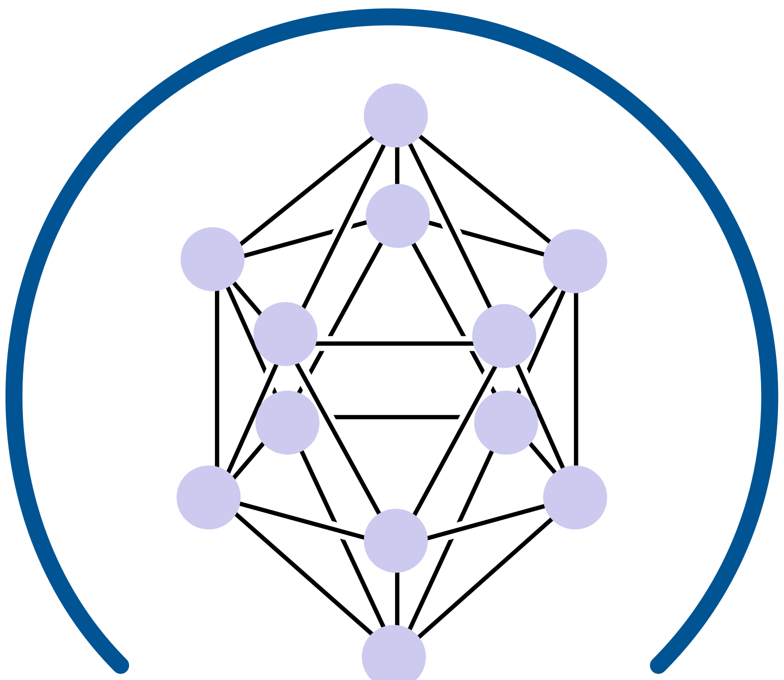
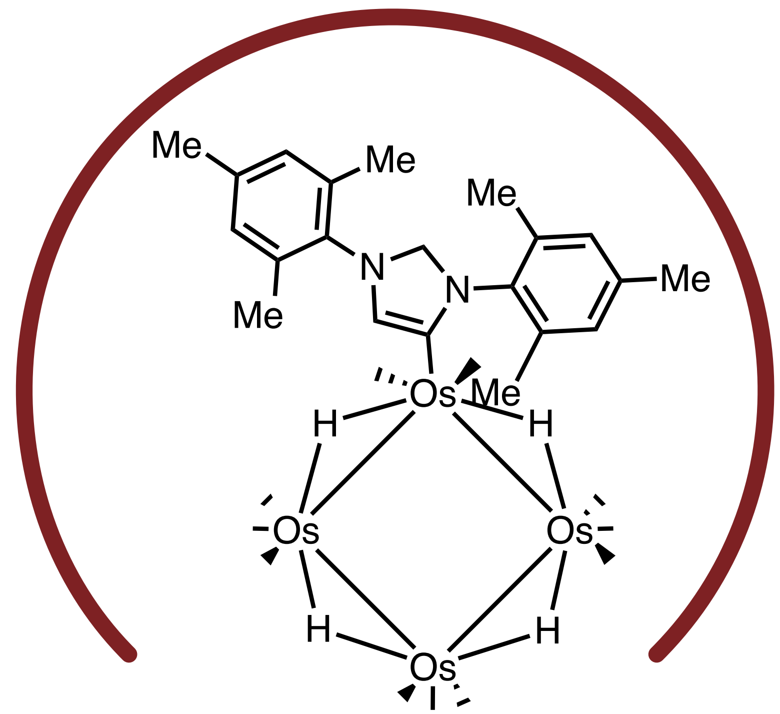
Clusters

An indroduction through case studies





Jerry Ruizhe Chen

MacMillan Group

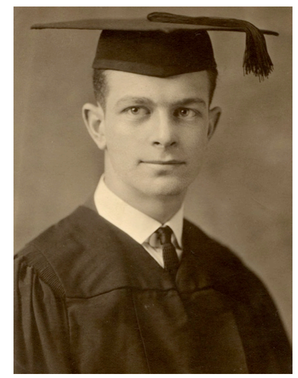
Literature Presentation

Dec 5th, 2023

It's not a long story

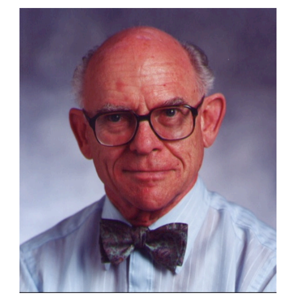
History

"Calomel" has been known in India for hundreds of years. Hg_2Cl_2 was later proven to have a Hg-Hg bond.



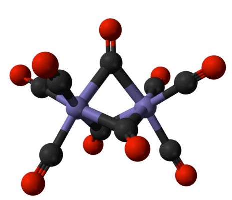
Young Linus Pauling found Mo_6 Octahedral in $MoCl_2$

Mainstream attention



F.A Cotton discovered $ReCl_3$ as Re_3Cl_9, followed by M-M multi bond

1300s — **1907** — **1928** — **1937** — **1960s** — **2023**



$Fe_2(CO)_9$ followed by a series of Fe, Mn clusters were discovered

Metal Carbonyl complexes

Alfred Stock: "Those are boranes in analogy to the alkanes."

Boron clusters

?

https://www.pharmaceutical-technology.com/features/history-of-als

It's not a long story

History

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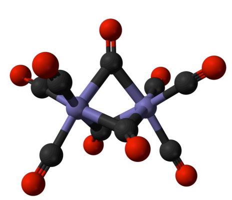
1300s



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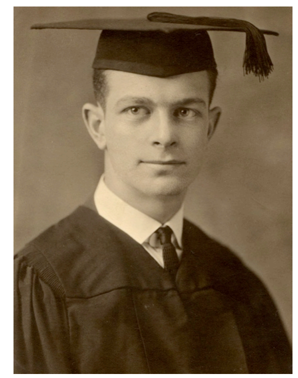
Metal Carbonyl complexes

1907



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1937

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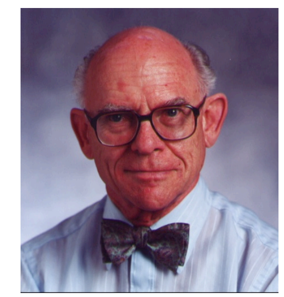


F.A Cotton discovered $ReCl_3$ as Re_3Cl_9, followed by M-M multi bond

1960s

2023

?

https://www.pharmaceutical-technology.com/features/history-of-als

Chemists have been discovering Clusters
But…
Much like we don't get all natural products from animals
Can we make them?

The synthesis of clusters

General procedures

Metal salts

Steel pressure vessel

Autoclave (100-150°C)

Days

Cluster crystal

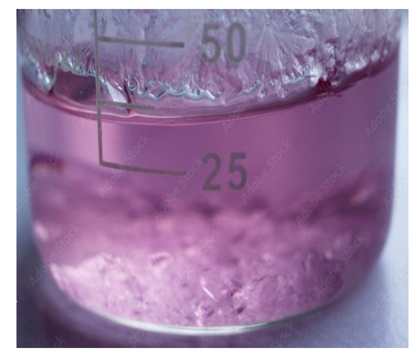
Frémont, P. d.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

The synthesis of clusters

General procedures

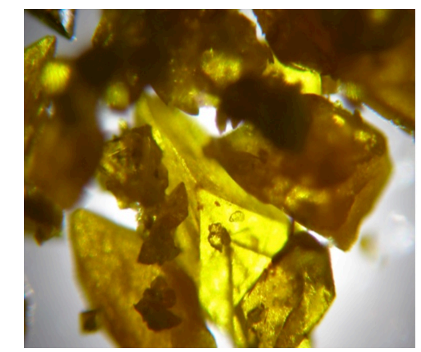
Metal salts

Solution



Crystalization

Weeks



Cluster crystal

Frémont, P. d.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

The synthesis of clusters

General procedures

Metal salts

High-Temp reactor (500-1200°C)

