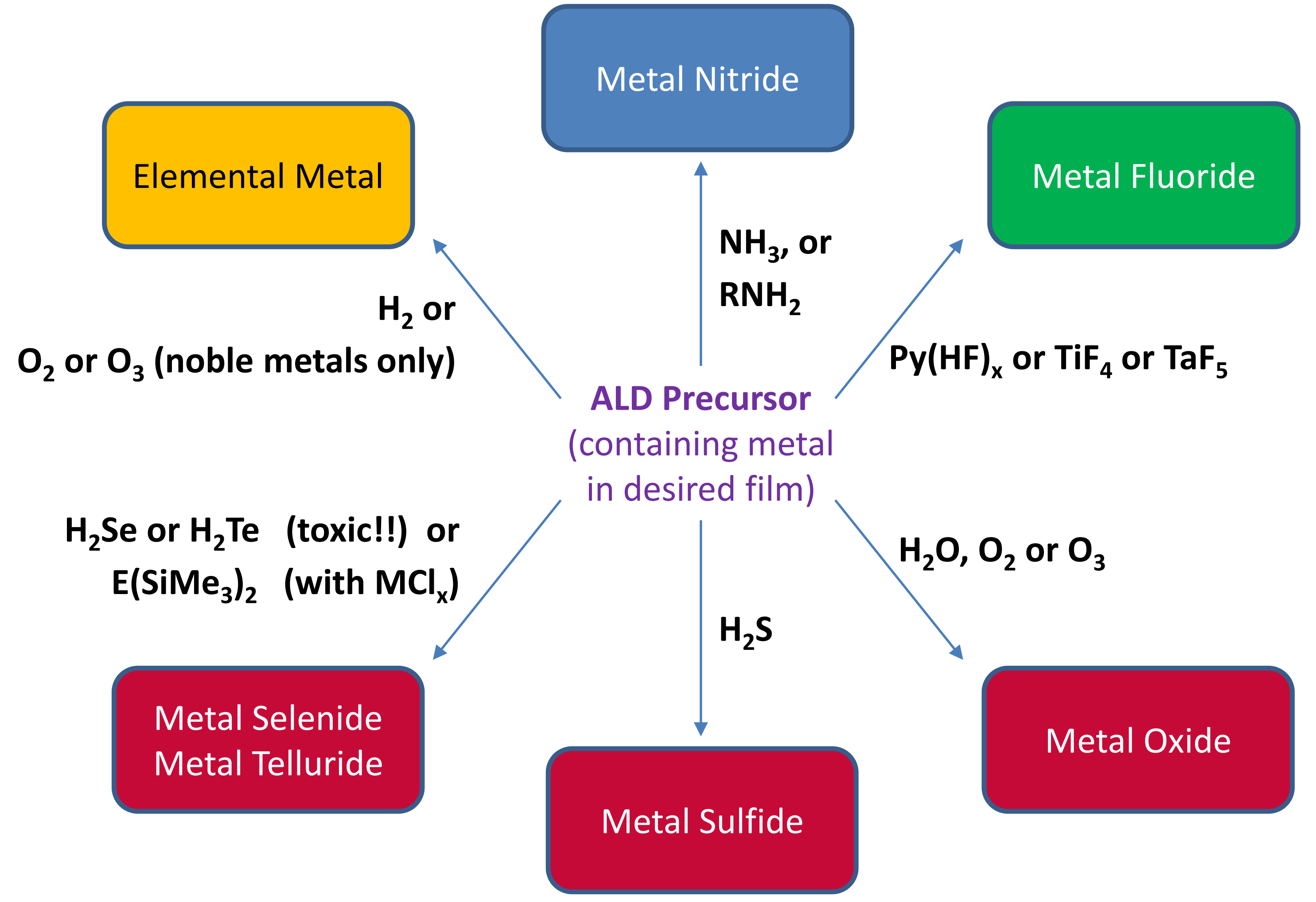
ALD is distinct in that it achieves *self-limiting growth and more conformal and uniform deposition*

ALD OVERVIEW – ACCESS TO DIFFERENT MATERIALS

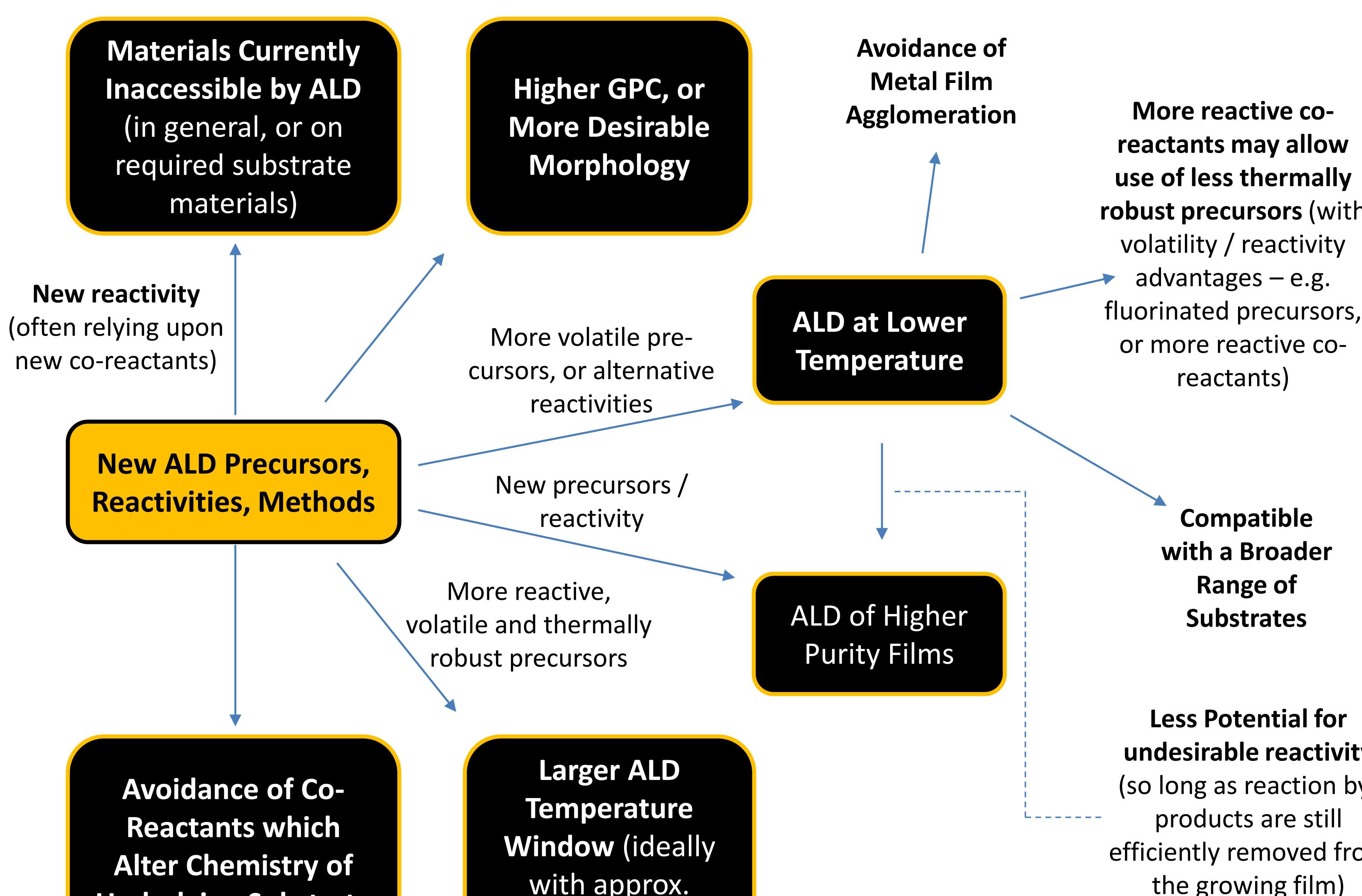
Co-reactants typically determine the type of thin film deposited (oxide, nitride etc).

Precursors are designed to exhibit the desired reactivity with a particular co-reactant.

Many Common precursors are halide, alkyl, Cp, amido, alkoxide, aminoalkoxide, acac, β-diketiminate, amidinate complexes.



WHY NEW ALD PRECURSORS AND REACTIVITIES ?



PRECURSOR DESIGN CONSIDERATIONS

Precursor Attributes	Additional Comments	Comments on Evaluation
Volatile	Ideally deliverable at low T (low molecular weight, alkyl or silyl > aryl, fluorination, sometimes less symmetrical compounds).	Sublimation/Distillation Temp (or measurement of vapor pressure vs temp.).
Thermally Stable	*Long timescale* --- Thermally stable for months at delivery temperature. *Short timescale* – no CVD until high temp.	Heating at delivery temp for 24h. TGA (thermogravimetric anal.), ideally at atm. and low pressure.
Reactive	Reacts with co-reactant at low T (with wide temp. window in which desired reactivity is observed, ideally with fairly constant GPC vs T).	Literature and solution reactivity can serve as a guide. In-reactor studies essential.
Reacts with co-reactant to form volatile and thermally robust products	Reaction by-products must be readily removed from the growing thin film.	Expected byproducts can be prepared. Alternatively, do ALD and assess film purity.
Low melting point (ideally)	Ideally, precursor will be liquid at the delivery temp (much less important for ALD vs CVD). Longer alkyl (e.g. n-Bu, i-Bu) groups can help, but sometimes at the expense of volatility…	---
Reactivity allowing ALD of multiple materials ?	One precursor for ALD of multiple materials could be beneficial.	---
No rapid exothermic decomp. upon heating	---	Exercise caution with certain classes of compound. TGA.
Scaleable synthesis	Synthesis can often be improved if initial ALD performance is promising.	---

Thermal ALD of Copper

Methods for Thermal Cu ALD:

Cu^{II} precursors with:

- H_2 (≥ 150 °C)
- ROH (300 °C)
- HCO_2H, then N_2H_4 (100-170 °C)
- $BH_3(NHMe_2)$ (130-160 °C)

Cu^{I} precursors with:

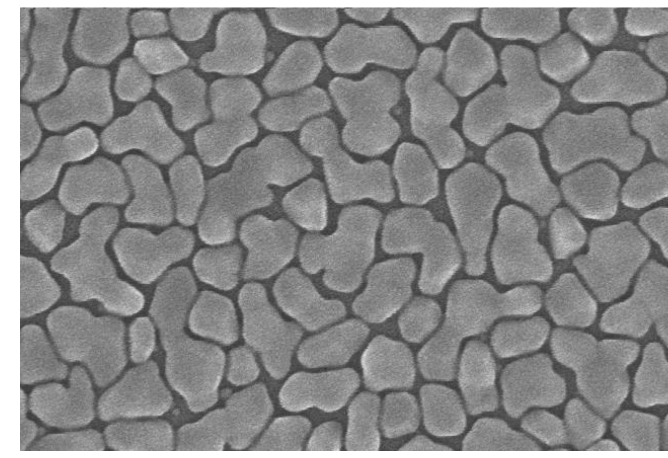
- Zn metal (>400 °C; impure films)
- H_2O, then H_2 (375-475 °C).

Emslie, D. J. H.; Chadha P.; J. S. Price, Metal ALD and pulsed-CVD: Fundamental reactions and links with solution chemistry, *Coord. Chem. Rev.*, **2013**, *257*, 3282-3296.

Knisley, T. J.; Kalutarage, L. C.; Winter, C. H., Precursors and chemistry for the ALD of metallic first row transition metal films, *Coord. Chem. Rev.*, **2013**, *257*, 3222-3231.

Kalutarage, L. C.; Clendenning, S. B.; Winter, C. H., Low-Temperature Atomic Layer Deposition of Copper Films Using Borane Dimethylamine as the Reducing Co-reagent, *Chem. Mater.* **2014**, *26*, 3731–3738.

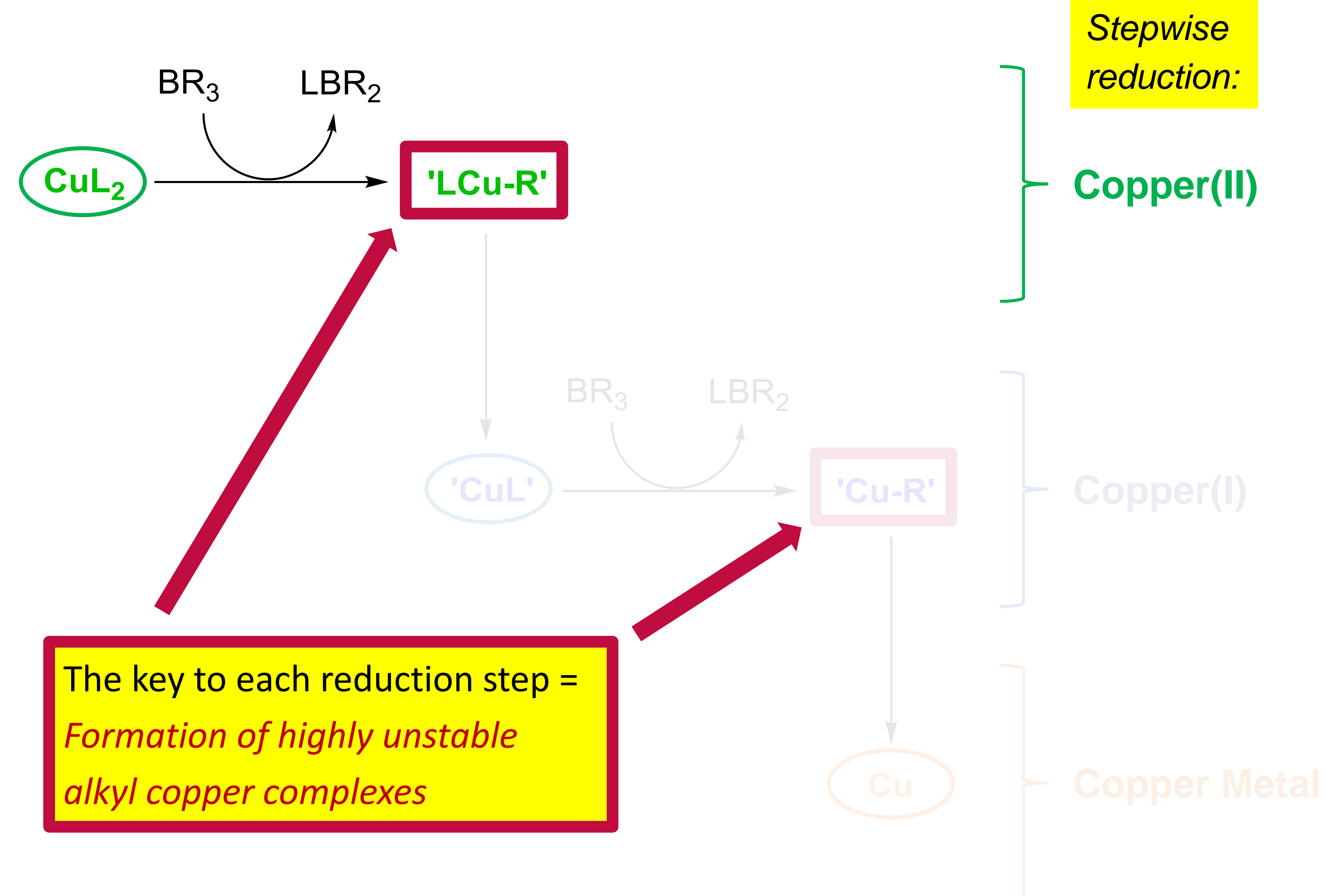
The above methods require the use of anhydrous hydrazine or operate at temperatures ≥ 130 °C, and in the case of very thin films, this can lead to agglomeration.