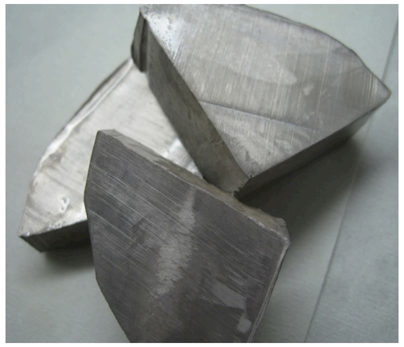
Cluster powder

Frémont, P. d.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

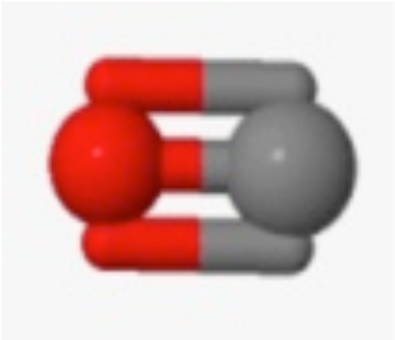
The synthesis of clusters

General procedures

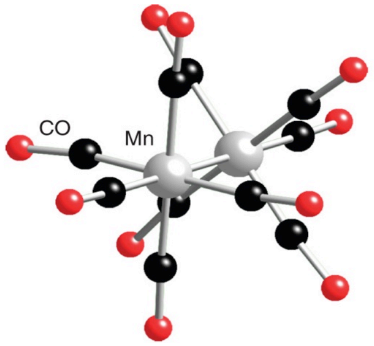
Oxidized salts



Metal reductant



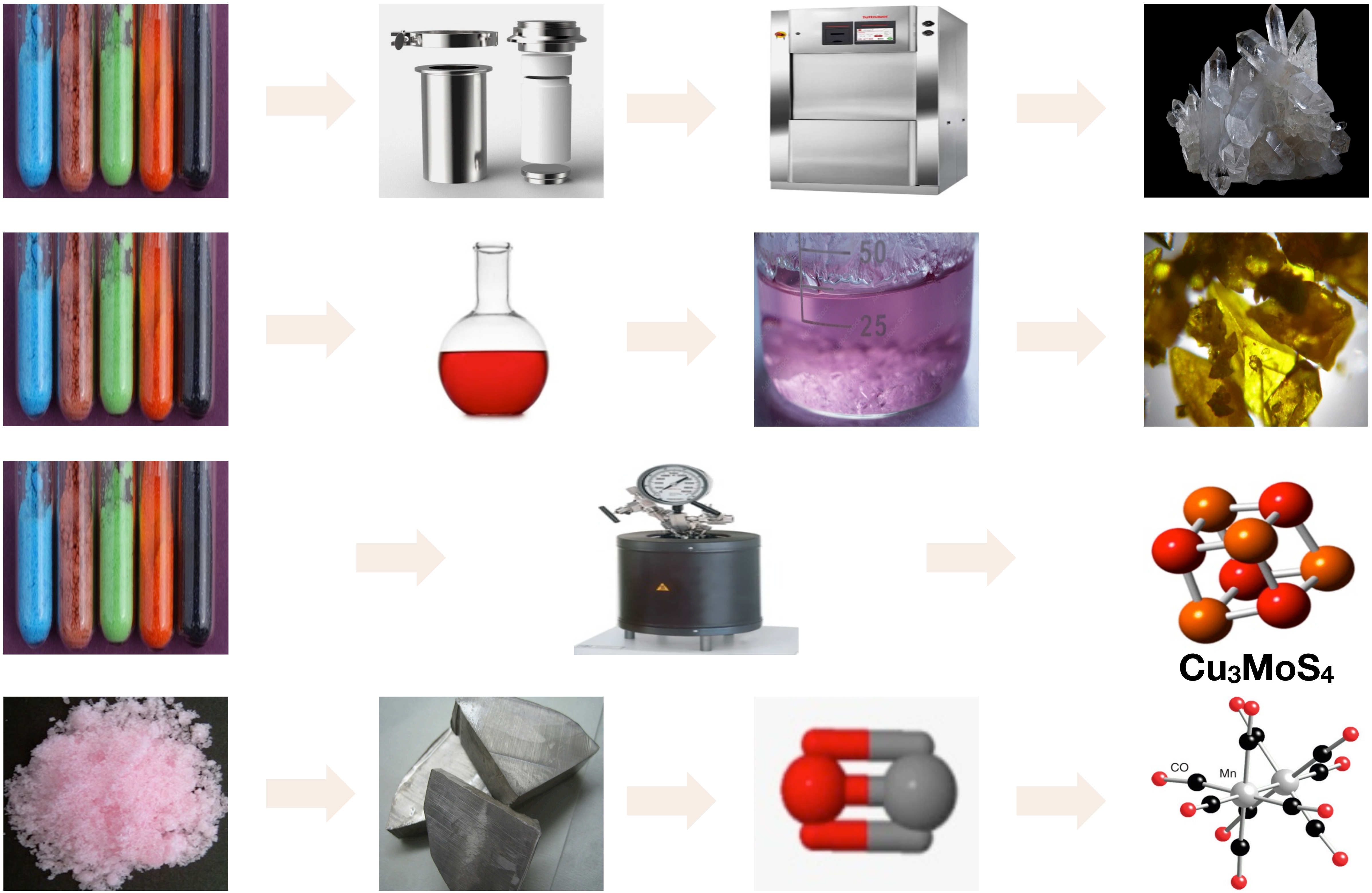
Carbon monoxide



Carbonyl clusters

The synthesis of clusters

General procedures



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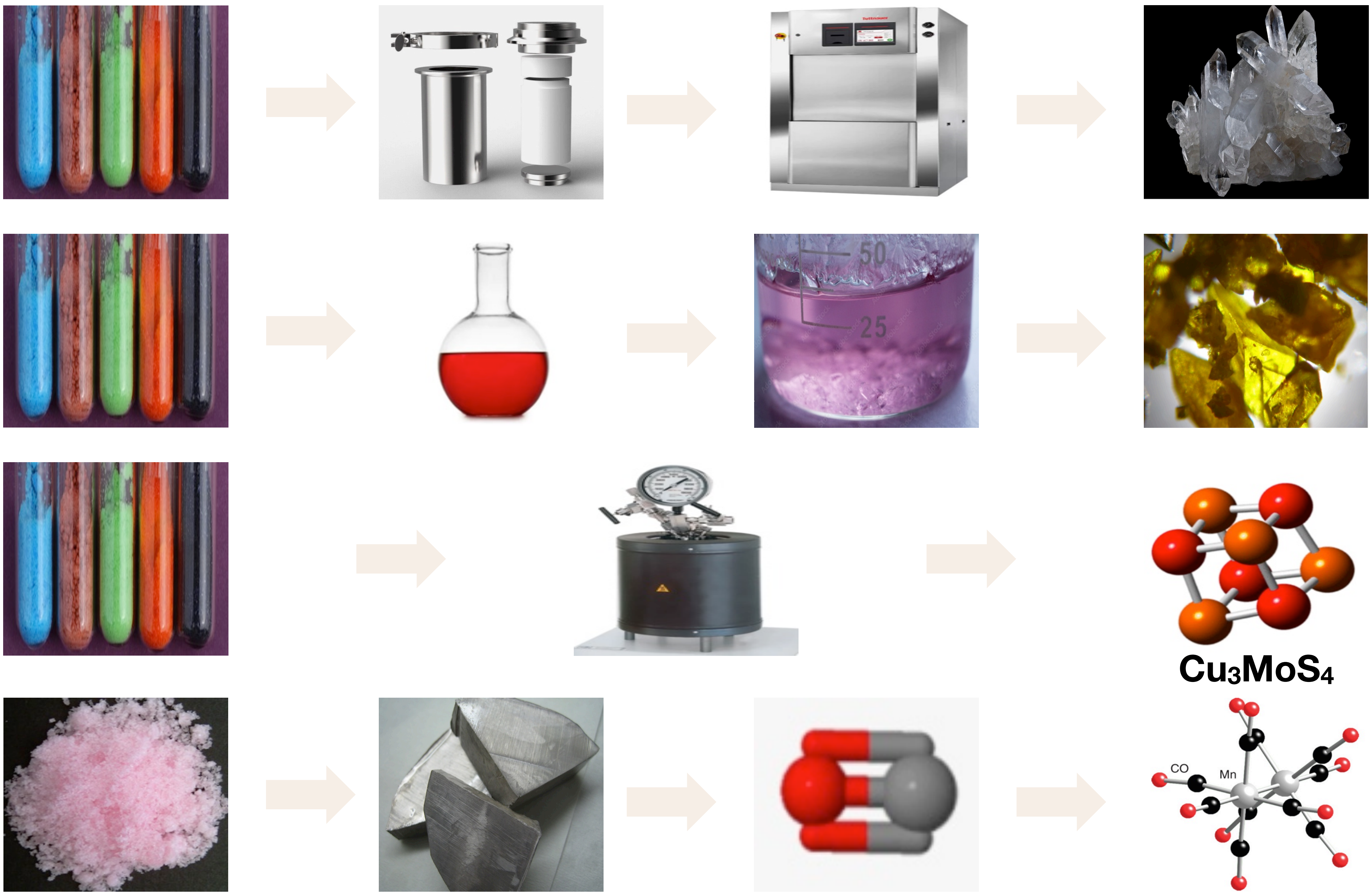
The synthesis of clusters

General procedures



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The synthesis of clusters

CO reductive synthesis

Case study I:
“The important one”
$Au_{55}[P(C_4H_5)_3]_{12}Cl_6$

Frémont, P. d.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

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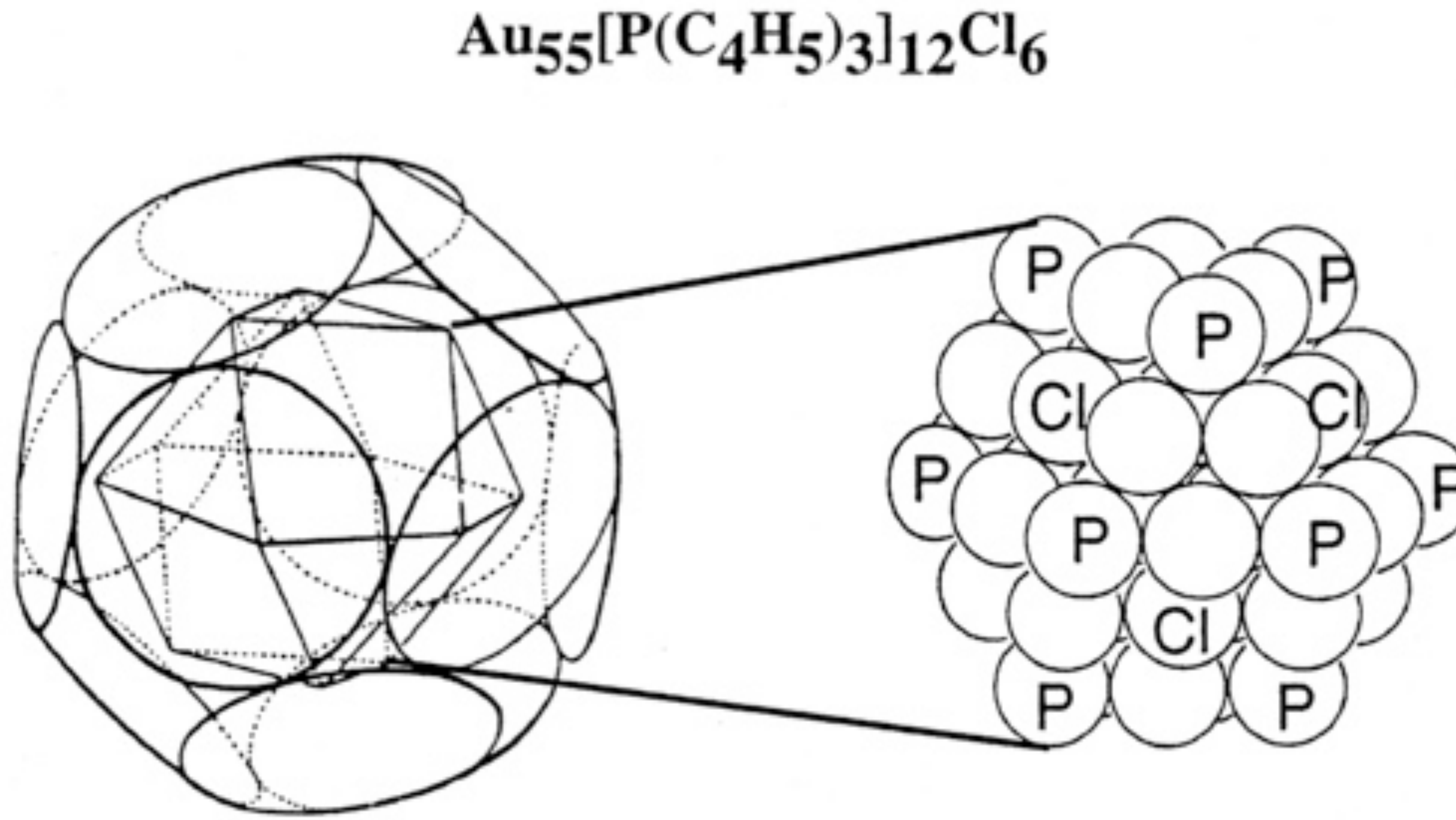

Frémont, P. d.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

$Au_{55}[P(C_4H_5)_3]_{12}Cl_6$

Synthesis

$$Ph_3P{-}Au{-}Cl \xrightarrow[\text{50-60°C, Benzene}]{B_2H_6} [Au_{9.2}(PPh_3)_2Cl]_n$$

Translatable strategy

Au_{55}, Ru_{55}, Rh_{55}, Pt_{55}, Co_{55} can all be made similarly

Generate M(0) waste

Poor thermo stablity

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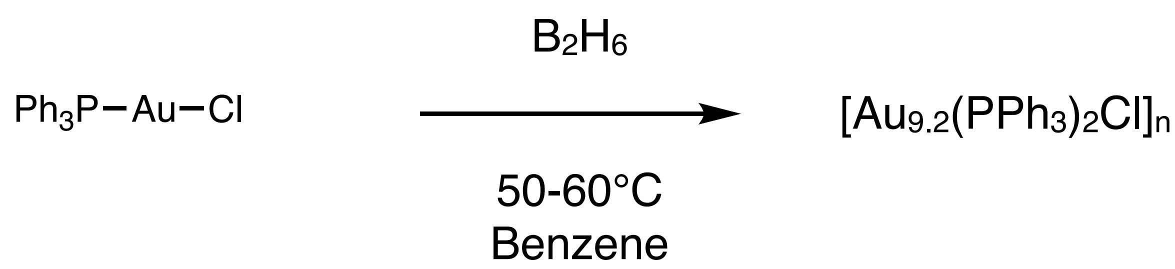
Synthesis



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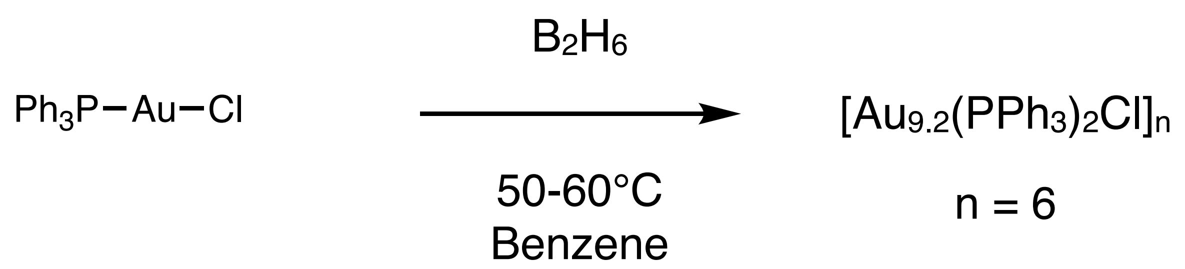

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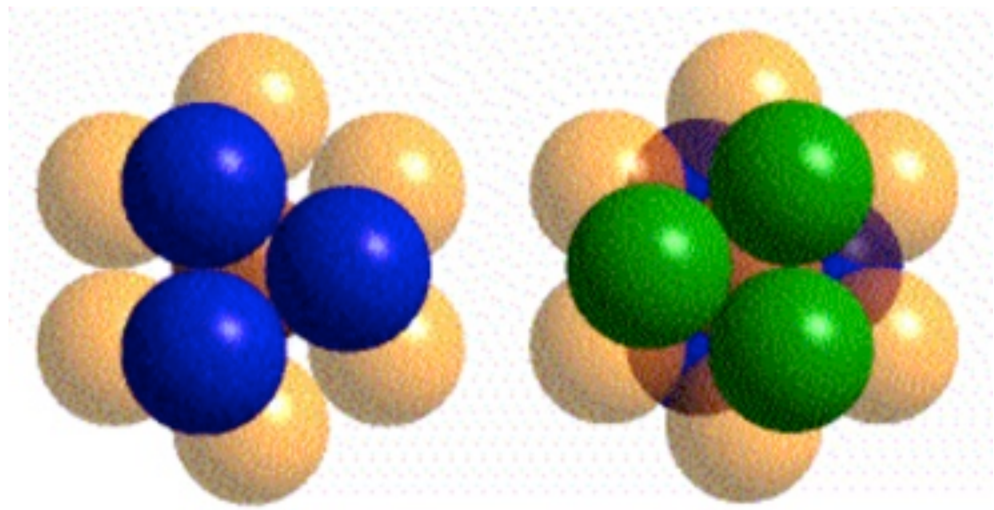
Why 55?

Generate M(0) waste

Poor thermo stablity

Metals really like to be close packed!



hcp **ccp**

Let's expand the packing from the simplest repeating unit.

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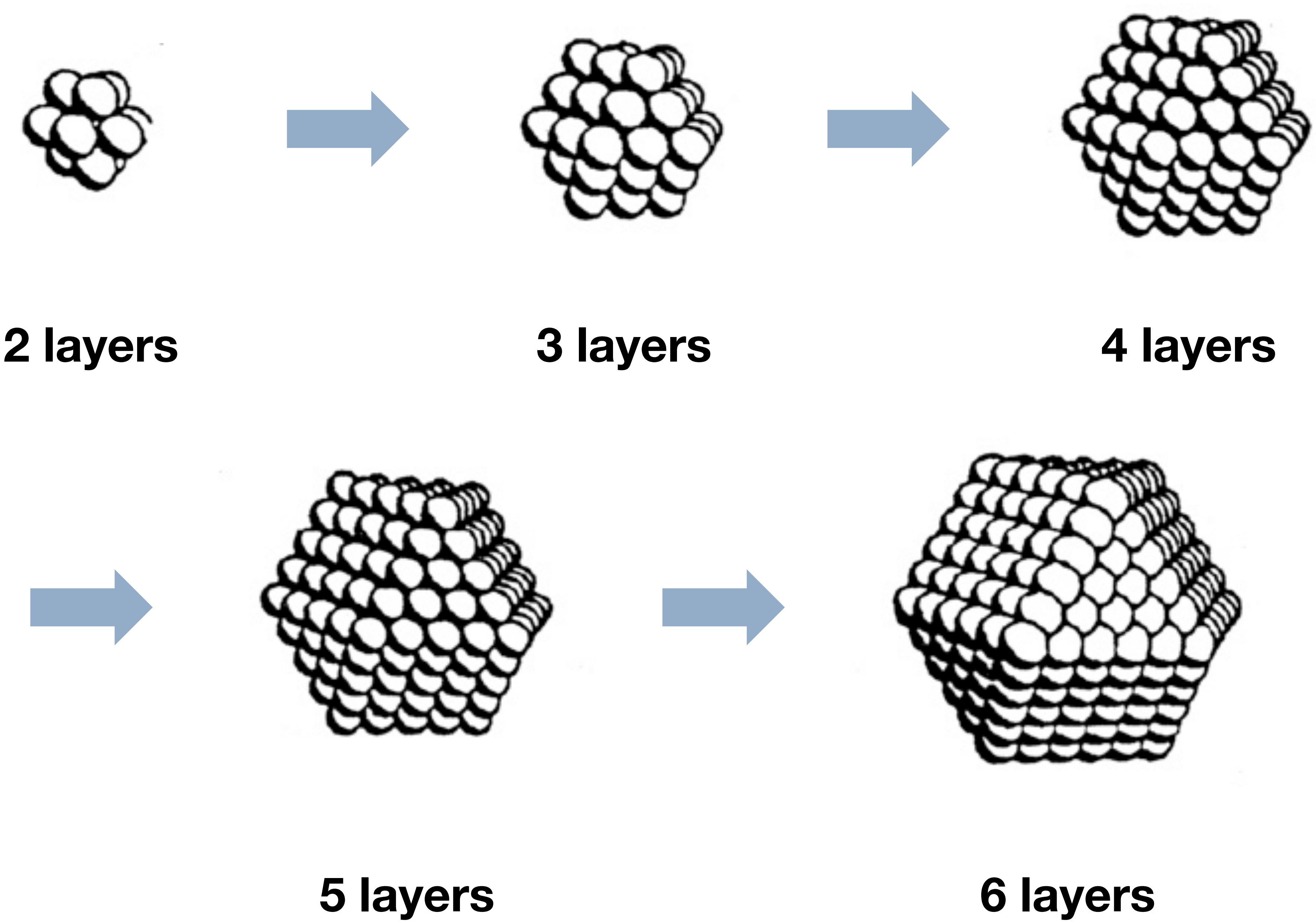

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The Magic number

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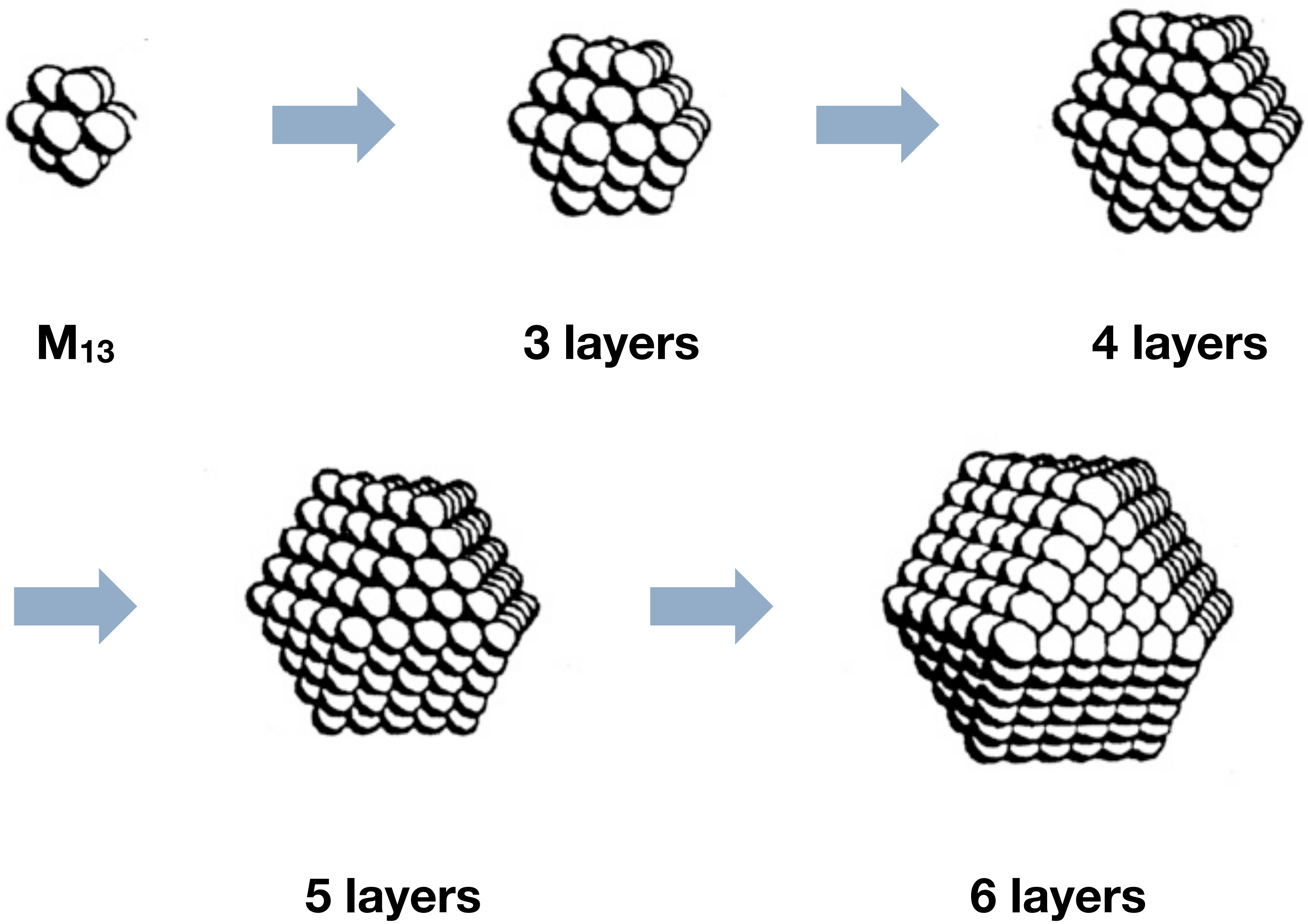

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The Magic number

Let's expand the packing from the simplest repeating unit.