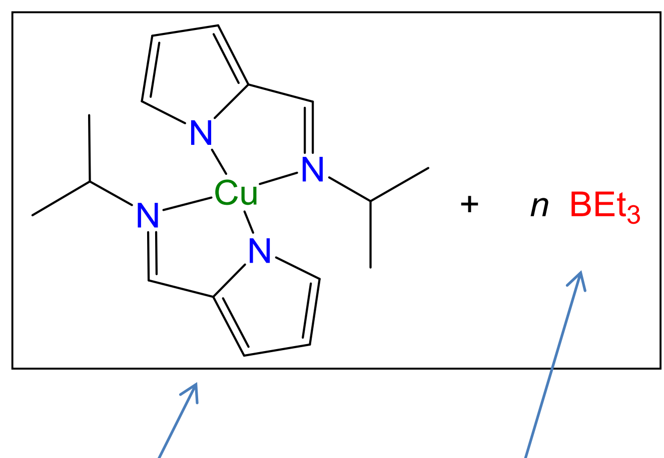
At outset of our work in this area, we asked:

Can $ZnEt_2$ be used as a co-reactant for Cu ALD (by introducing Et groups onto Cu, resulting in unstable Cu alkyl species) ?

PROPOSED REACTION SCHEME



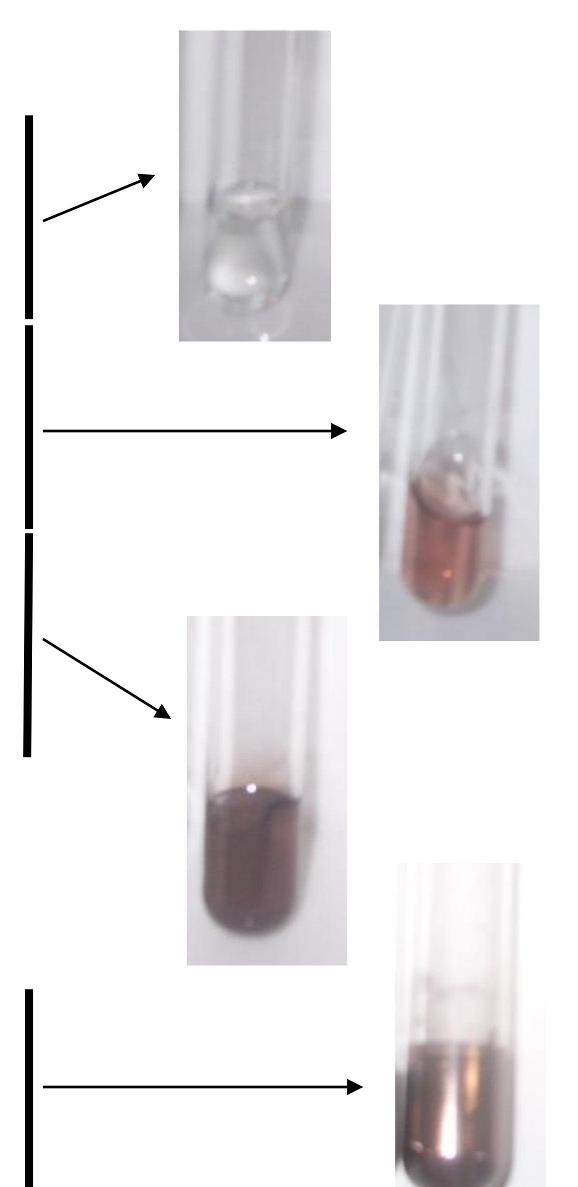
Screening Reactions – A Typical Reaction



Order of Reactivity from Solution Screening:

$ZnEt_2$ >
$AlMe_3$ >>
BEt_3

Temp	5 eq.
25 °C	Very pale yellow soln
50 °C	Pale pink soln
75 °C	**Cu mirror** with reddish pink soln
100 °C	**Cu mirror** with colorless soln
120 °C	**Cu mirror** with colorless soln



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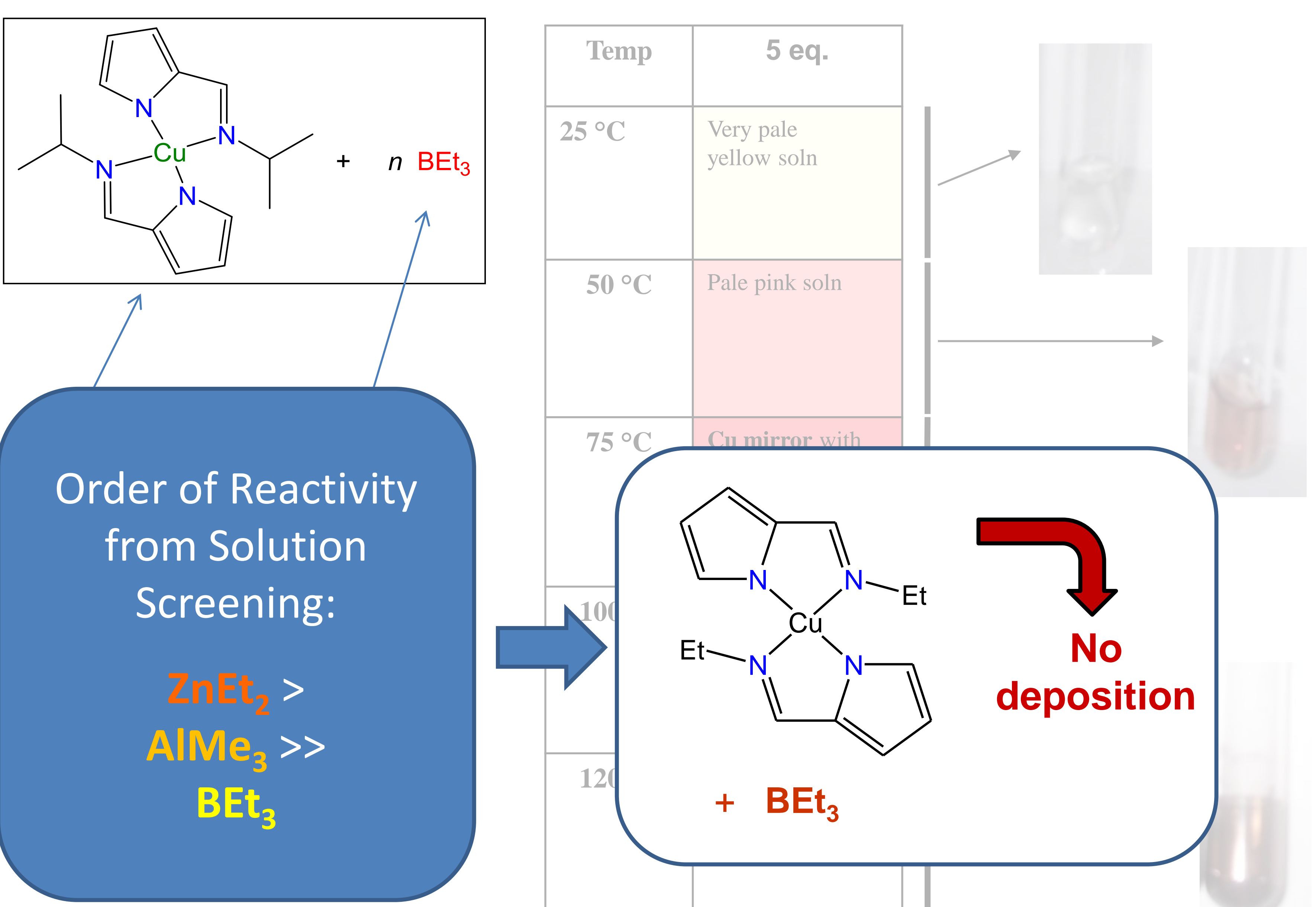
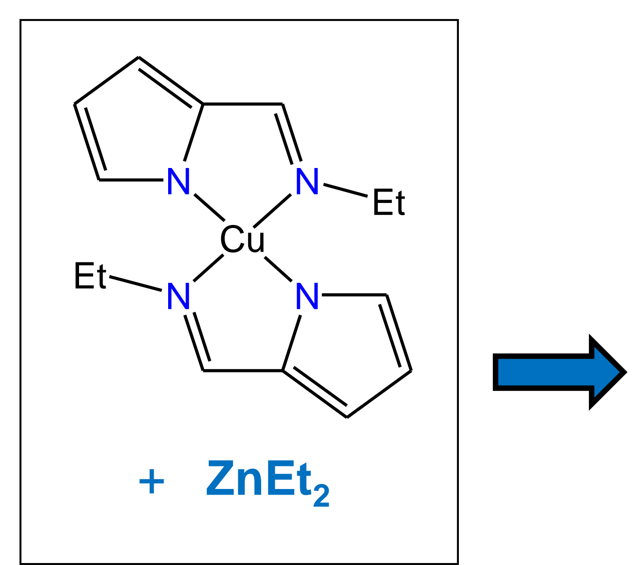
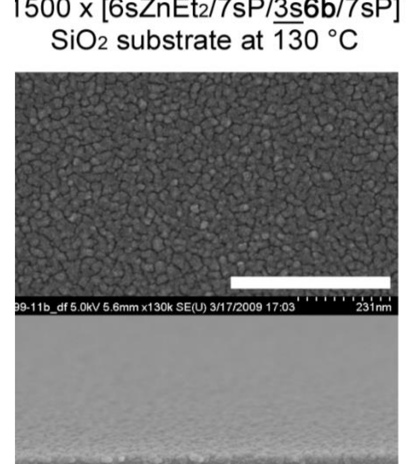
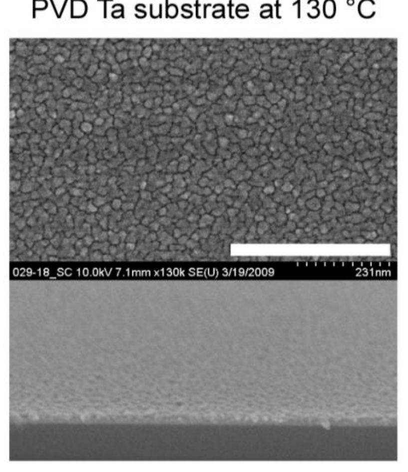






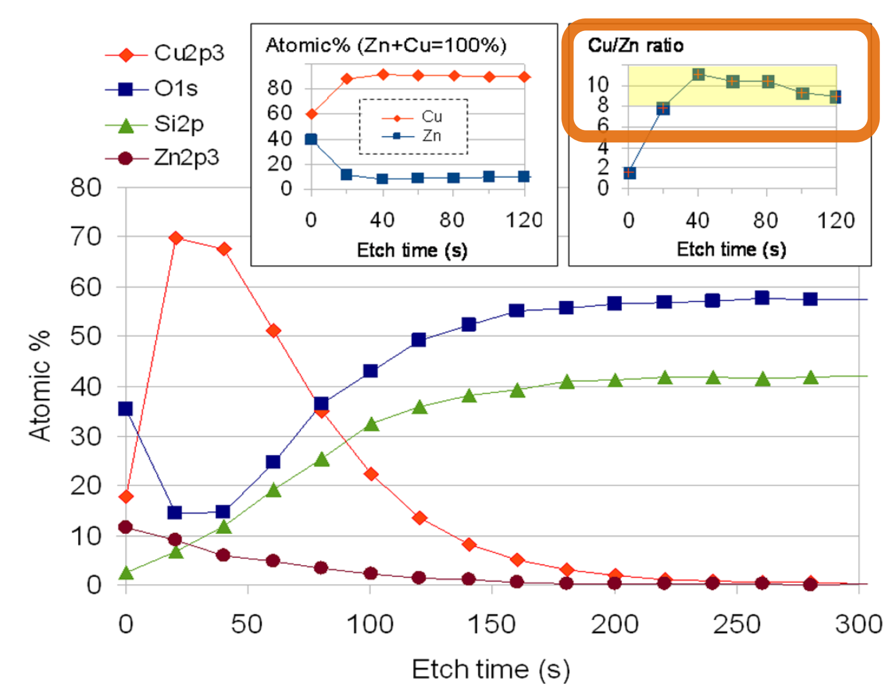


Dr. Scott B. Clendenning, Intel

Pulsed-CVD of Cu Metal using $[Cu(PyrIm^{Et})_2]$ with $ZnEt_2$ at 130 °C

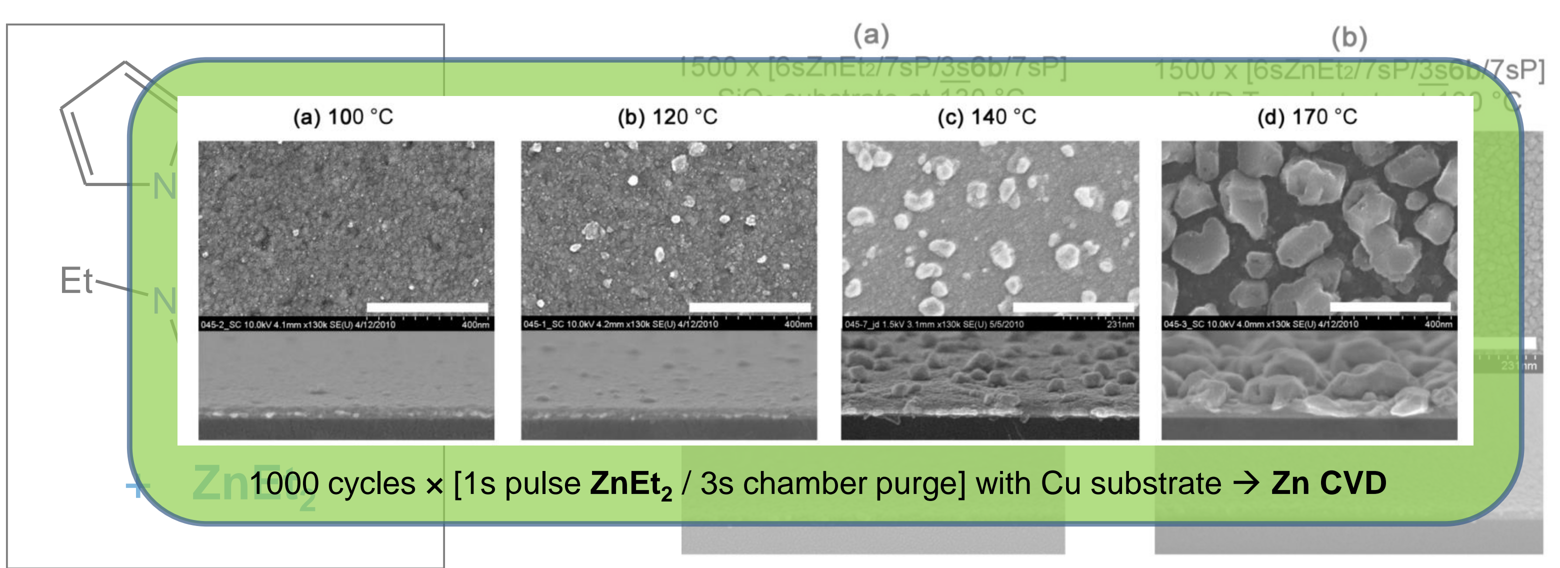
Deposition on SiO_2

1500 x [6s DEZ / 7s P / 9s CuL_2 / 7s P]
Appearance: Metallic Cu
Cu Film thickness ~ 470Å
GPC ~0.31 Å/cycle
Rs: 6.5 Ω/sq; ρ~ 31 μΩ•cm



Not Self Limiting → pulsed-CVD

B. Vidjayacoumar, D. J. H. Emslie, S. B. Clendenning and J. M. Blackwell *et al. Chem. Mater.*, **2010**, *22*, 4844-4853.