M_{13}

M_{55}

4 layers

5 layers

6 layers

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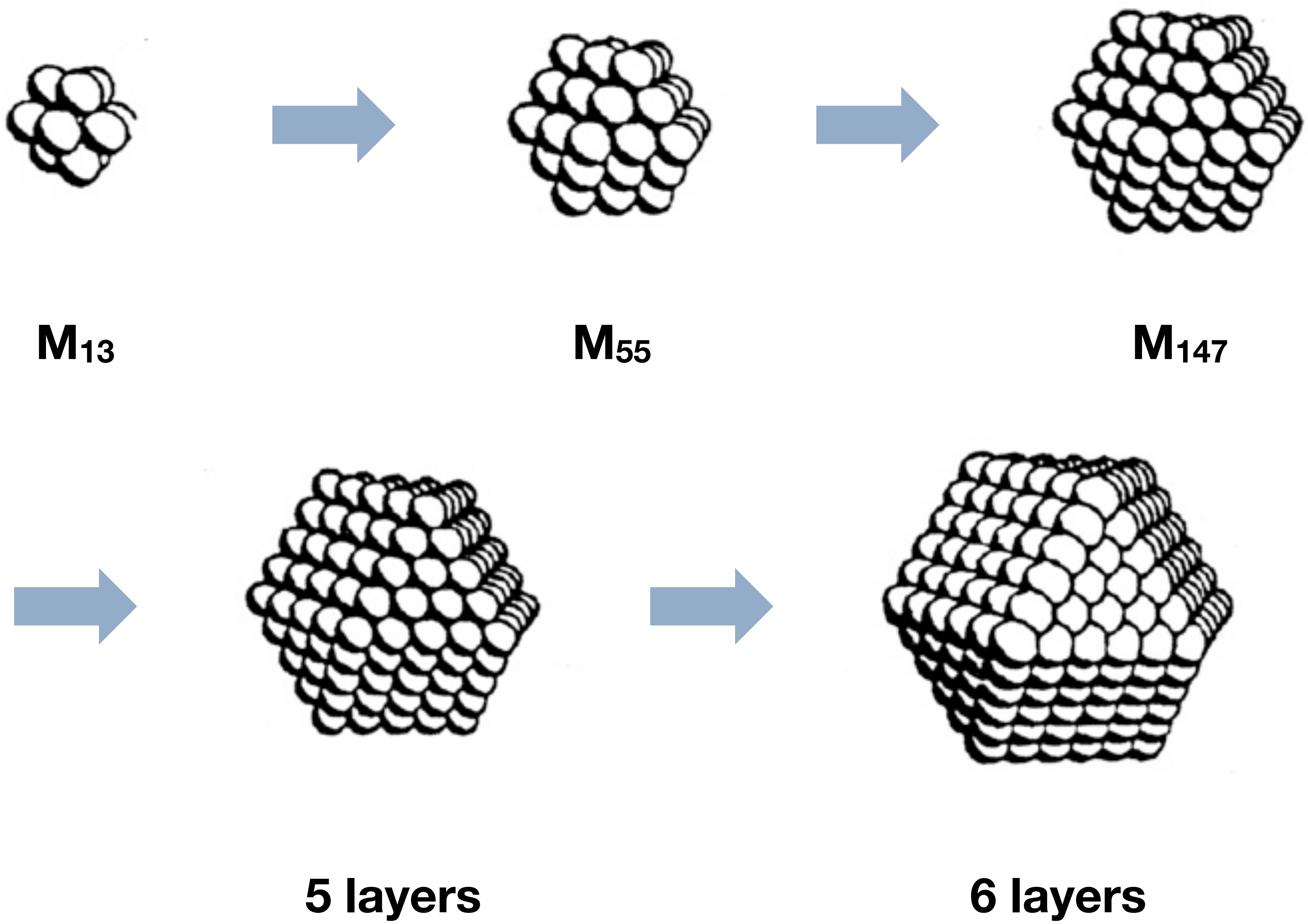

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Let's expand the packing from the simplest repeating unit.

M_{13}

M_{55}

M_{147}

M_{309}

6 layers

Frémont, P. d.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

Let's expand the packing from the simplest repeating unit.

M_{13}

M_{55}

M_{147}

M_{309}

M_{561}

Frémont, P. d.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

Let’s expand the packing from the simplest repeating unit.

M_{13}

M_{55}

M_{147}

M_{309}

M_{561}

$y=10n^2+2$

Frémont, P. d.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

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Heterogeneous catalysis

$Ph_3P-Au-Cl$

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B_2H_6

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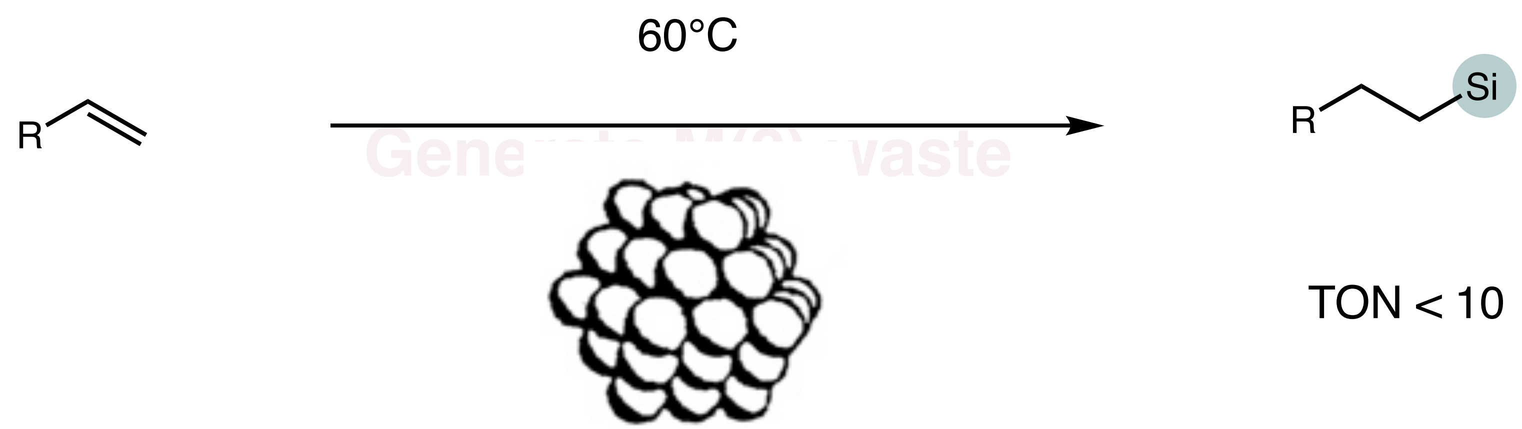

TON < 10

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B_2H_6

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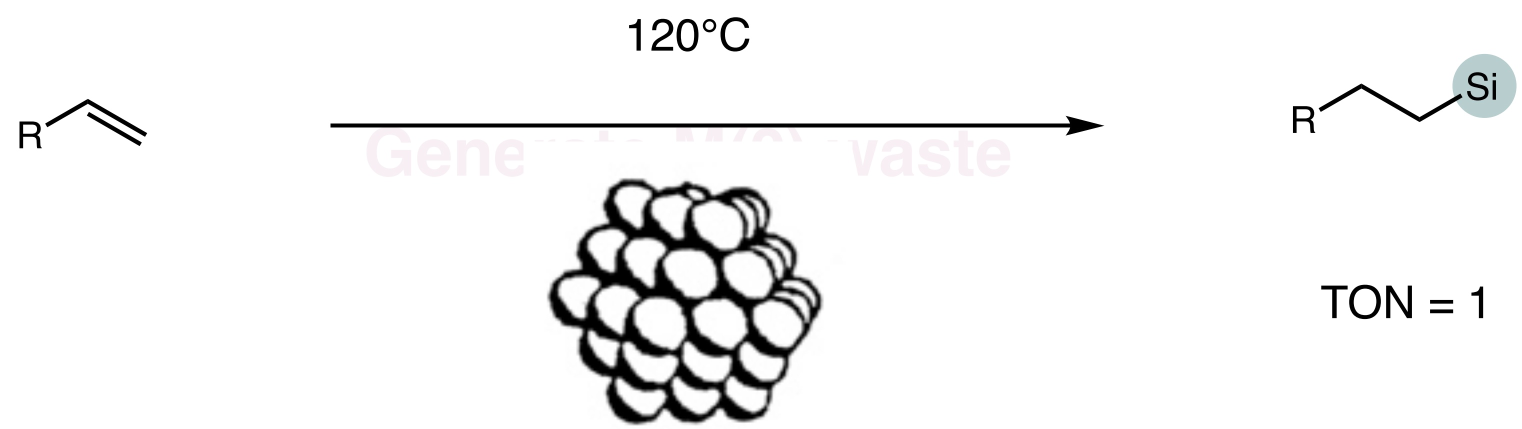


TON = 1

Can we make more stable clusters?