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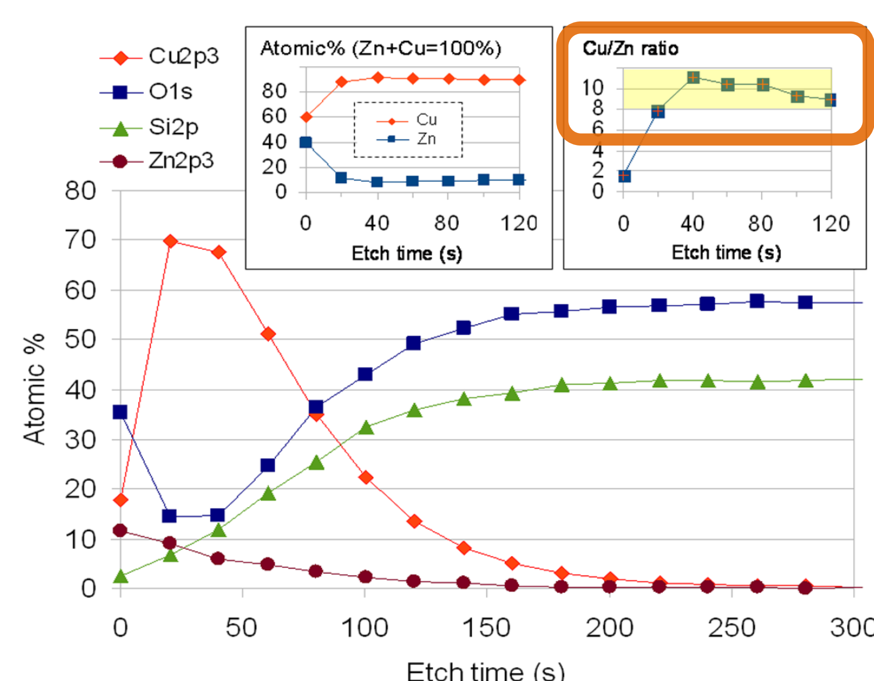

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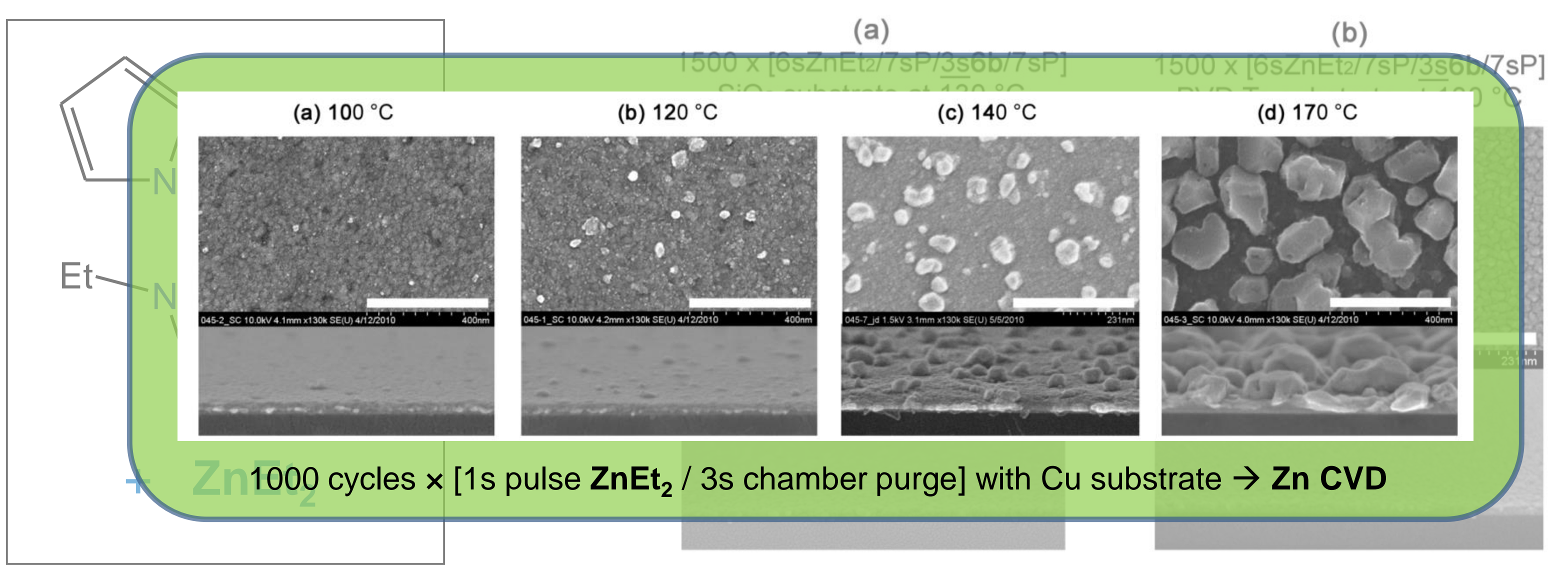

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- Zinc incorporation results from **Zn CVD**, which is significant at **> 100 °C**

- **Minimum delivery temperature** for our copper precursor was 120 °C.

- With a **more volatile copper precursor**, Fischer, Sung *et al.* demonstrated Cu metal ALD using $ZnEt_2$ at 100 °C (*Angew. Chem. Int. Ed.* **2009**, *48*, 4536-4539)

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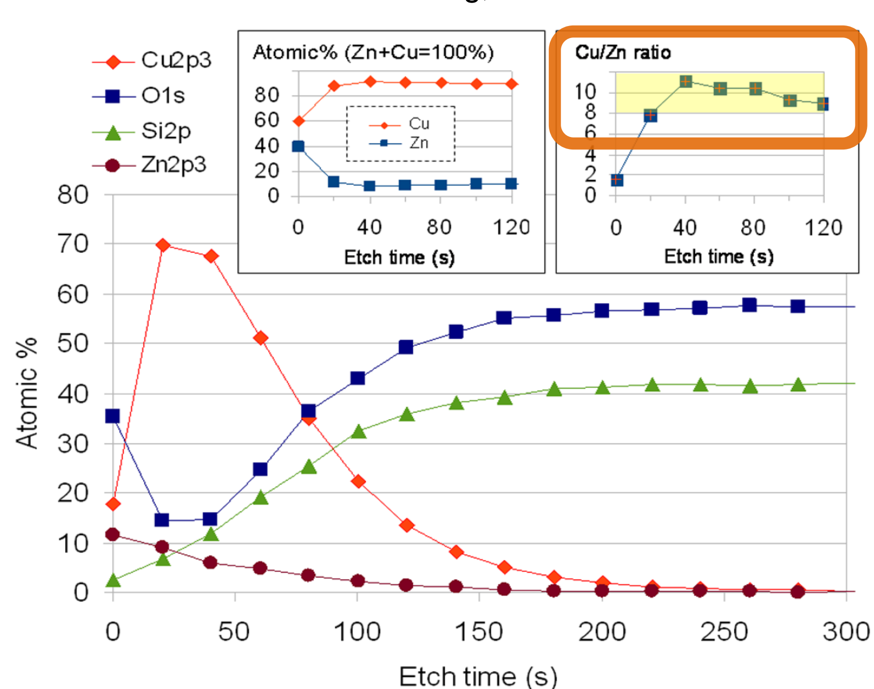

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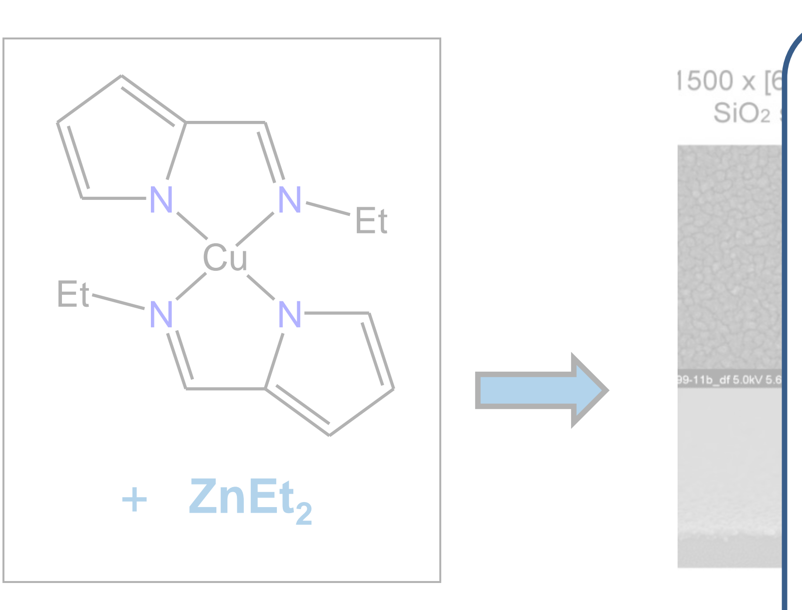

100-120 °C

Cu + ZnEt₂ → Zn + Cu

XRD

Cu on Si/SiO₂

SEM

Cu nanotubes formed by deposition into pores in a polycarbonate membrane

SEM

TEM

- Zinc incorporation results from **Zn CVD**, which is significant at **> 100 °C**

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Not Self Limiting → pulsed-CVD

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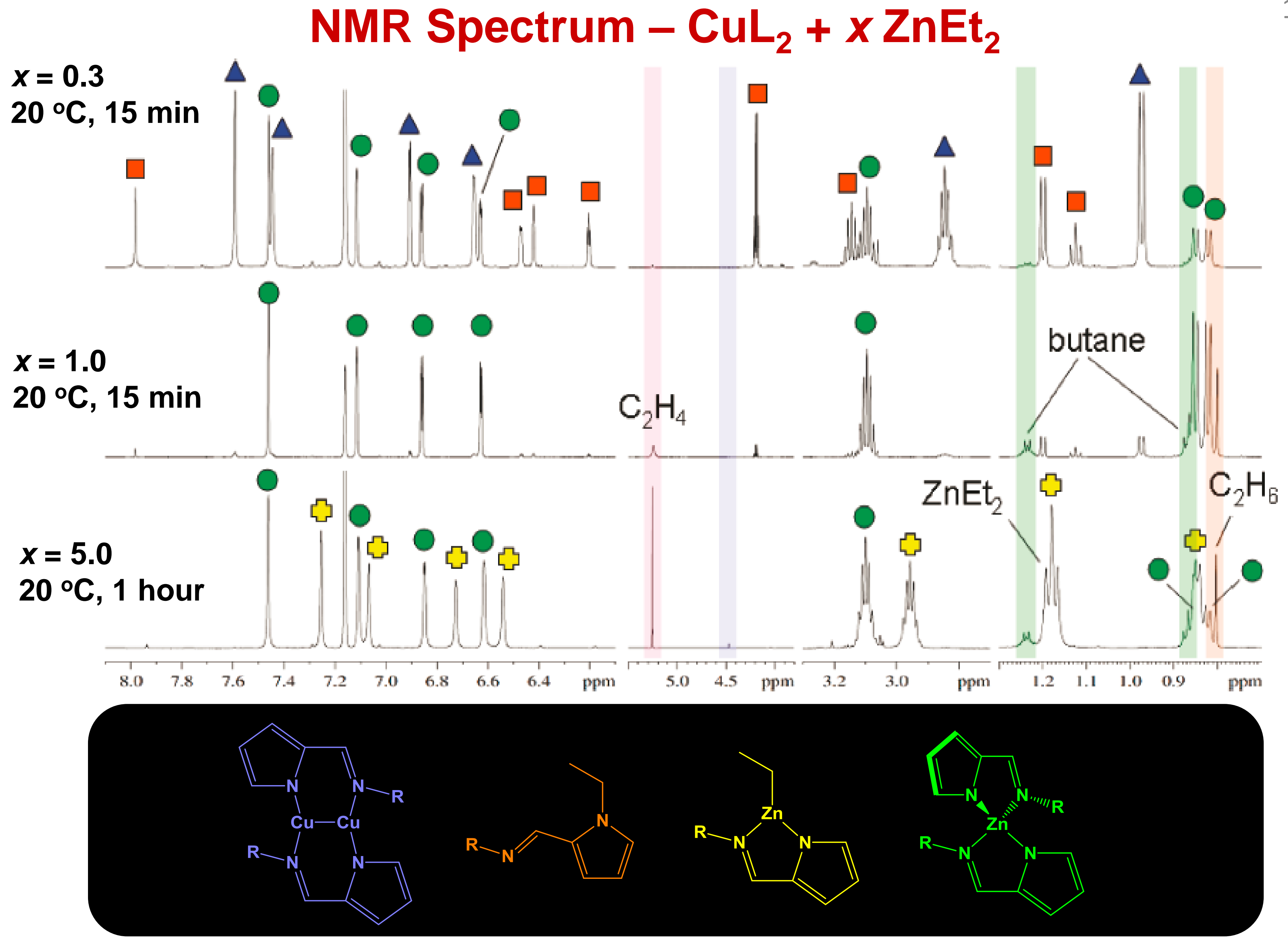
What Can we learn from NMR Spectroscopy?

For compounds without any unpaired electrons:

Prepare NMR samples in the glovebox

Record NMR Spectra as Reactions Proceed (increasing temperature incrementally if necessary)

NMR Spectrum – CuL_2 + *x* $ZnEt_2$

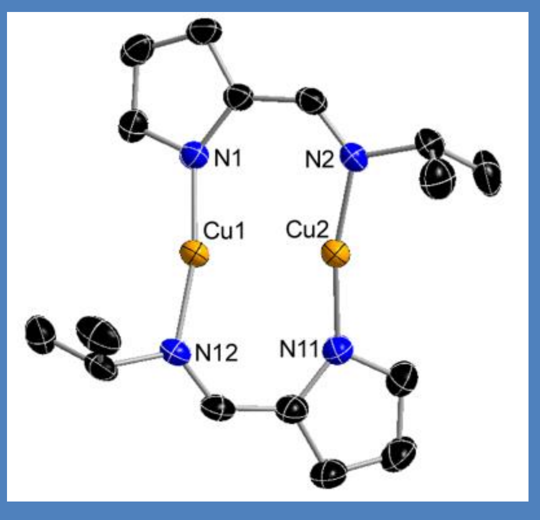


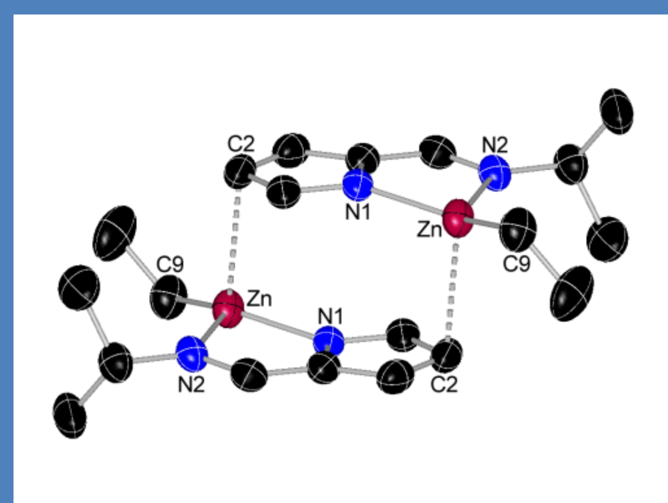
B. Vidjayacoumar, D. J. H. Emslie, J. M. Blackwell and S. B. Clendenning *et al. Chem. Mater.*, **2010**, *22*, 4854-4866.