The Magic number

M_{13}

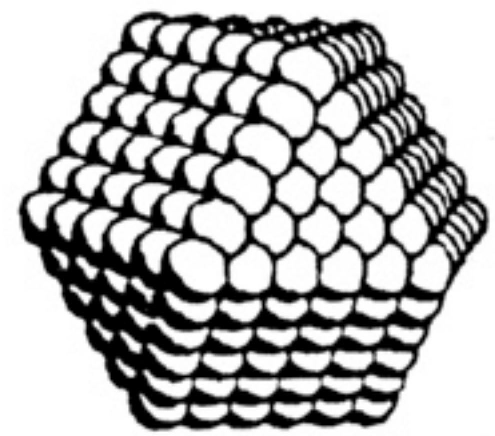
M_{55}

M_{147}

M_{309}

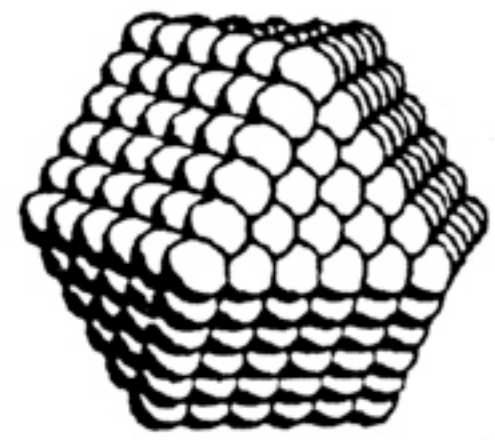
M_{561}

The Magic number



Case study II:
The most studied cluster catalyst system

The Magic number



Case study II:
The most studied cluster catalyst system
$Pd_{561}L_{60}(OAc)_{180}$

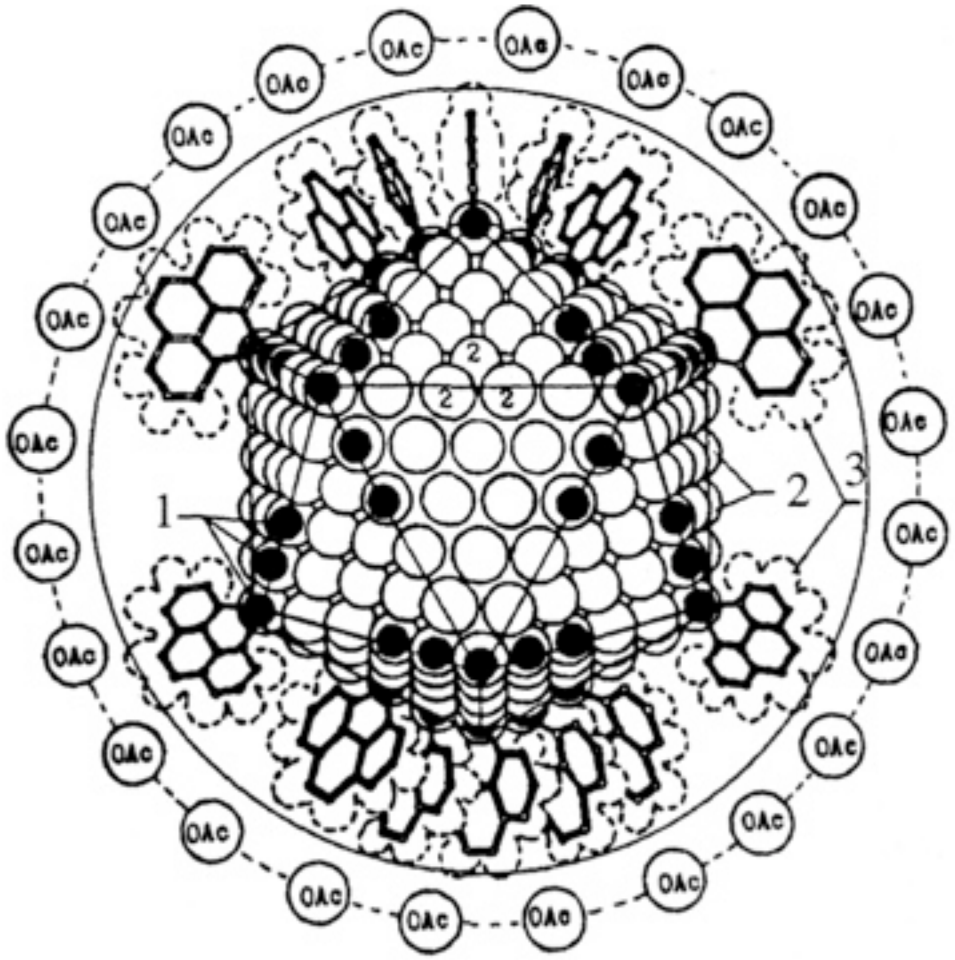
$Pd_{561}L_{60}(OAc)_{180}$

Synthesis

Frémont, P. d.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

$Pd_{561}L_{60}(OAc)_{180}$

Synthesis



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$Pd_{561}L_{60}(OAc)_{180}$

Synthesis

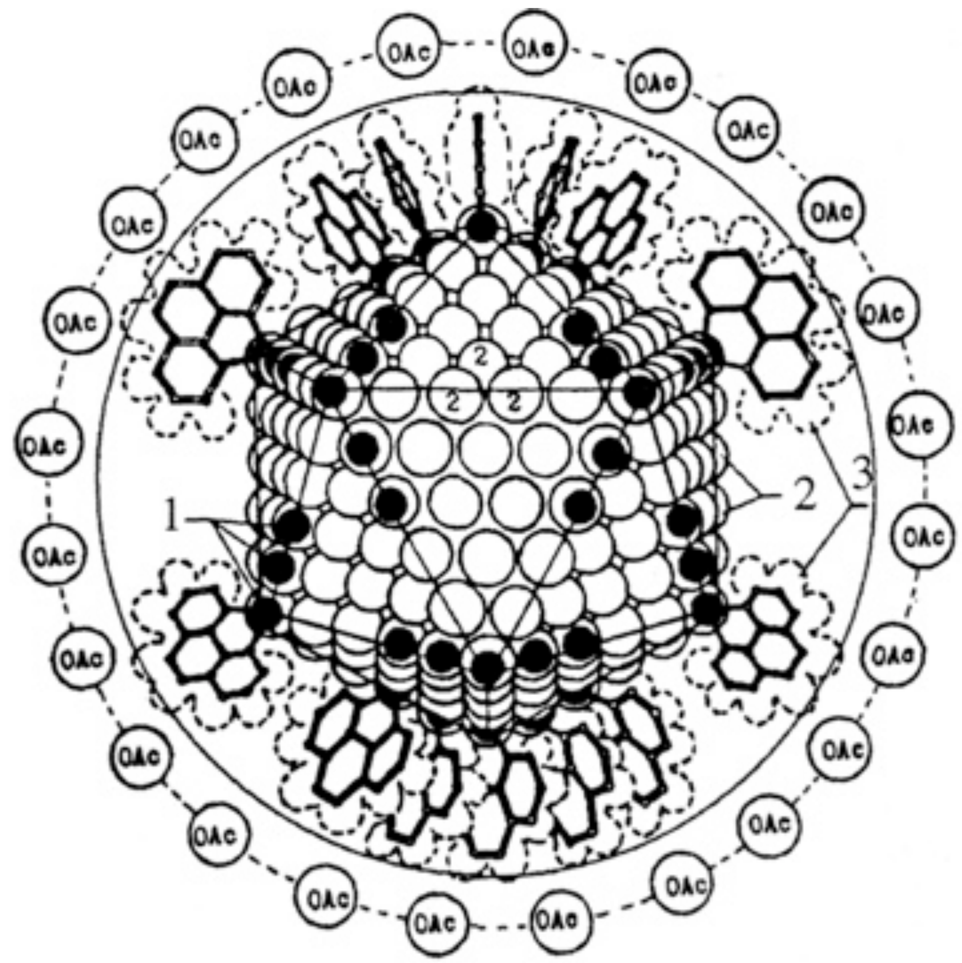
$$Pd(OAc)_2 \xrightarrow[\text{phen}]{H_2} [Pd_4(OAc)_2phenH_4]_n \quad n = 100$$

$$[Pd_4(OAc)_2phenH_4]_n \;(n = 100) \xrightarrow[O_2]{} Pd_{561}(OAc)_{180}(phen)_{60}$$

Wait…I think it should be Pd_{540}

$Pd_{561}L_{60}(OAc)_{180}$

Characterization

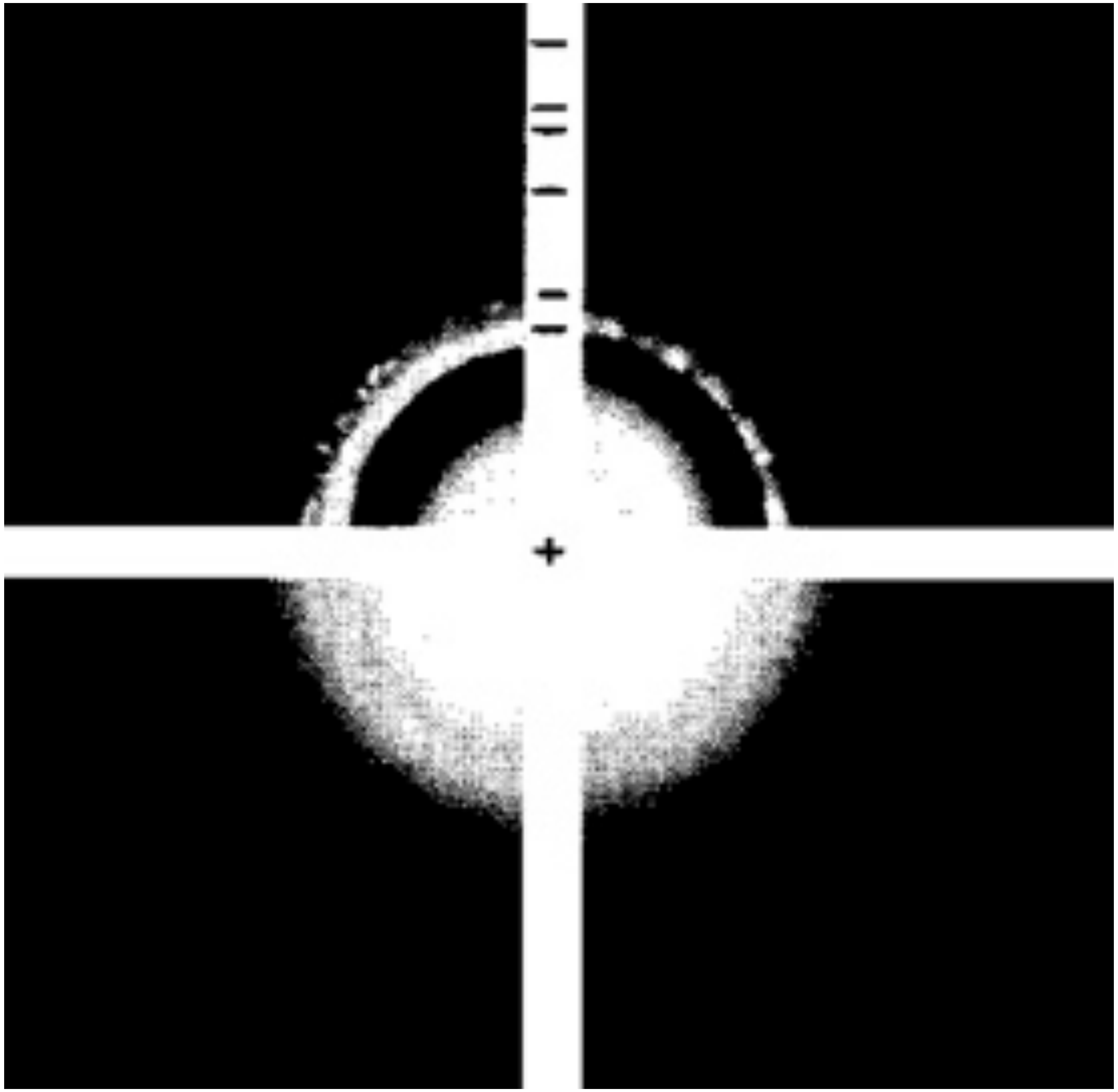


How do we arrive at the formula

$Pd_{561}L_{60}(OAc)_{180}$?