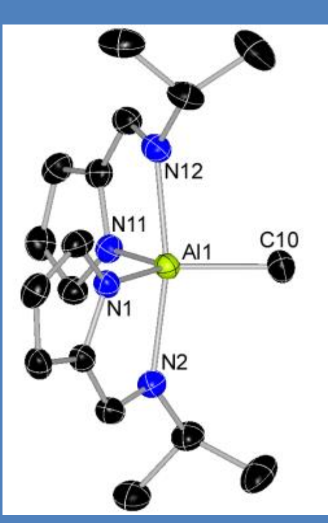
NMR Spectrum – CuL_2 + *x* $ZnEt_2$

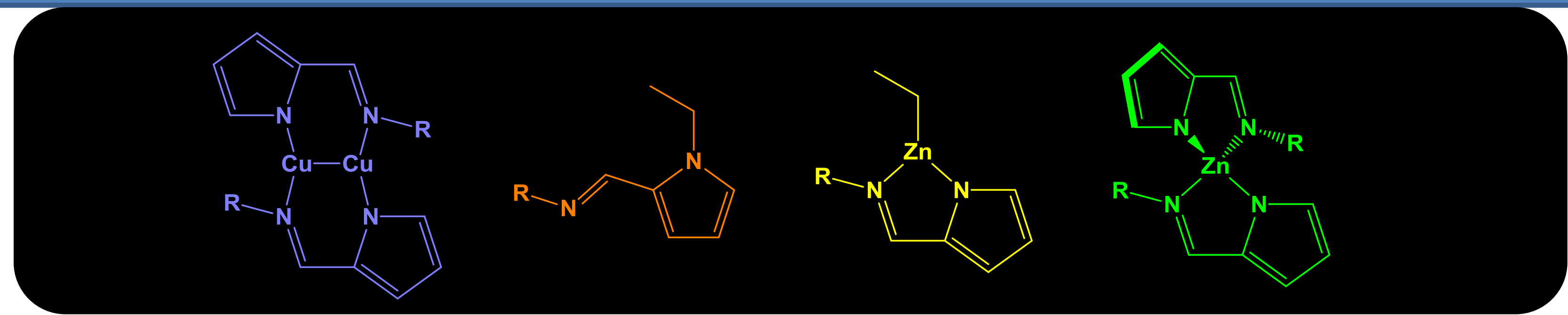
x = 0.3
20 °C, 15 min

All Stable Intermediates / Byproducts Independently Synthesized.
Selected X-ray Crystal Structures:









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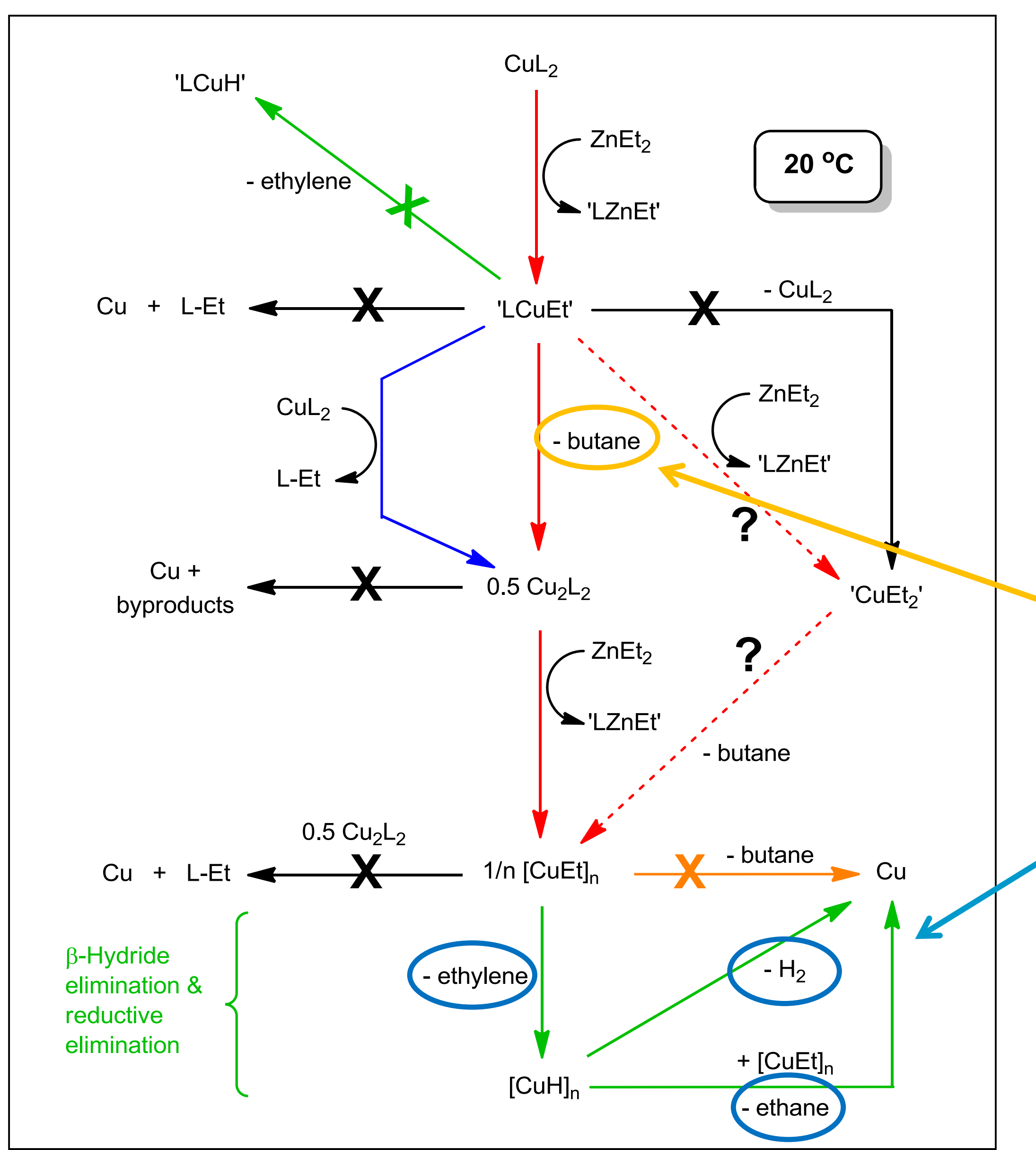
CuL_2 + *n* $ZnEt_2$ → Cu metal + byproducts



- Multi step mechanism with several different available pathways
- Reaction steps identified by observation and synthesis of intermediates and byproducts
- *n*-Butane is the only gas formed during reduction from Cu^{II} to Cu^{I}.
- Ethylene, ethane and hydrogen (not *n*-butane) are formed during reduction from Cu^{I} to Cu^{0} (copper metal).

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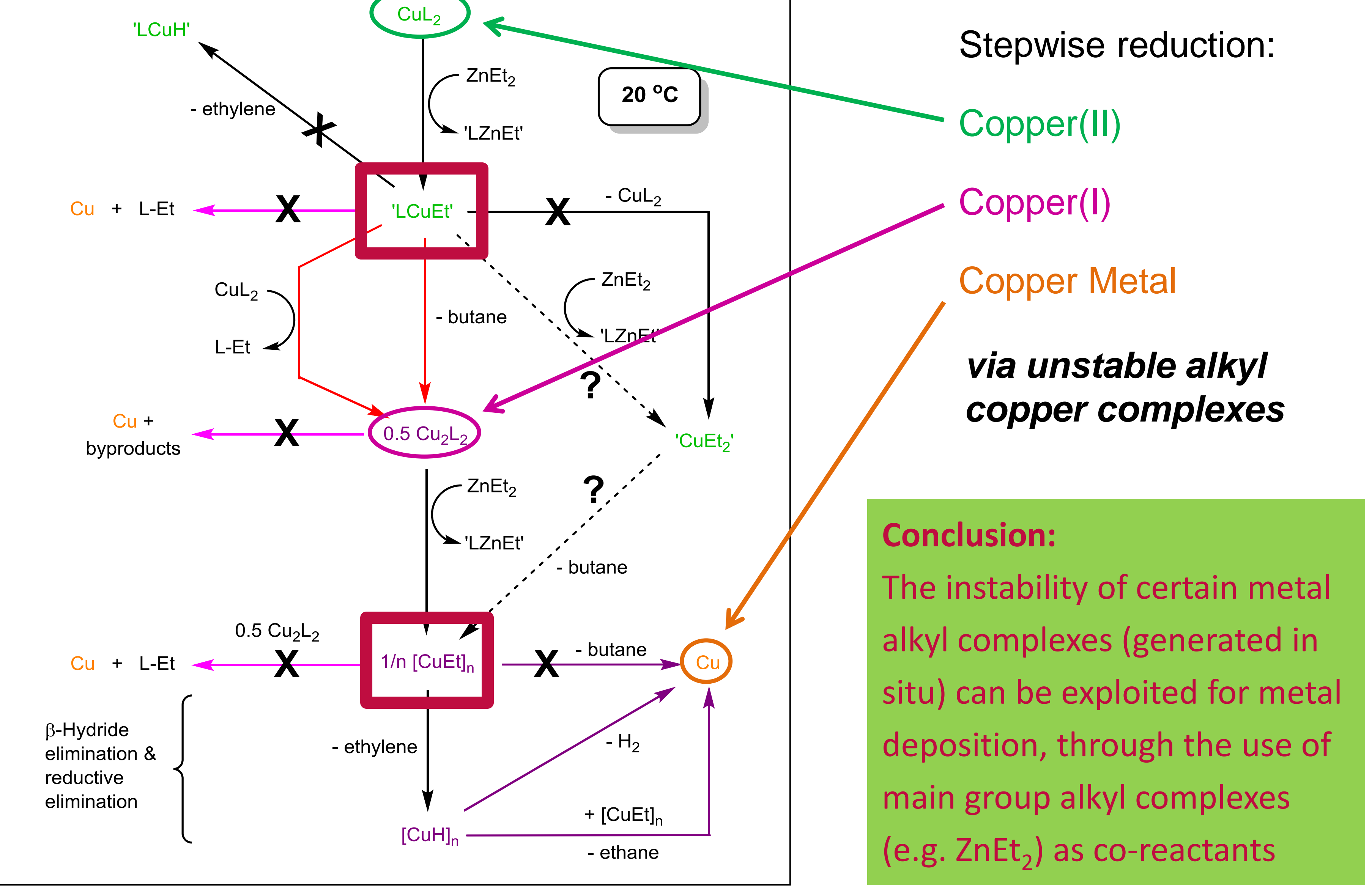
SOLUTION Reaction Pathway



Conclusion:
The instability of certain metal alkyl complexes (generated in situ) can be exploited for metal deposition, through the use of main group alkyl complexes (e.g. $ZnEt_2$) as co-reactants

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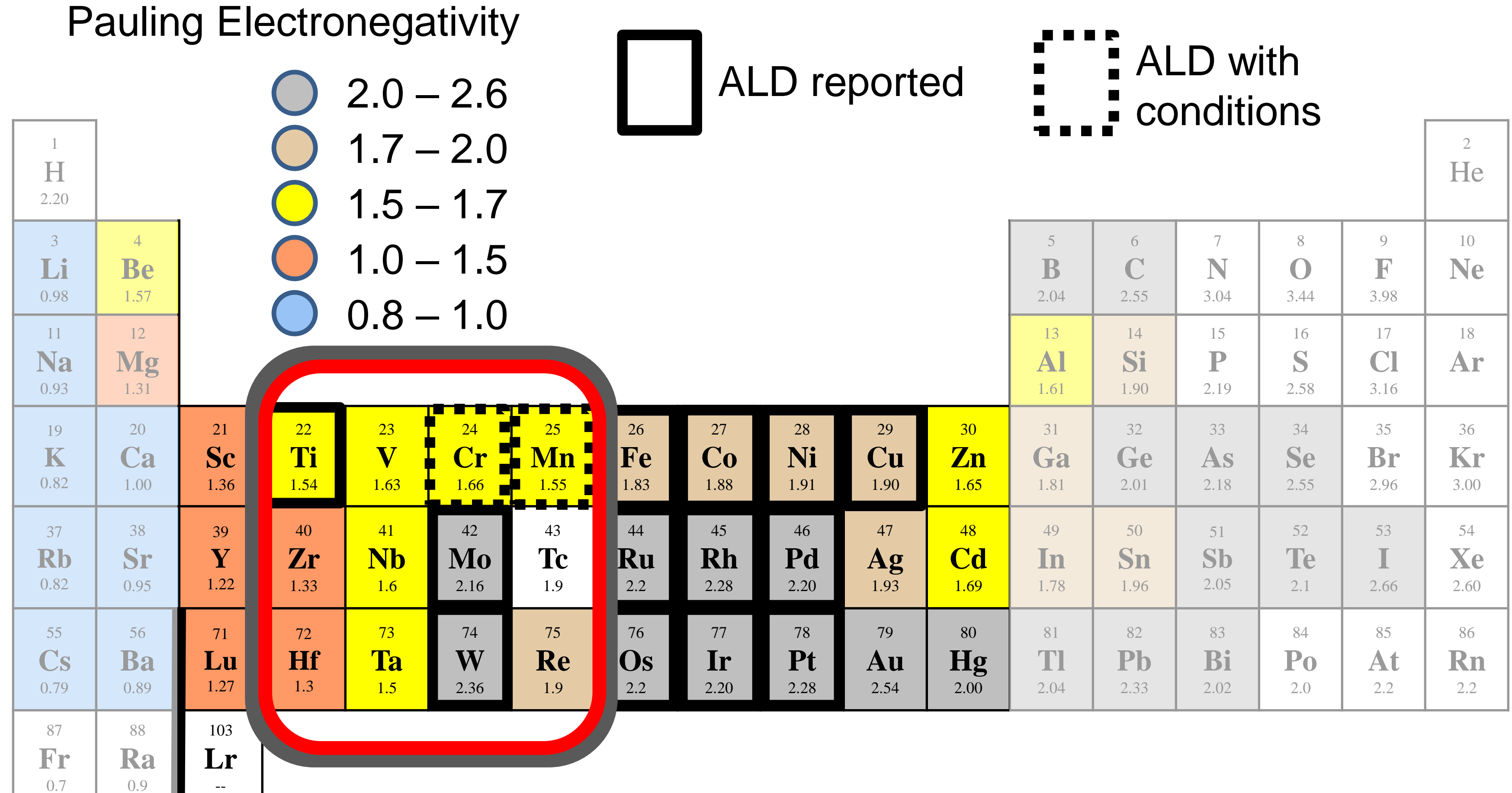
Thermal ALD of Transition Metals (or pulsed-CVD)



	57 La 1.10	58 Ce 1.12	59 Pr 1.13	60 Nd 1.14	61 Pm --	62 Sm 1.17	63 Eu --	64 Gd 1.20	65 Tb --	66 Dy 1.22	67 Ho 1.23	68 Er 1.24	69 Tm 1.25	70 Yb --
An	89 Ac 1.1	90 Th 1.3	91 Pa 1.5	92 U 1.38	93 Np 1.36	94 Pu 1.28	95 Am 1.3	96 Cm 1.3	97 Bk 1.3	98 Cf 1.3	99 Es 1.3	100 Fm 1.3	101 Md 1.3	102 No 1.3

THE CHALLENGE OF EARLY TRANSITION METAL ALD

$WF_6 + H_3Si\text{-}SiH_3 \longrightarrow W + H_{4-n}SiF_n$

J.W. Klaus, S.J. Ferro, S.M. George, Atomically controlled growth of tungsten and tungsten nitride using sequential surface reactions, *Appl. Surf. Sci.*, **2000**, *162–163* 479–491.

Analogous reaction with TaF_5 generated Ta silicide

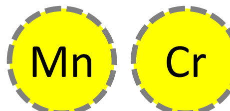
Lemonds, A.M.; White, J.M.; Ekerdt, J.G., Surface science investigations of atomic layer deposition half-reactions using TaF_5 and Si_2H_6, *Surf. Sci.*, **2003**, *538*, 191.

Ti

Klesko, J. P.; Thrush, C. M.; Winter, C. H., Thermal Atomic Layer Deposition of Titanium Films Using Titanium Tetrachloride and 2-Methyl-1,4-bis(trimethylsilyl)-2,5-cyclohexadiene or 1,4-Bis(trimethylsilyl)-1,4-dihydropyrazine, *Chem. Mater.* **2016**, *28*, 700.

0.5 $TiCl_4$ + [1,4-bis(trimethylsilyl)-1,4-dihydropyrazine] or [2-methyl-1,4-bis(trimethylsilyl)-2,5-cyclohexadiene] ⟶ 0.5 Ti + 2 Me_3SiCl + [pyrazine] or [toluene]

GPC 0.06 Å/cycle. Rapid oxidation to TiO_2 in air, but some Ti metal remains deeper in the film, according to XPS



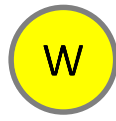
Kalutarage, L. C.; Martin, P. D.; Heeg, M. J.; Winter, C. H., Volatile and Thermally Stable Mid to Late Transition Metal Complexes Containing α-Imino Alkoxide Ligands, a New Strongly Reducing Coreagent, and Thermal Atomic Layer Deposition of Ni, Co, Fe, and Cr Metal Films, *J. Am. Chem. Soc.* **2013**, *135*, 12588.