$Pd_{561}L_{60}(OAc)_{180}$

Characterization

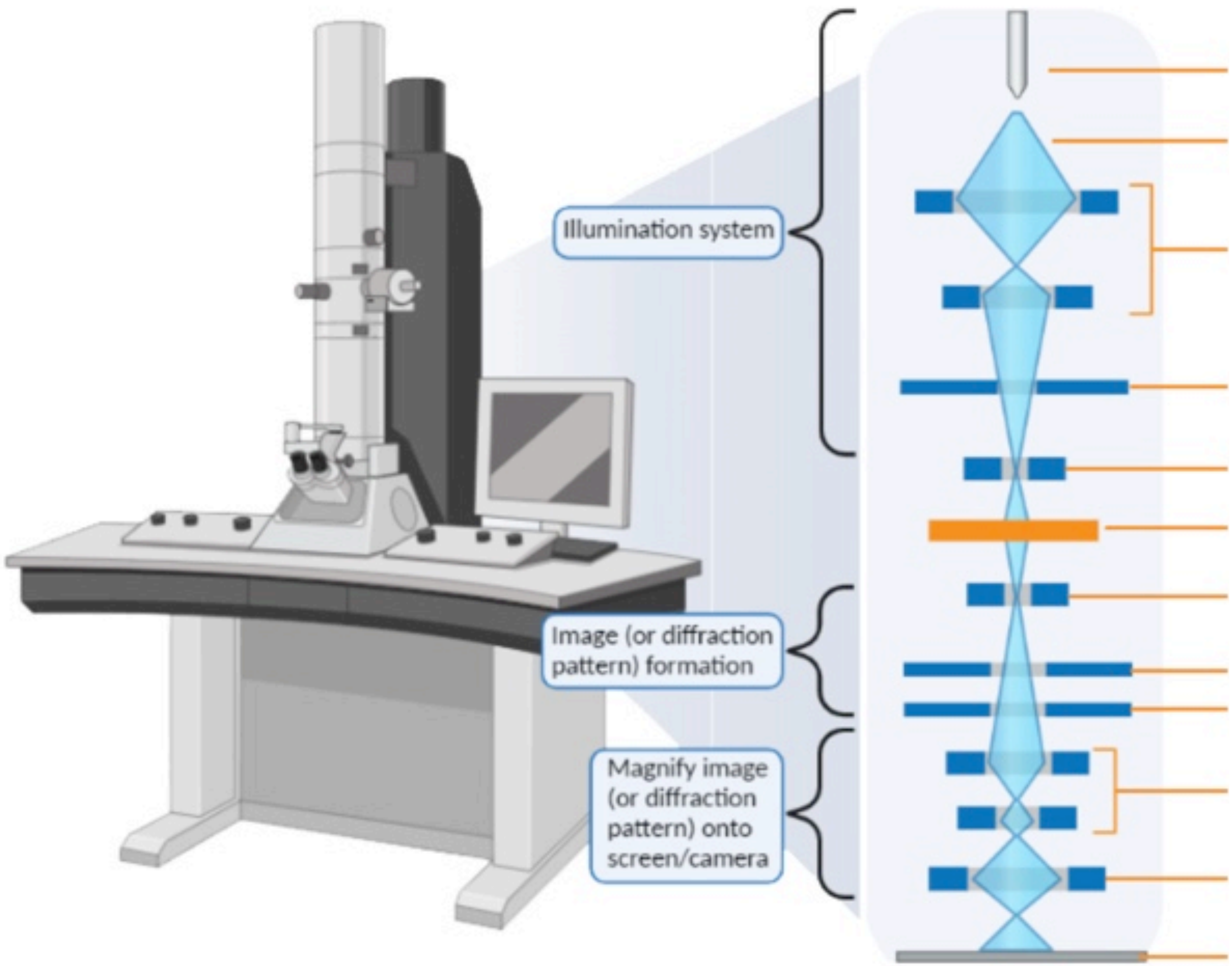


$Pd_{561}L_{60}(OAc)_{180}$

Characterization

Transmission electron microscopy
(TEM)

How does it work?



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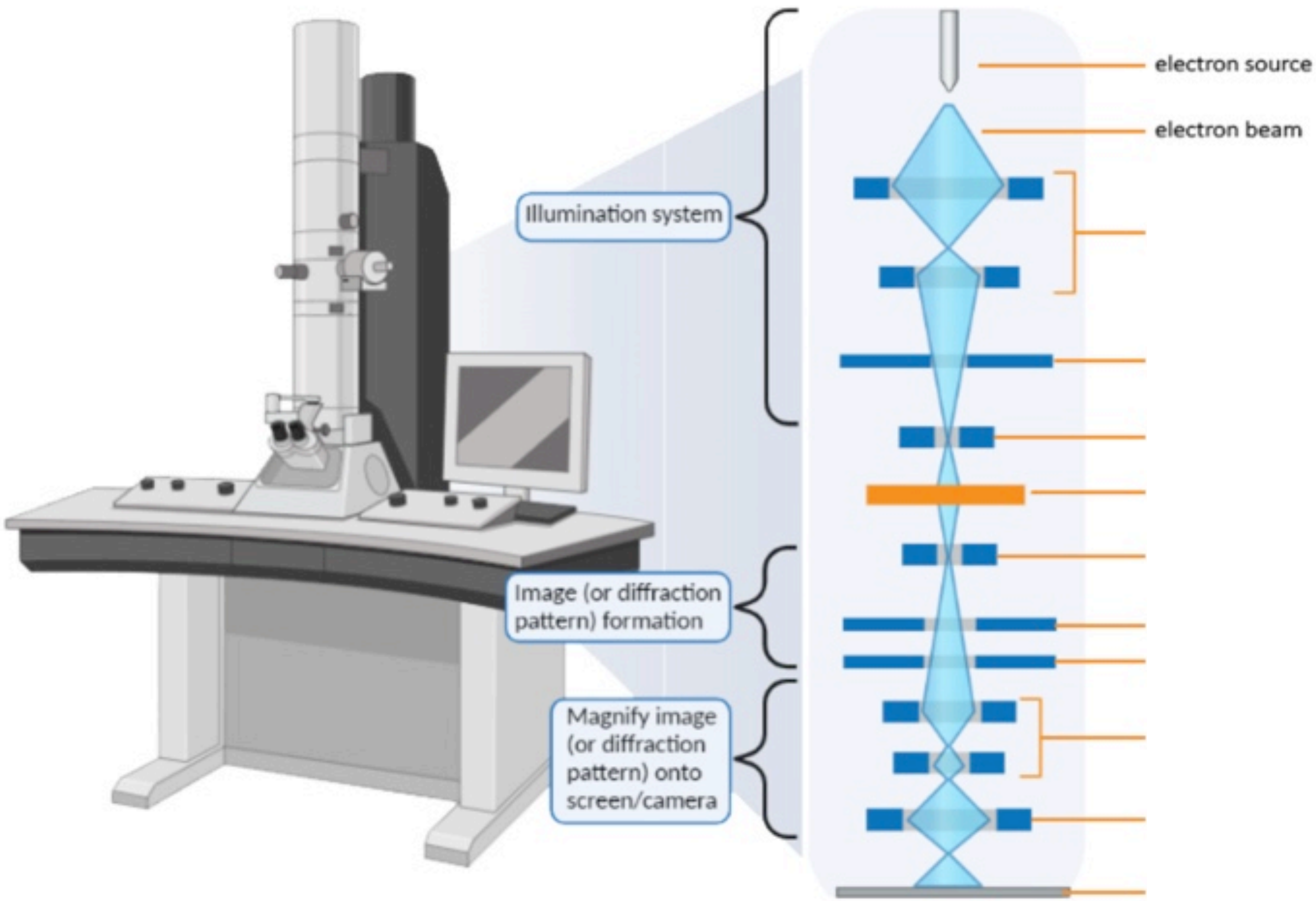