[Mn dimer complex] or [M complex]

M = **Cr**, Co; R = ^tBu
M = Fe, Ni; R = ^iPr

$BH_3(NHMe_2)$ ⟶ **Metal**

- Ru substrate
- 180-225 °C
- GPC 0.07-0.10 Å/cycle



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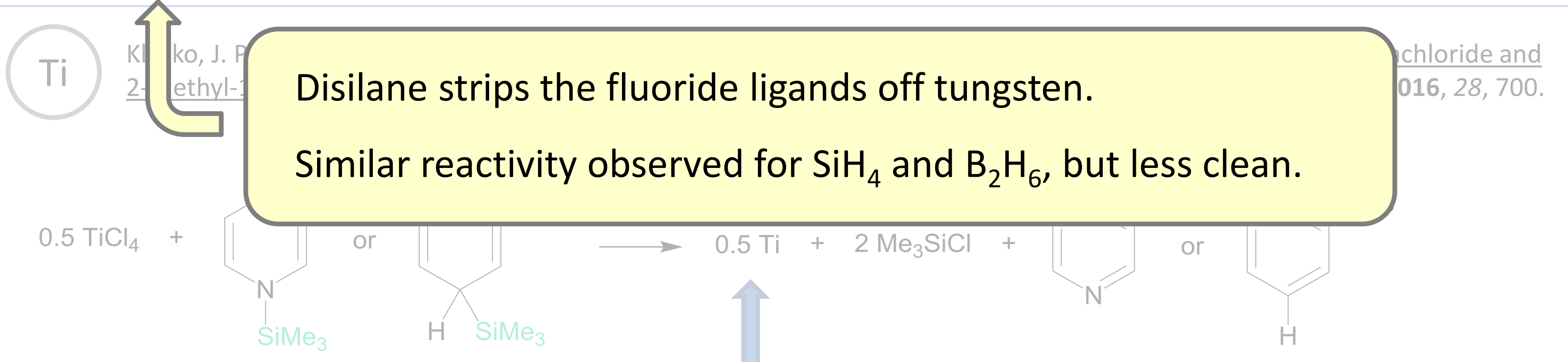

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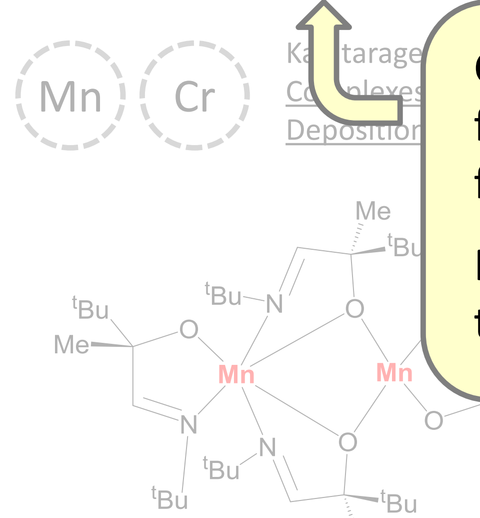
$0.5\ TiCl_4$ + 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (N-$SiMe_3$) or 2-methyl-1,4-bis(trimethylsilyl)-2,5-cyclohexadiene (H, $SiMe_3$, Me) → 0.5 Ti + $2\ Me_3SiCl$ + pyrazine or toluene

GPC 0.06 A/cycle. Rapid oxidation to TiO_2 in air, but some Ti metal remains deeper in the film, according to XPS

Mn Cr

Conceptually, the two precursors serve as a more reactive form of a disilane ($Me_3Si\text{-}SiMe_3$), which strips chloride ligands from titanium.

Requires a volatile metal chloride, which is likely to limit translation of methodology to most other early transition metals.



Me O M N O Me R tBu

- GPC 0.07-0.10 Å/cycle

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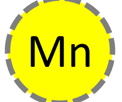
$0.5\ TiCl_4$ +

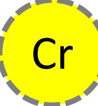
GPC 0.06 Å

Deposition only observed on a ruthenium substrate after a lengthy surface pre-treatment with $BH_3(NHMe_2)$.

Deposition ceased at a film thickness of ~ 10 nm.

For Mn, immediate oxidation of the film upon removal from reactor prevented determination of whether Mn metal or MnO had been deposited.





Kalutarage, L. C.; Martin, P. D.; Heeg, M. J.; Winter, C. H., Volatile and Thermally Stable Mid to Late Transition Metal Complexes Containing α-Imino Alkoxide Ligands, a New Strongly Reducing Coreagent, and Thermal Atomic Layer Deposition of Ni, Co, Fe, and Cr Metal Films, *J. Am. Chem. Soc.* **2013**, *135*, 12588.

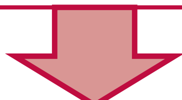
M = **Cr**, Co; R = ^{t}Bu
M = Fe, Ni; R = ^{i}Pr

[Mn dimer complex] or [M complex] $\xrightarrow{BH_3(NHMe_2)}$ **Metal**

- Ru substrate
- 180-225 °C
- GPC 0.07-0.10 Å/cycle

An Alternative Approach: Organometallic Precursors for Electropositive Metal ALD ?

- **Reduction** to elemental metal becomes increasingly challenging for more electropositive metals
- Electropositive metals have a high tendency to form **oxides, nitrides and halides**, making many coordination complexes poorly suited for electropositive metal ALD



Can highly reactive ***organometallic* precursors** (acyclic hydrocarbyl complexes, rather than cyclopentadienyl complexes) be used for electropositive metal ALD?

Organometallic Complexes	***Metal-organic Complexes***
Contain direct M-C (or M-Si, or M-H) bonds	*Contain a metal and organic ligands*
More Reactive	***Less Reactive***

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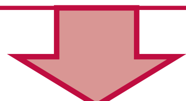

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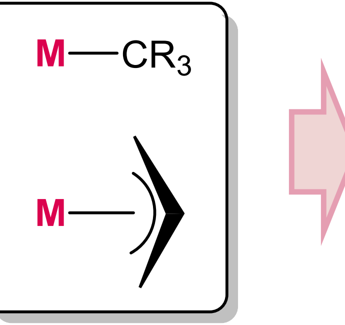
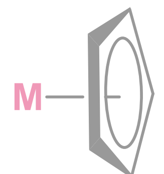
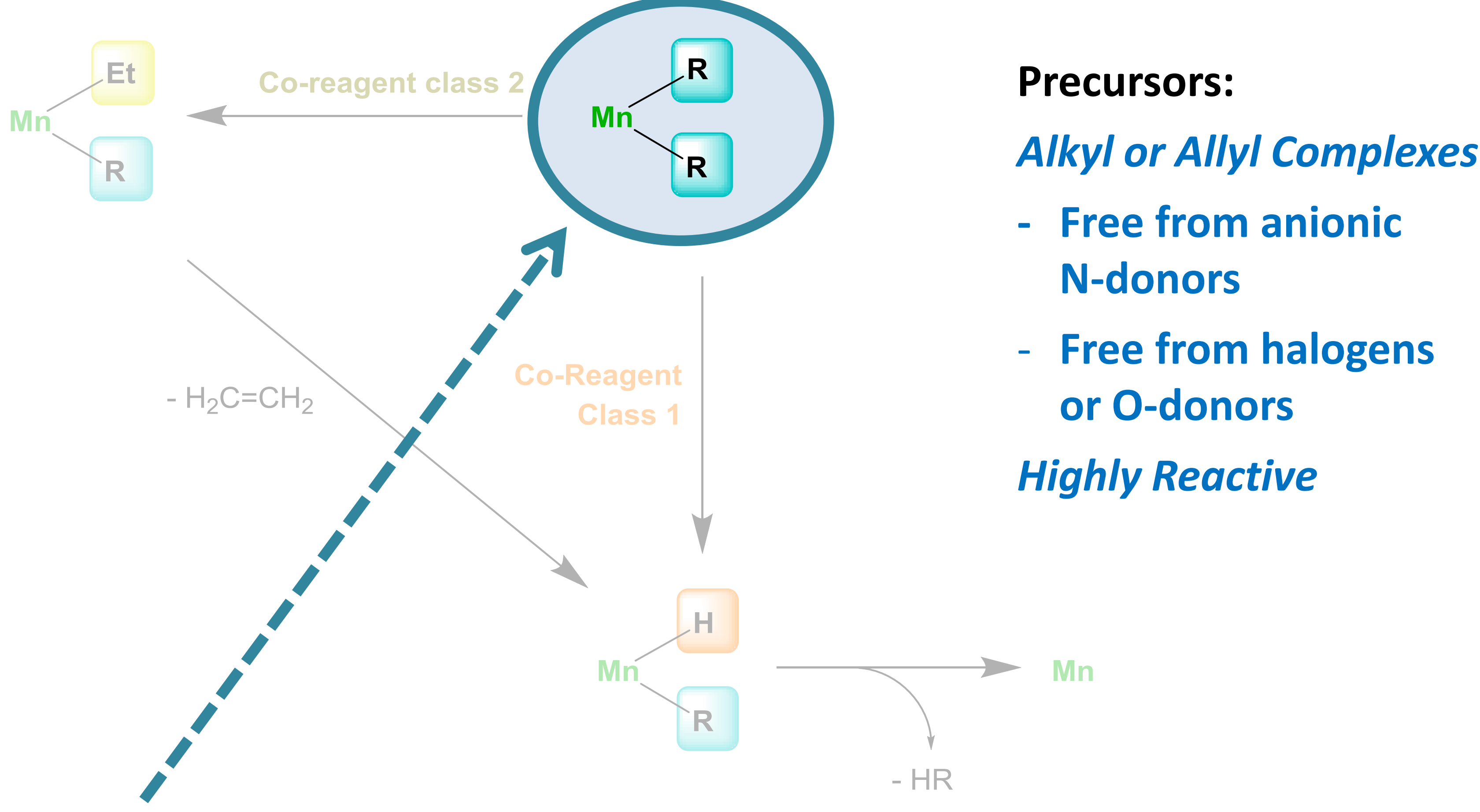




How will the necessary ***thermal stability*** be achieved without compromising:
(a) ***volatility*** and
(b) ***reactivity***?

OVERALL STRATEGY FOR MANGANESE DEPOSITION



Precursors:

Alkyl or Allyl Complexes

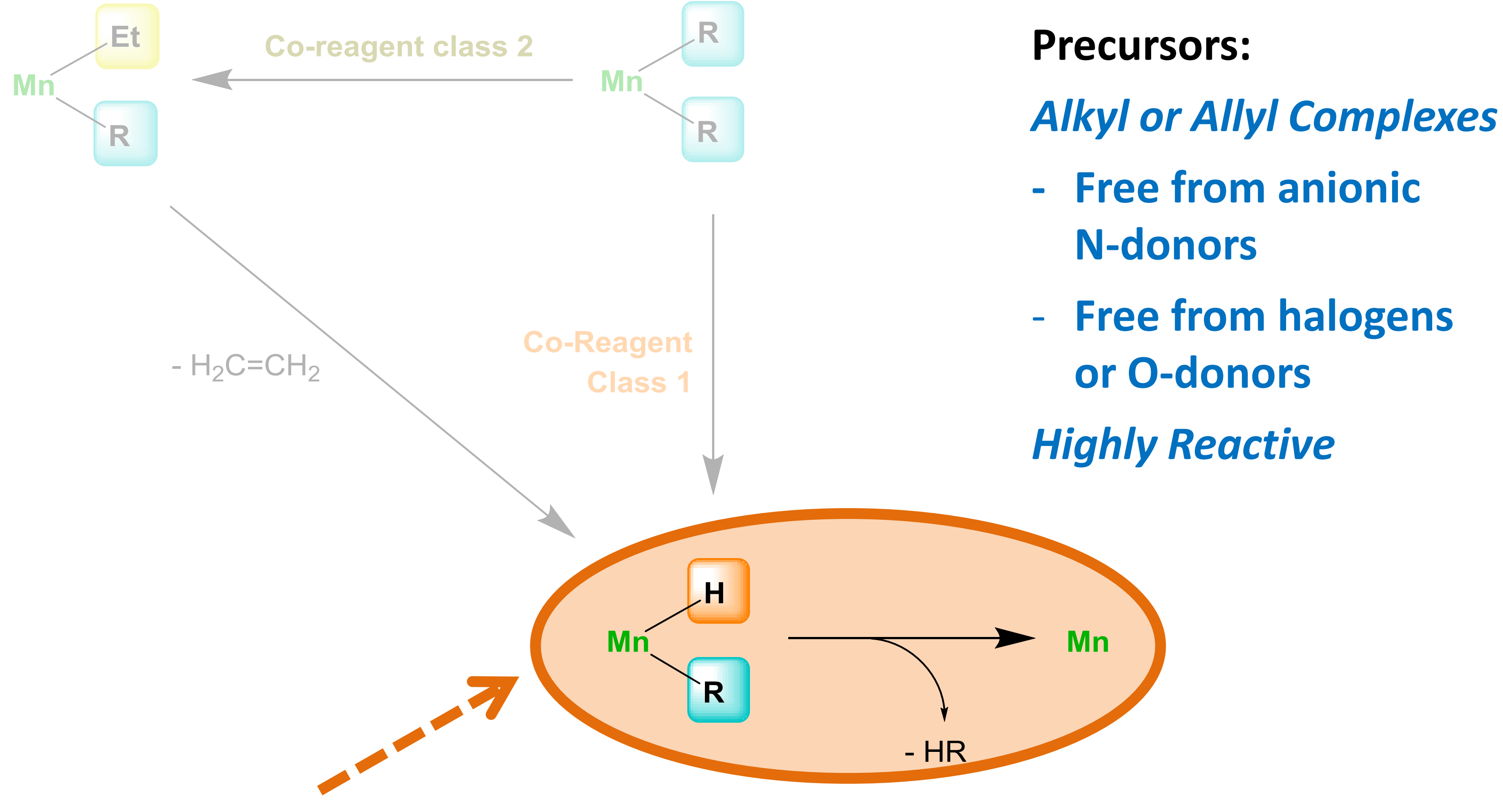
- **Free from anionic N-donors**
- **Free from halogens or O-donors**

Highly Reactive

The metal precursor must be:

- Thermally robust & volatile
- Reactive towards the desired co-reactant --- for this reason, ***highly reactive metal alkyl and allyl complexes*** are the focus of this work

OVERALL STRATEGY FOR MANGANESE DEPOSITION



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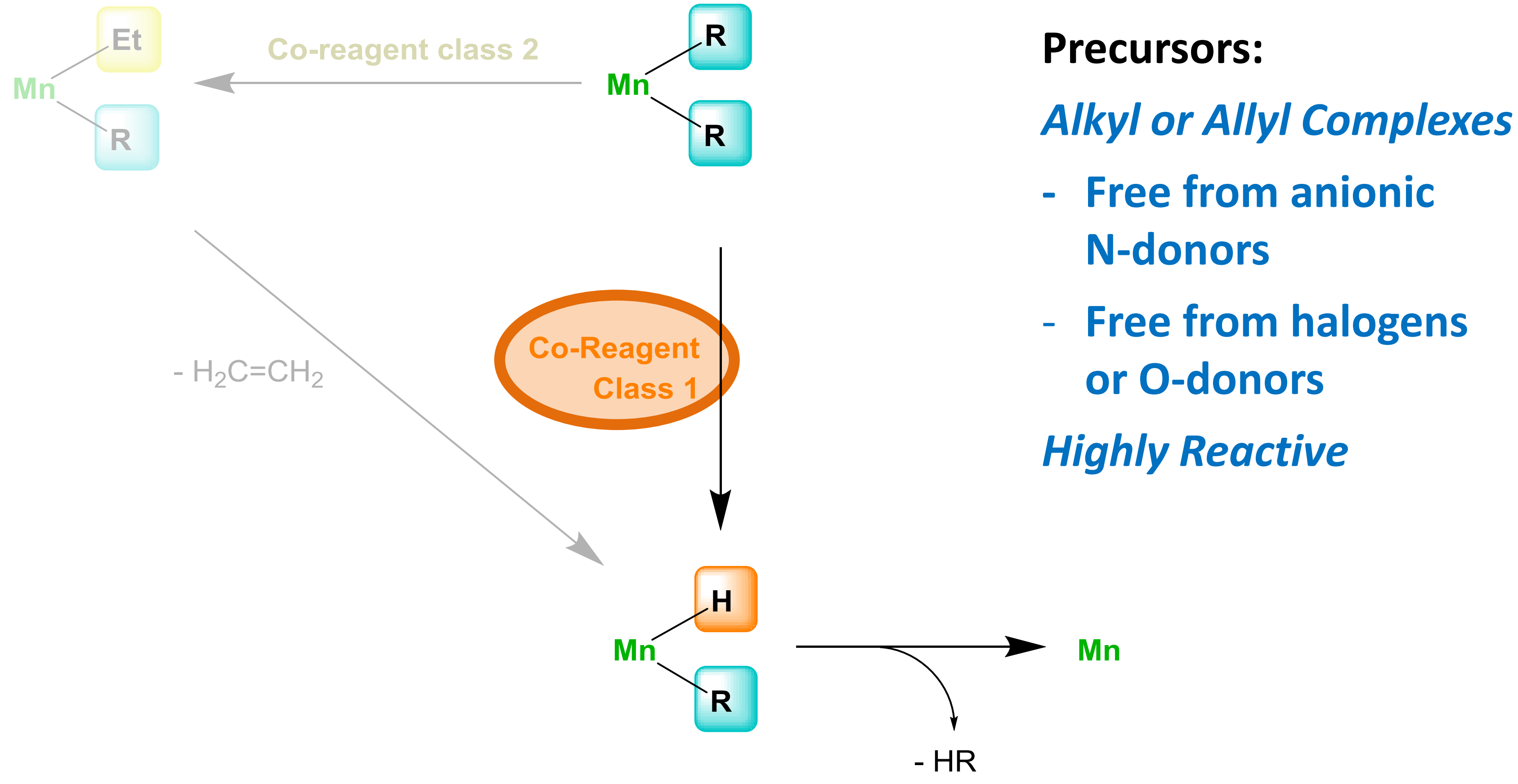
Highly Reactive

Co-Reactants Selected to form Alkyl / Hydride Intermediate which should be particularly prone to reductive elimination

OVERALL STRATEGY FOR MANGANESE DEPOSITION



Co-reactants:

- **Class 1** co-reactants (H_2, $PhSiH_3$, R'_2BH) form the alkyl / hydride complex directly
- **Class 2** co-reactants (BEt_3, $AlEt_3$, $ZnEt_2$) initially form an unstable ethyl complex

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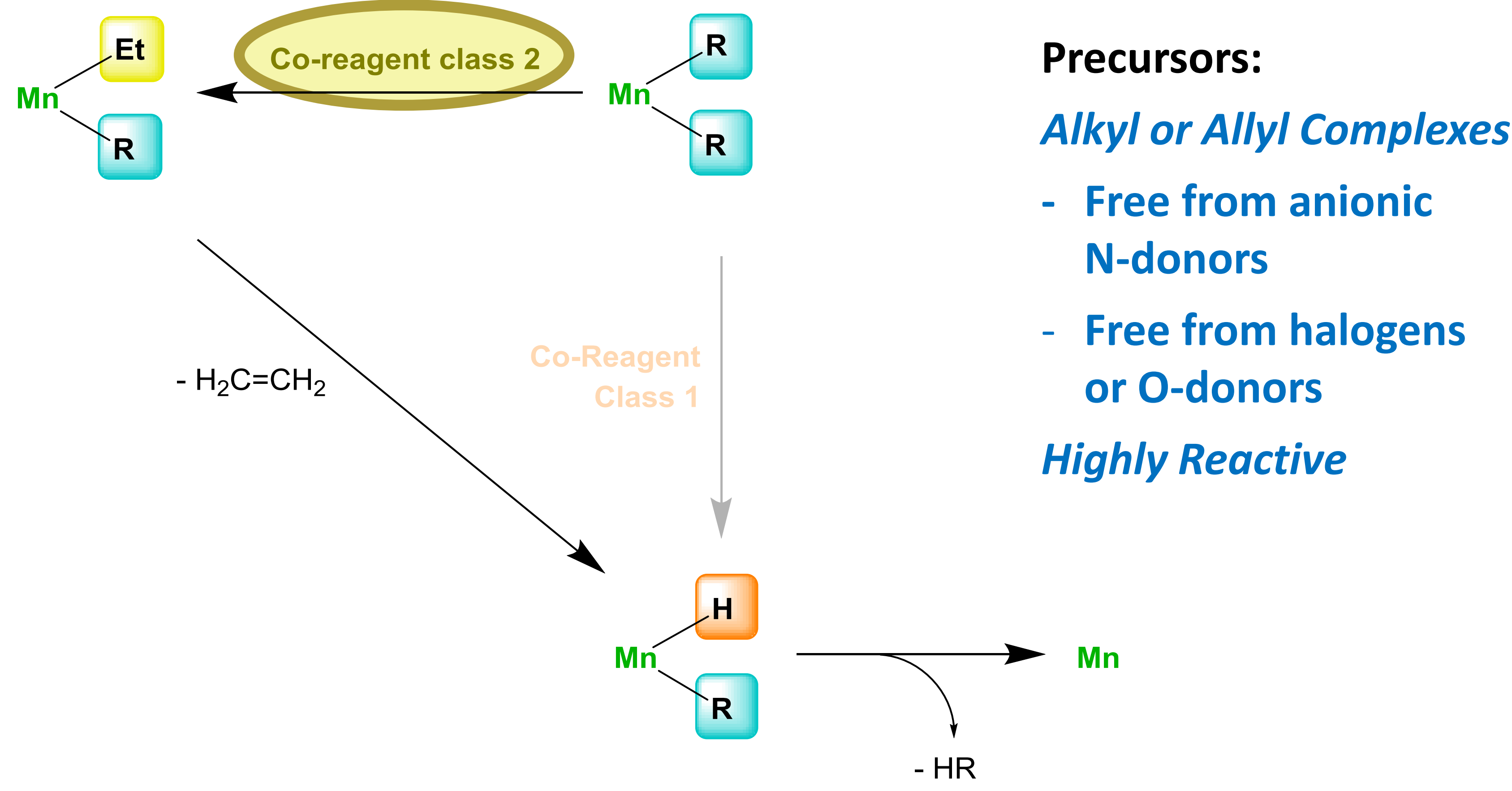

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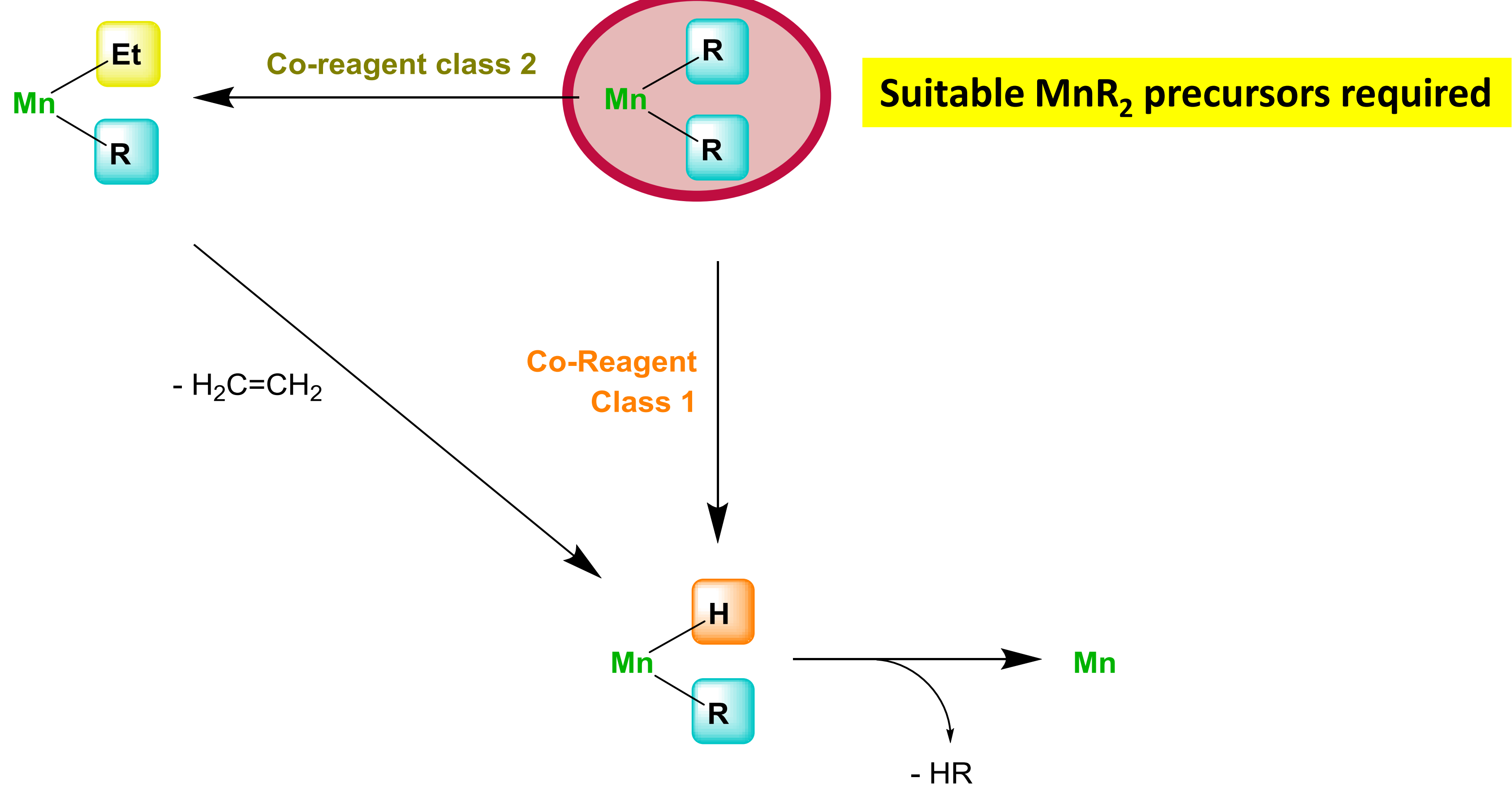

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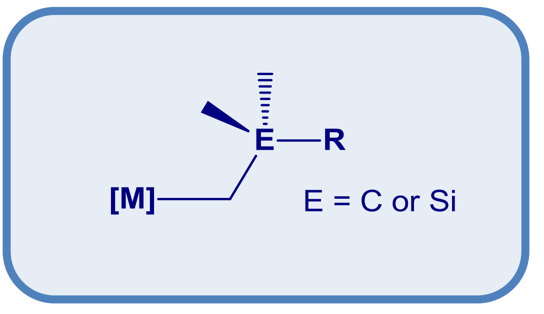
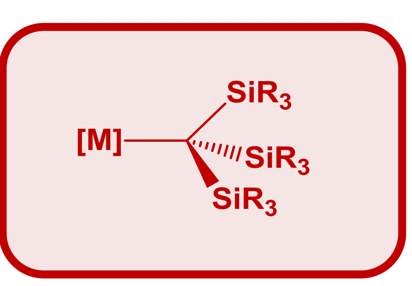
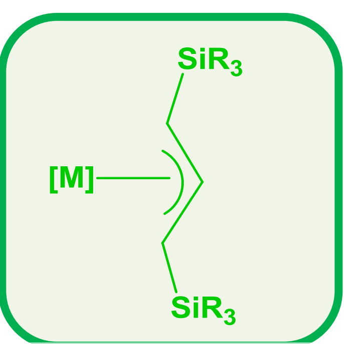
Precursor Design

- *Oxygen-free alkyl and allyl complexes*
- **All complexes will be *highly reactive* due to the presence of metal-carbon bonds**







(1) Primary alkyl complexes

- **fairly straightforward to prepare**
- presence of α-hydrogen atoms may render complexes **less thermally stable**

(2) Tertiary alkyl complexes [$C(SiR_3)_3$ complexes]

- **α-hydrogen free**, and **β-hydrogen free**
- Complexes expected to exhibit **high thermal stability** (resistance to carbide formation)

(3) Bulky allyl complexes

- resistant to common decomposition pathways
- allyl complexes often have **higher thermal stability than alkyl complexes**
- allyl complexes are **much more reactive than cyclopentadienyl complexes**

Tertiary ALKYL and ALLYL Complexes

High thermal stability due to steric bulk and absence of α-hydrogens

1

Me_3Si, Me_3Si, Me_3Si – Mn – $SiMe_3$, $SiMe_3$, $SiMe_3$

J. Chem. Soc. Chem. Commun. **1985**, 1380-1381.

Synthetically inaccessible in gram quantities due to extreme steric bulk

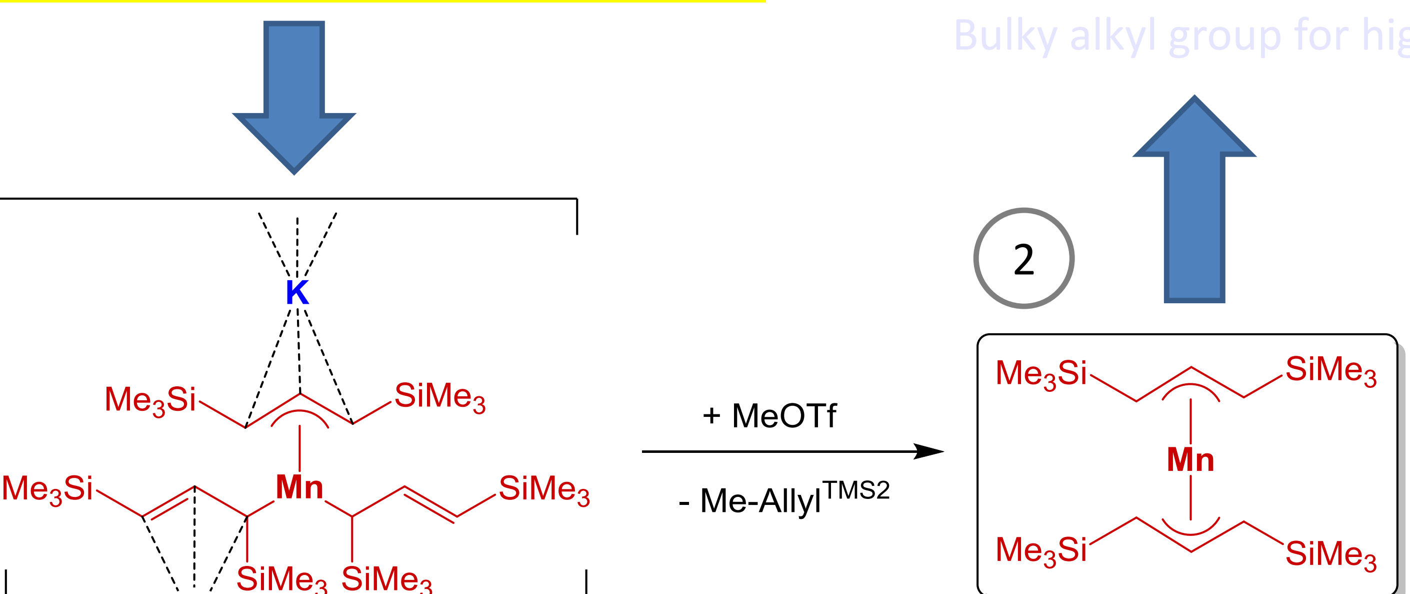
3

Me_3Si / $SiMe_3$ allyl – $Mn(L)_x$ – $C(SiMe_3)_3$

Allyl group for increased **reactivity** and improved **synthetic accessibility**

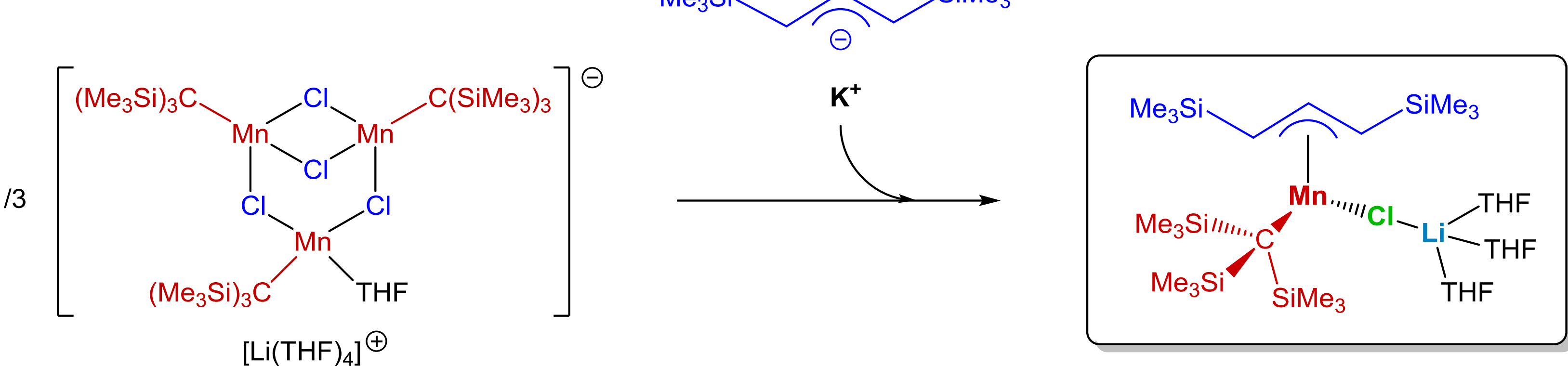
Lower symmetry for increased **volatility** ?