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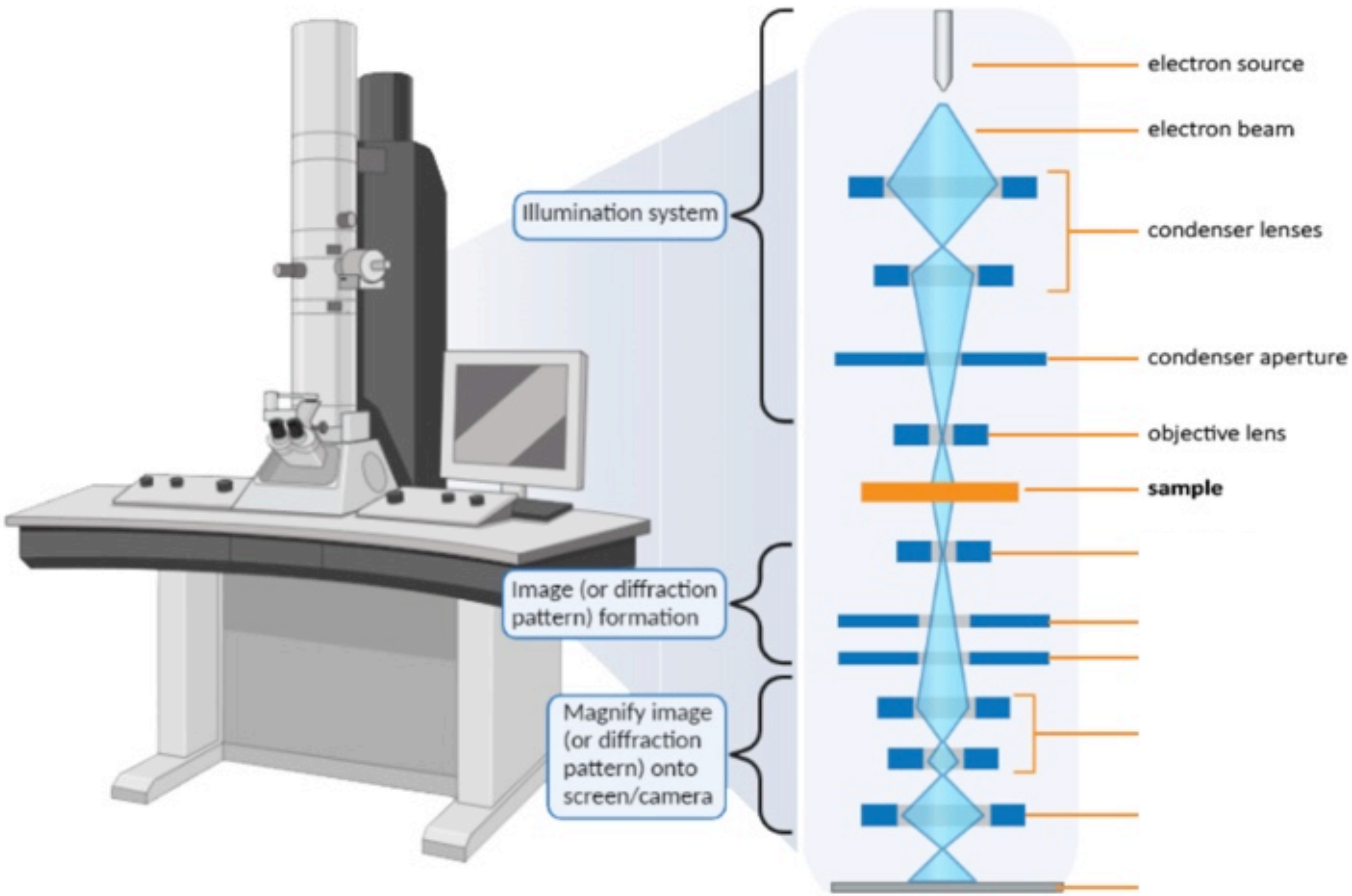

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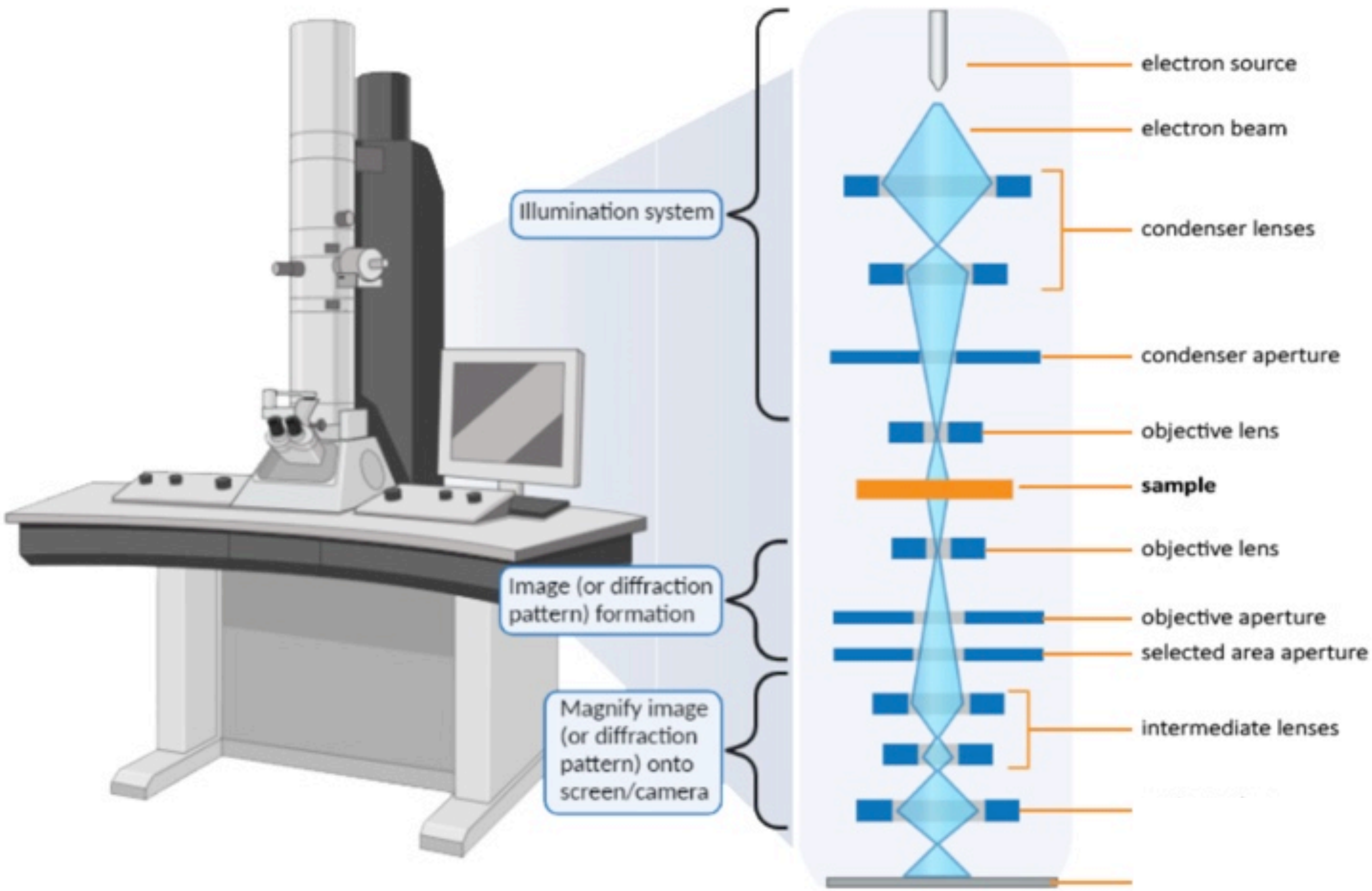

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Transmission electron microscopy (TEM)

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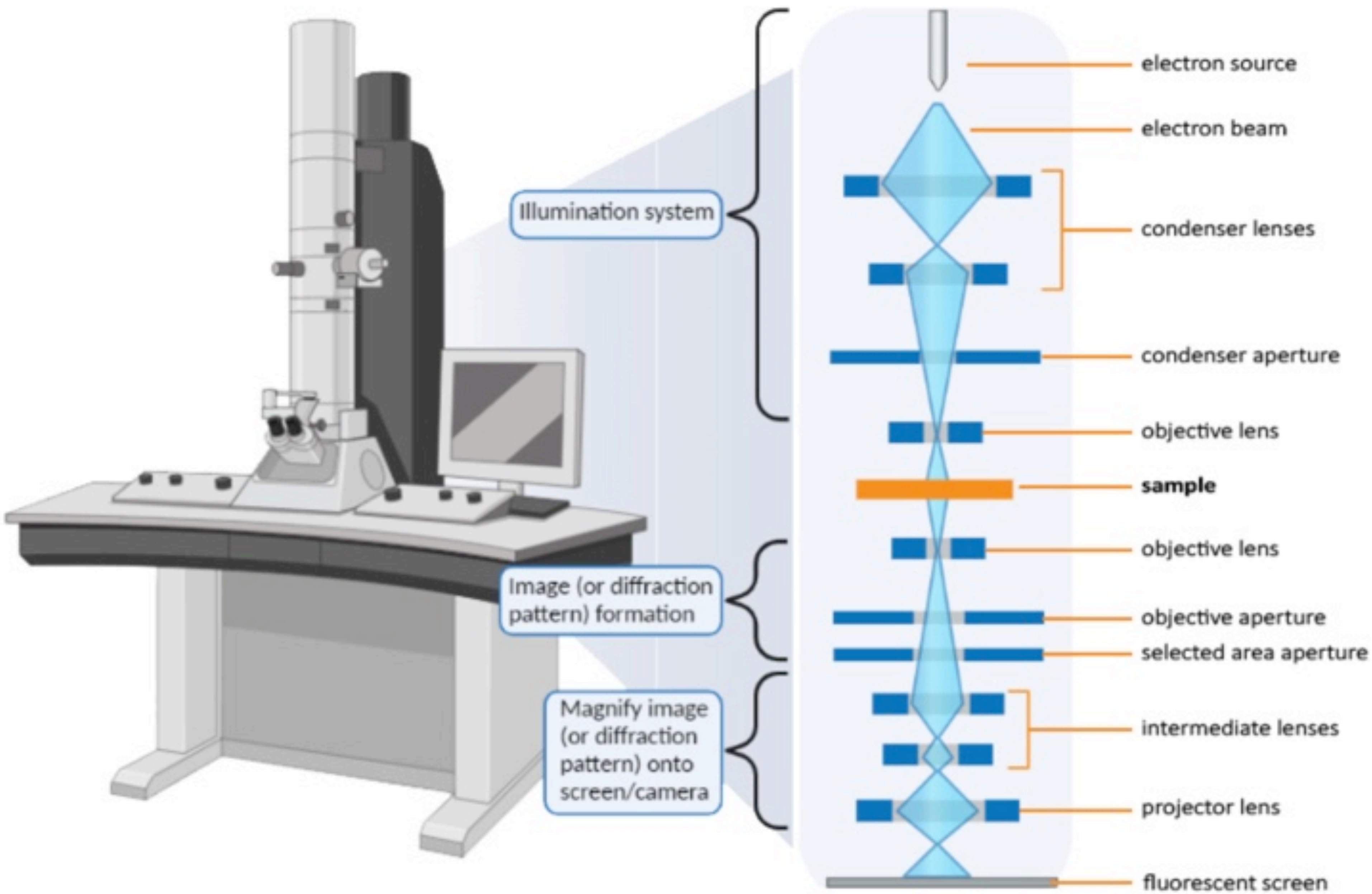