Bulky alkyl group for high **thermal stability**



Insufficient thermal stability for use as an ALD precursor

MIXED ALKYL (TSI) / ALLYL (allyl^{TMS2}) MANGANESE(II) COMPLEXES



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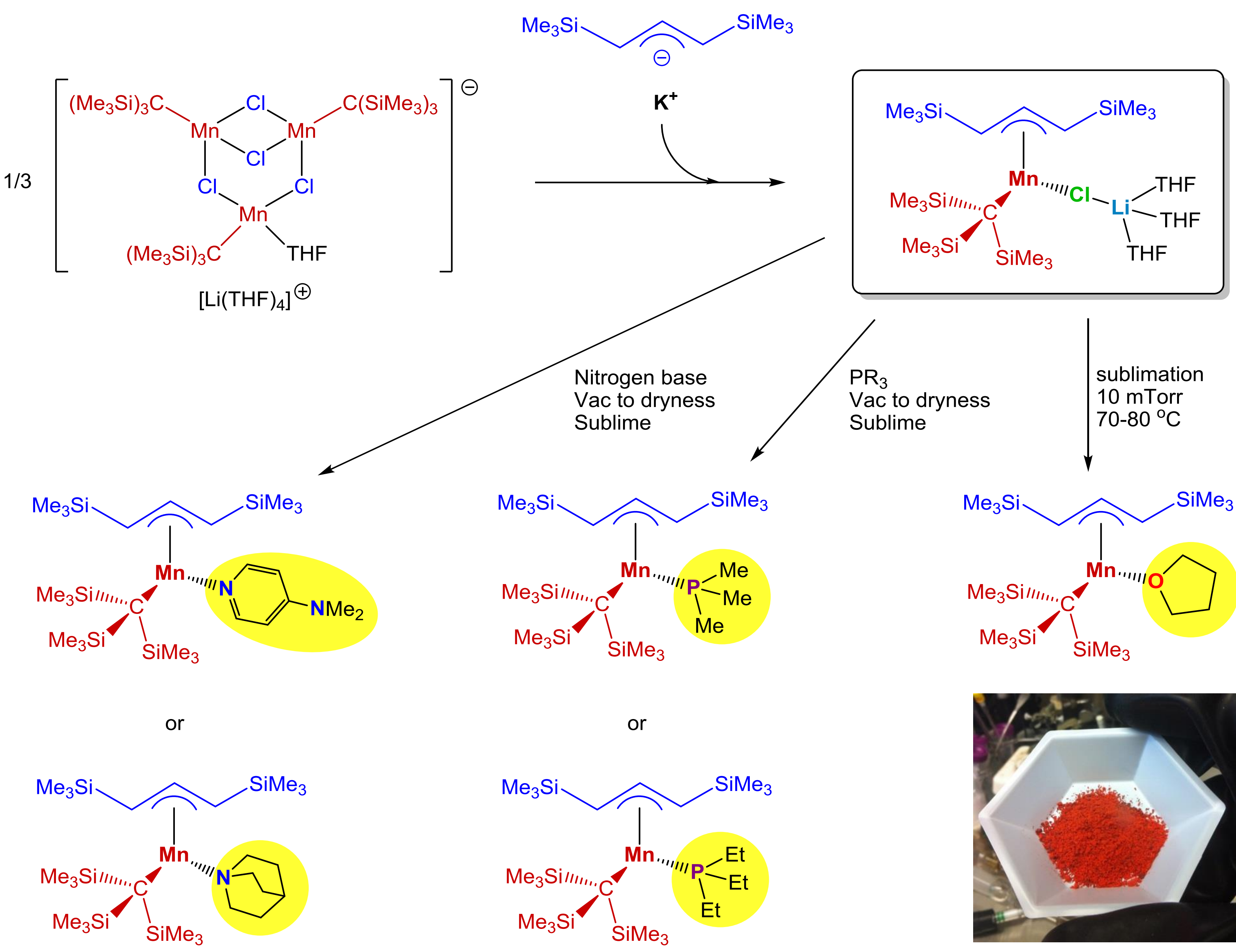
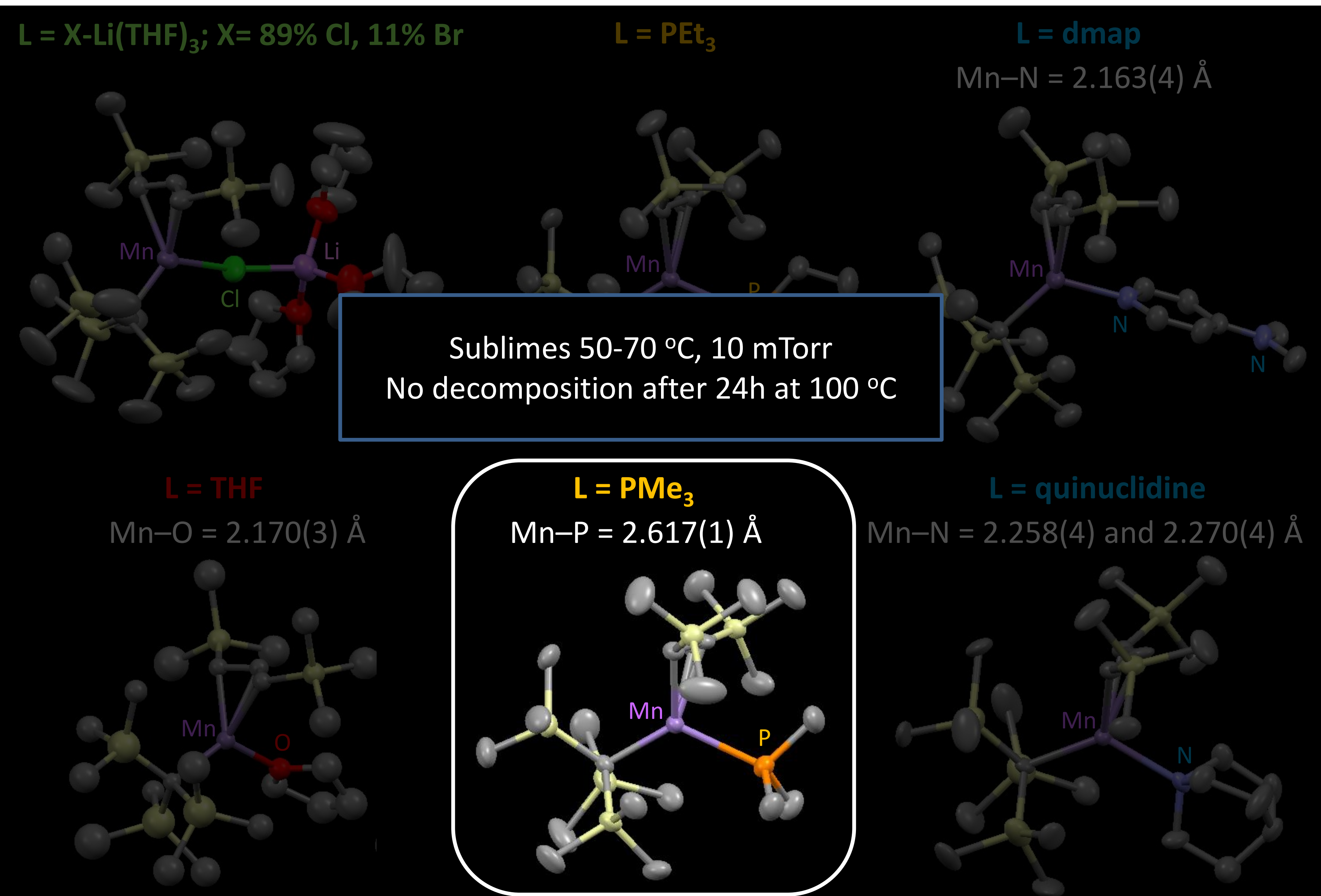
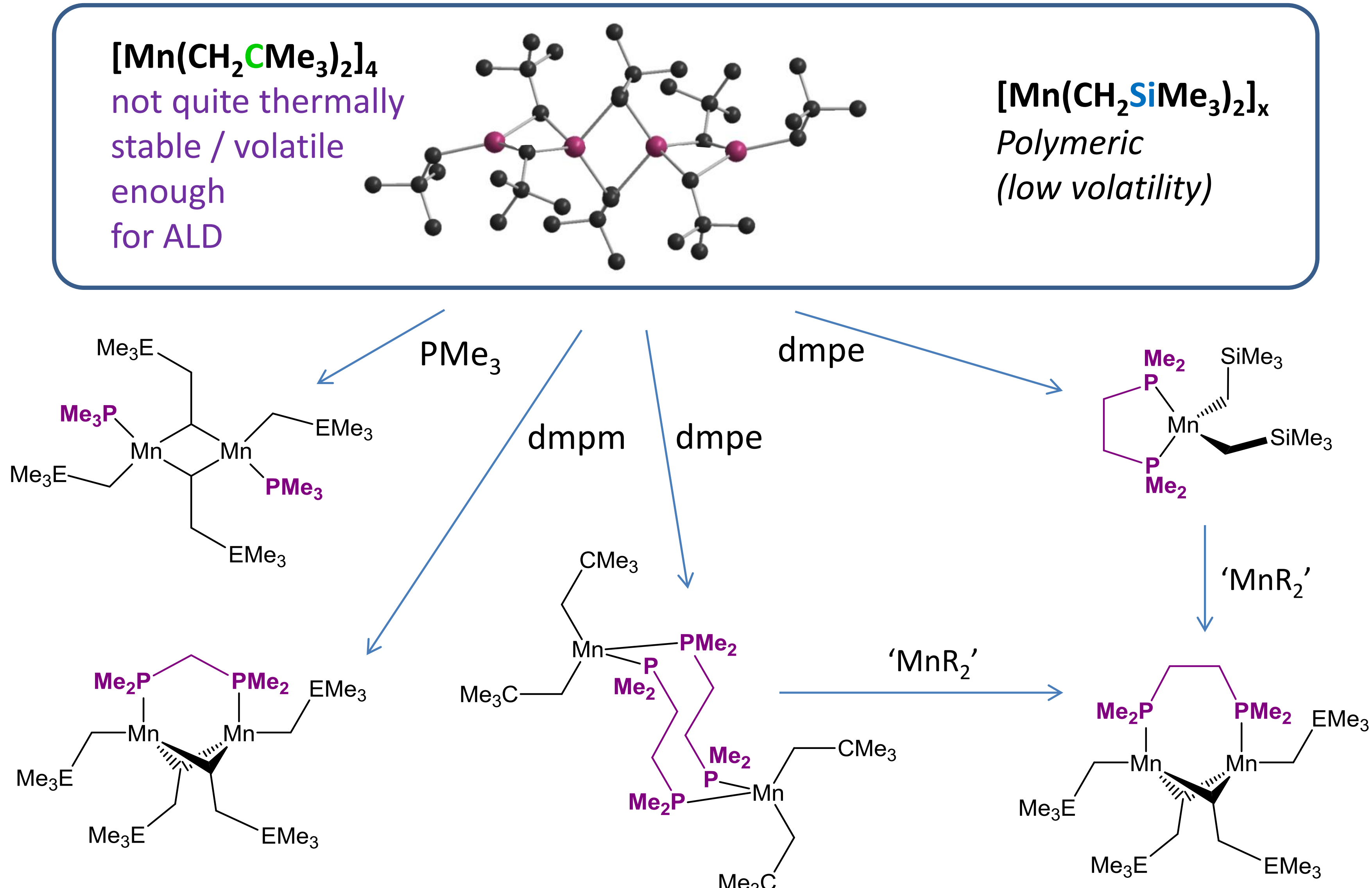


X-Ray Crystal Structures of [(allyl^{TMS2})Mn(TSI)L] Complexes



PRIMARY ALKYL MANGANESE(II) COMPLEXES: R = CH_2CMe_3



J. S. Price, P. Chadha, D. J. H. Emslie, *Organometallics*, **2016**, *35*, 168-180.

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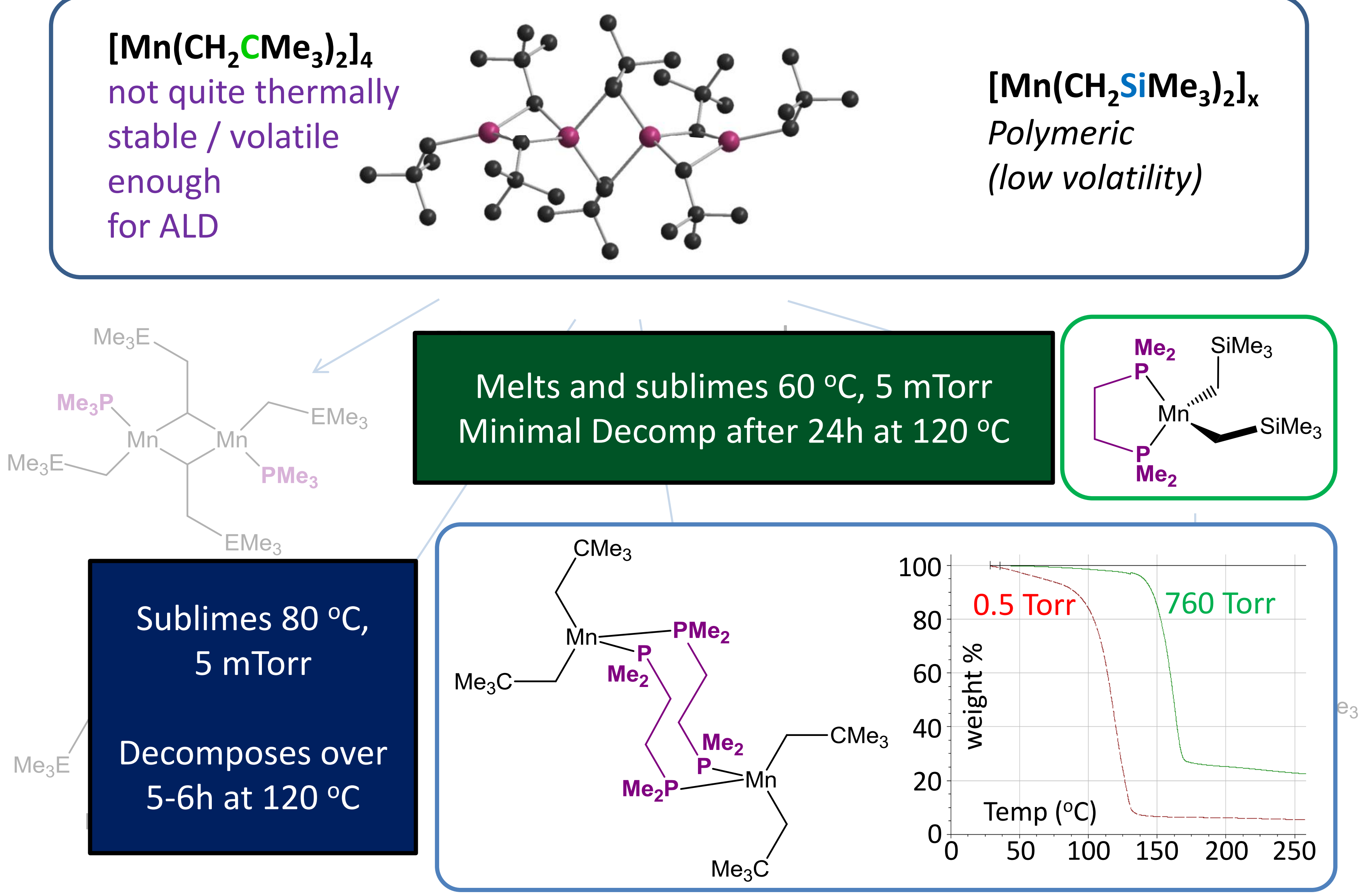

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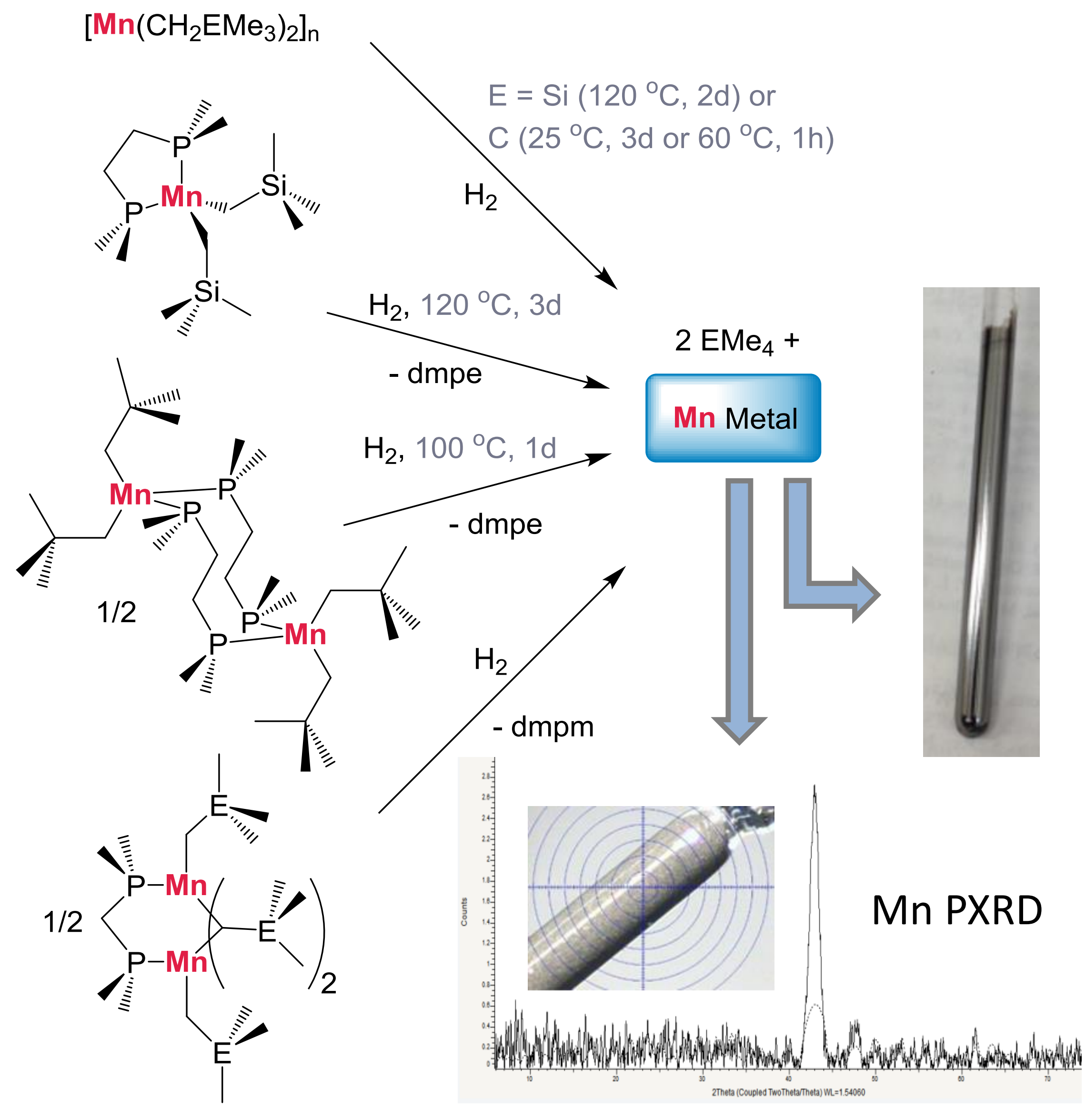
Solution Reactivity of Primary Alkyl Manganese(II) Complexes with H_2



ALD using forming gas (5% H_2 in N_2)

- With substrate = 125 °C, a GPC of 0.2 Å / cycle was observed on Ru seed.
- The film was non-conductive after air-exposure, likely due to complete oxidation…

Ru seed
Thickness ~ 80 Å (ellipsom),
GPC ~ 0.2 Å/cycle

400 x [3s Mn / 5s purge / 2s FG / 15 s purge]

196-2_SH 5.0kV 4.7mm x180k SE(U) 6/17/2014 300nm

J. S. Price, P. Chadha, D. J. H. Emslie, *Organometallics*, **2016**, *35*, 168-180.

Solution Reactivity of Primary Alkyl Manganese(II) Complexes with H_2

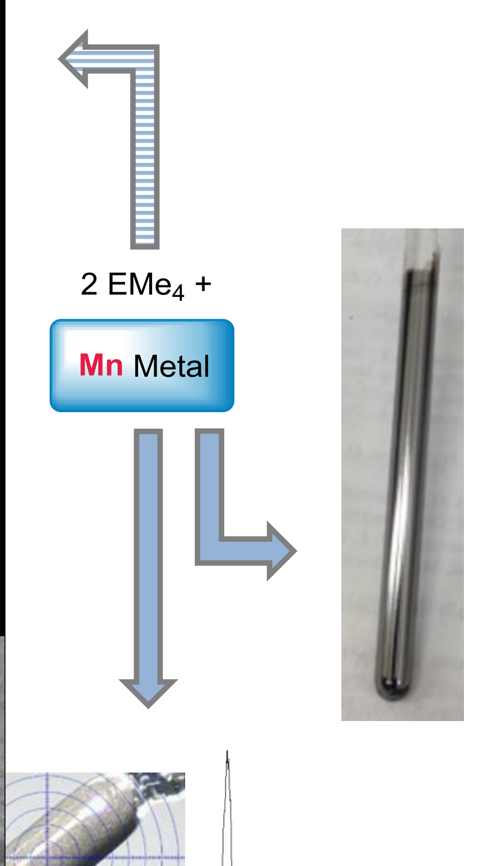
MnS ALD using H_2S (one precursor for multiple materials)

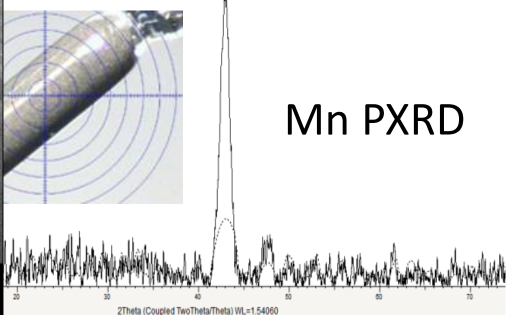
- With substrate = 110 °C, a GPC of 0.3 Å / cycle was observed on Ru seed.
- XPS: ~ 1:1 ratio of Mn:S with no P and low C. 5-10% O, presumably due to air exposure…

Ru seed
Thk ~ 390 Å (XSEM)
GPC ~ 0.33 Å/cycle

1200x [3s Mn / 8s purge / 3s Mn / 4s purge / 0.4s H_2S / 8s purge]

196-3B_SH 5.0kV 4.8mm x180k SE(U) 6/26/2014 300nm





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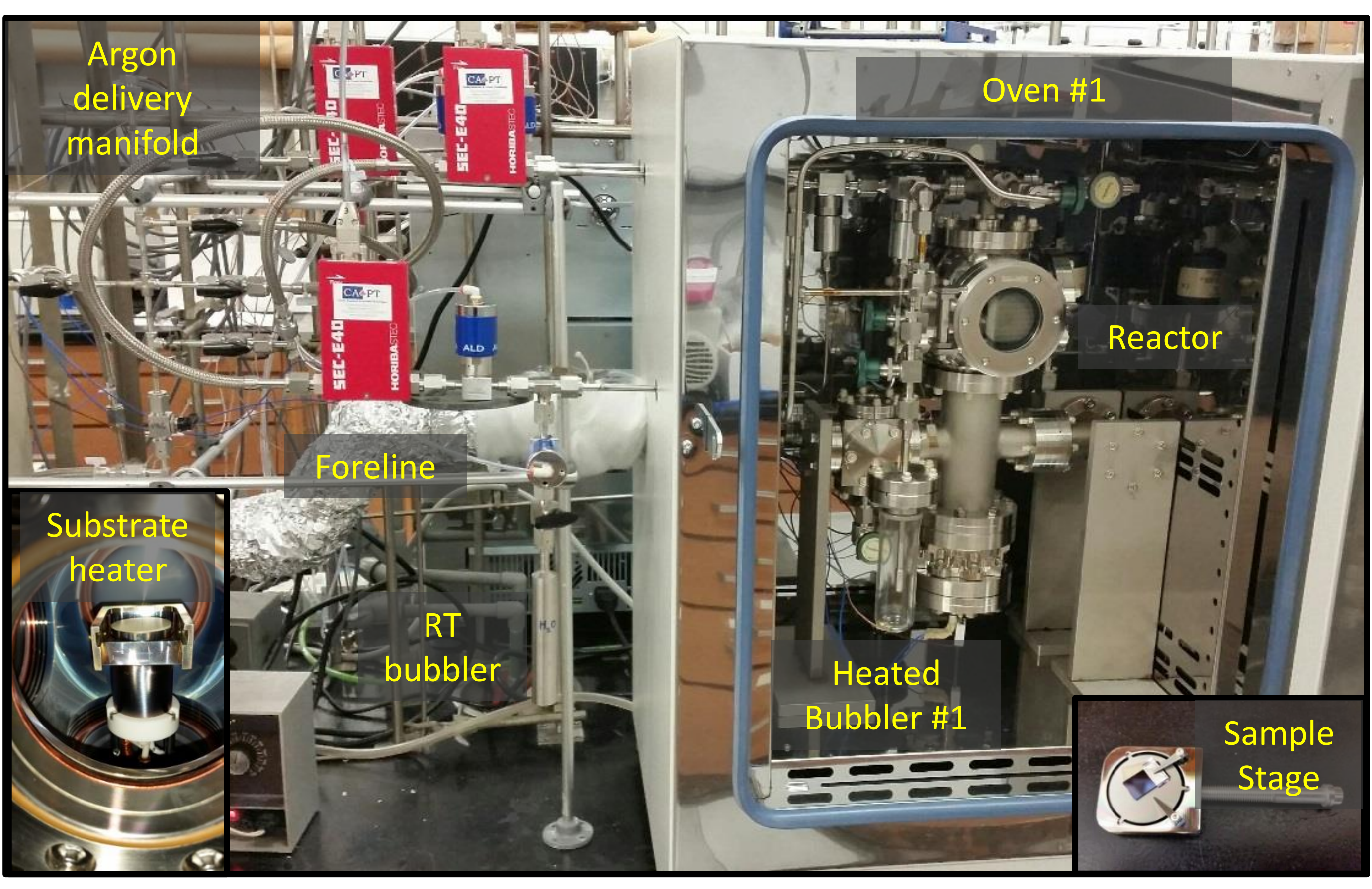
ALD Reactor Studies

- Until recently, all ALD studies on our compounds were conducted by collaborators.
- We now have a home-built ALD reactor, so further studies on our Mn cpds are on the schedule for this summer...



Summary / Conclusions

- **Many reported ALD processes are far from ideal:**

- Also, many materials (especially pure elements) simply cannot yet be deposited by thermal ALD.

- High deposition temperature (leading to agglomeration, low film purity, incompatibility with certain substrates, limited selection of precursors with appropriate thermal stability)
- Limited ALD temperature window
- Very low GPC
- Low film purity
- Undesirable film morphology
- Undesirable substrate selectivity (e.g. no deposition on H-terminated Si)
- Undesirable reactivity between the co-reactant and the underlying substrate.

below 100 ^{o}C. --- Solution reactivity studies can provide mechanistic insight.

- **The Mn chemistry** highlights a new approach for electropositive metal ALD: harnessing the high reactivity of manganese alkyl and allyl complexes for Mn metal deposition.

- Highly reactive organometallic precursors have the disadvantage of high air-sensitivity. However, they may allow deposition of multiple materials from a single precursor.

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- **ALD at lower temperature (may require more reactive precursor/co-reactant combinations and/or more volatile precursors and co-reactants) offers various advantages:**
- For metal ALD, most new ALD methods leading to ALD of previously inaccessible materials rely upon new co-reactants rather than new metal precursors.

- Avoids agglomeration of thin metal films.
- Compatible with a broader range of substrates, perhaps including those with polymer patterning.
- Leads to more predictable chemistry, potentially generating higher purity films.
- Can allow use of less-thermally robust but higher-volatility (and perhaps higher reactivity) precursors and co-reactants.

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  --- The initial focus was not on Cu precursor design. However, limitations in $ZnEt_2$ thermal stability brought the work full circle, where precursor volatility now appears to be the limitation in terms of accessing Cu deposition significantly below 100 ^{o}C. --- Solution reactivity studies can provide mechanistic insight.
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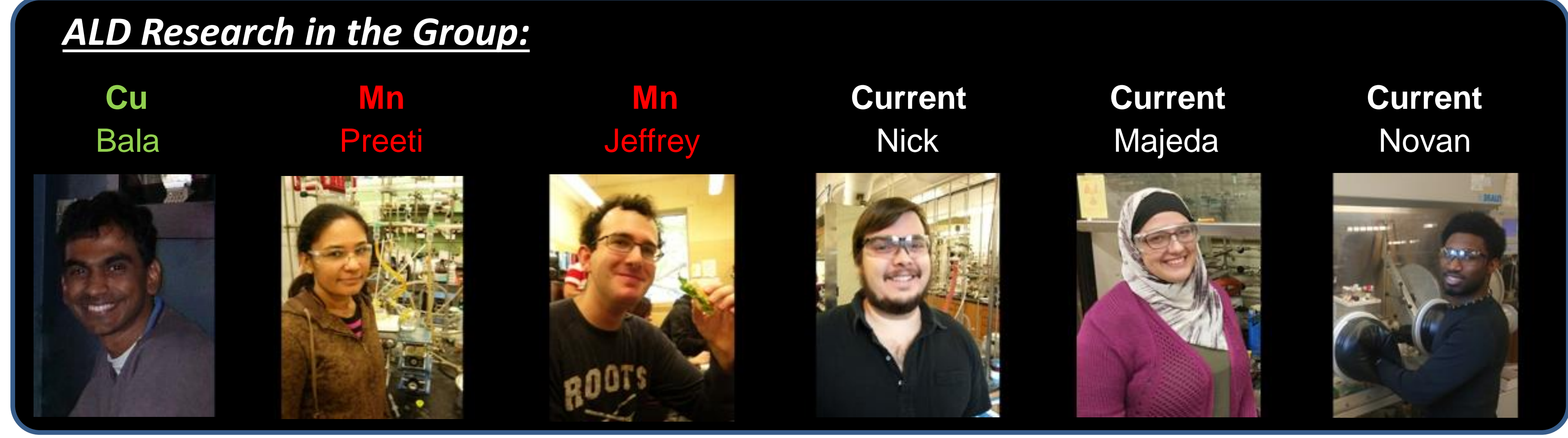
ACKNOWLEDGEMENTS



Funding for the Cu and Mn work:

through:

Questions ?