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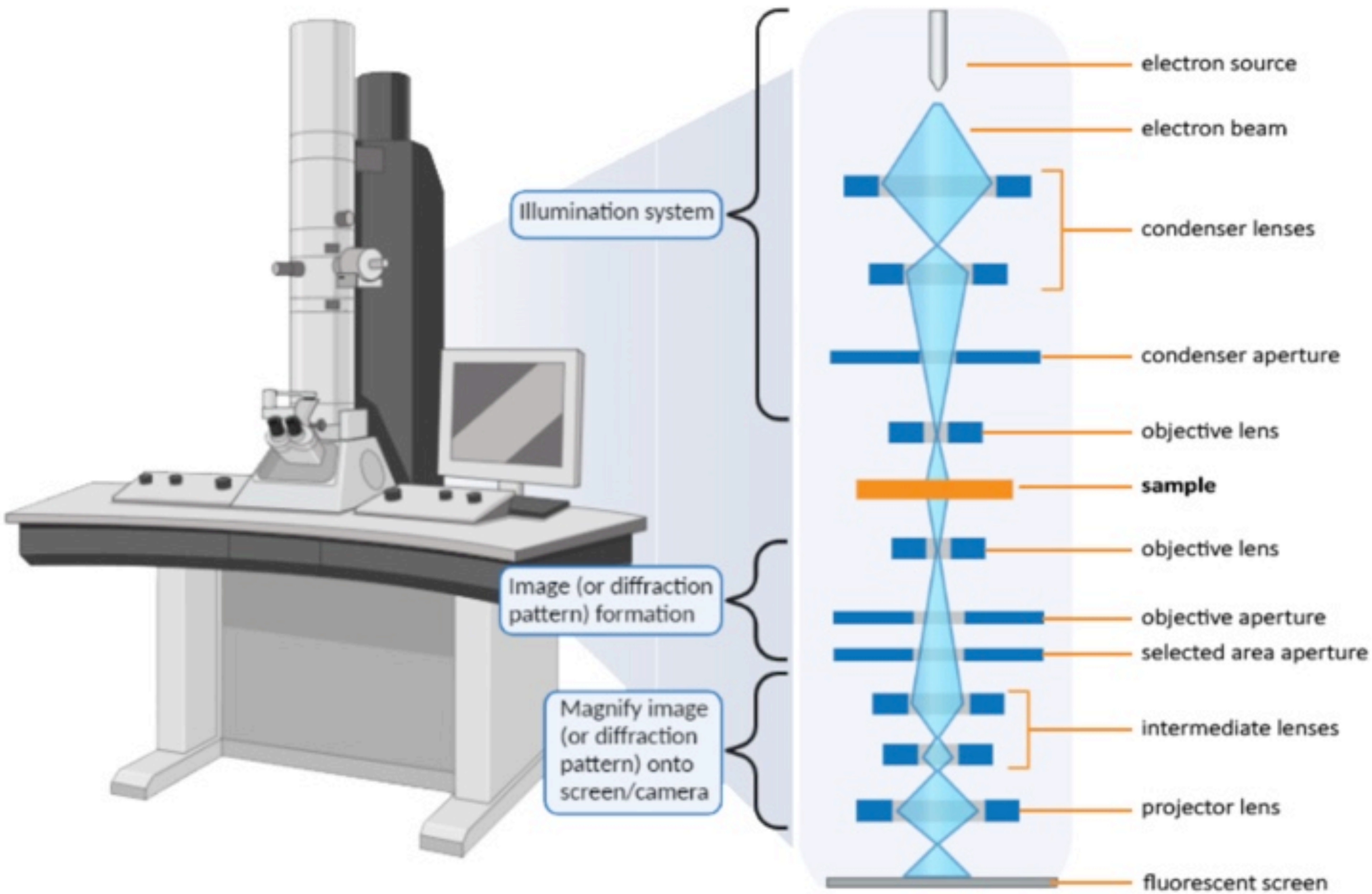
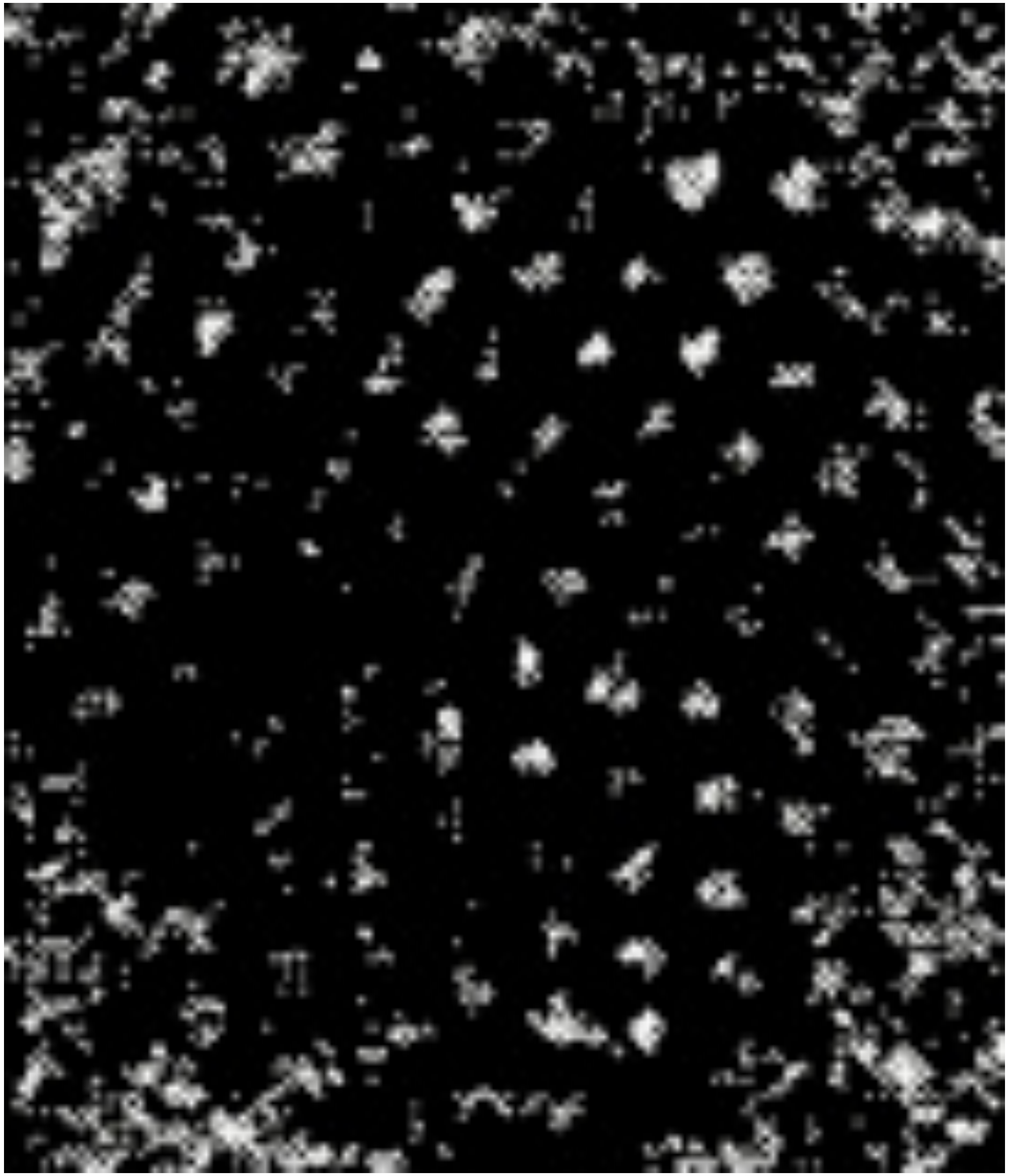
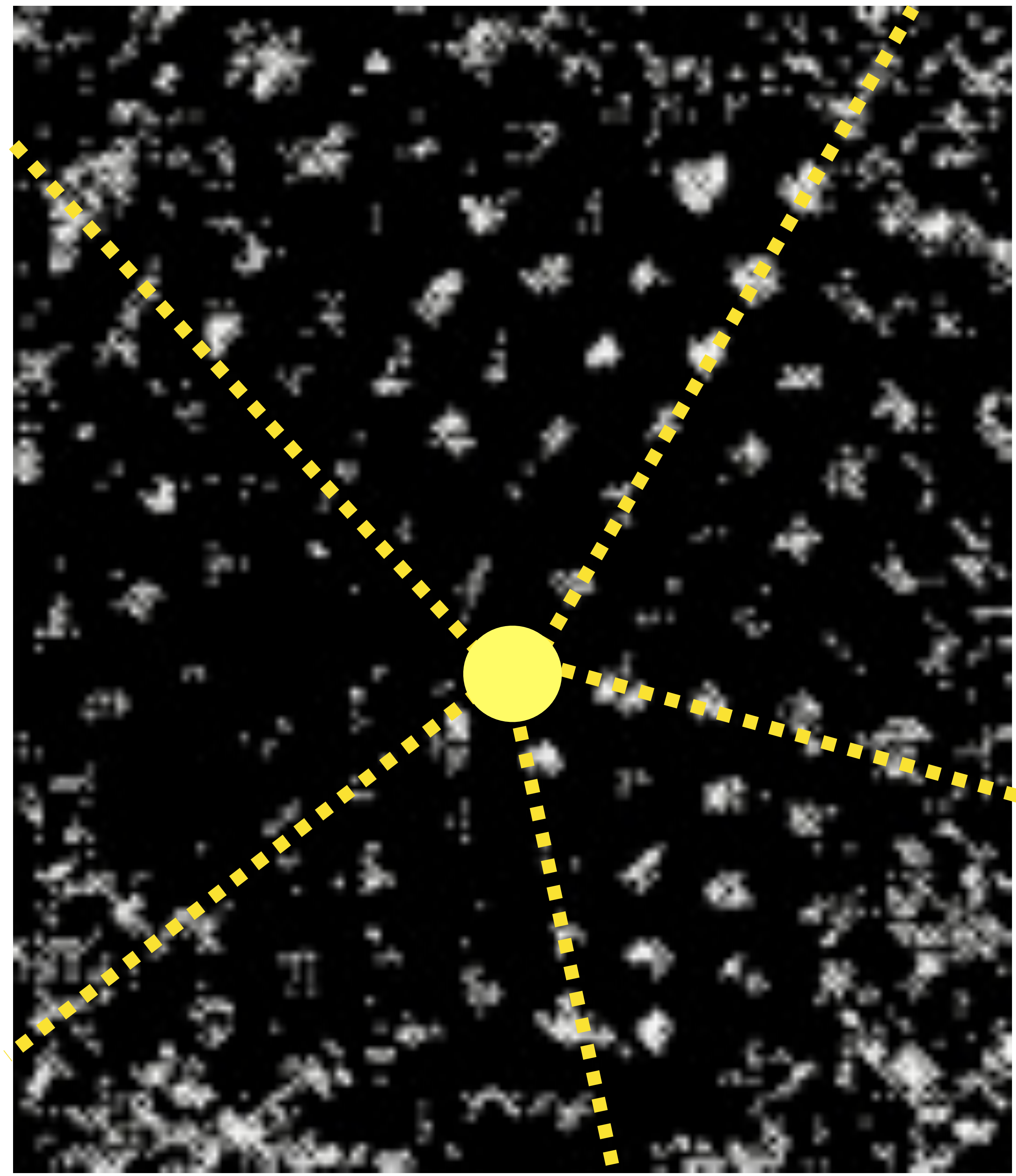


Orders of magnitude more resolution than optical spectroscopy

Transmission electron microscopy
(TEM)



Transmission electron microscopy (TEM)



Transmission electron microscopy
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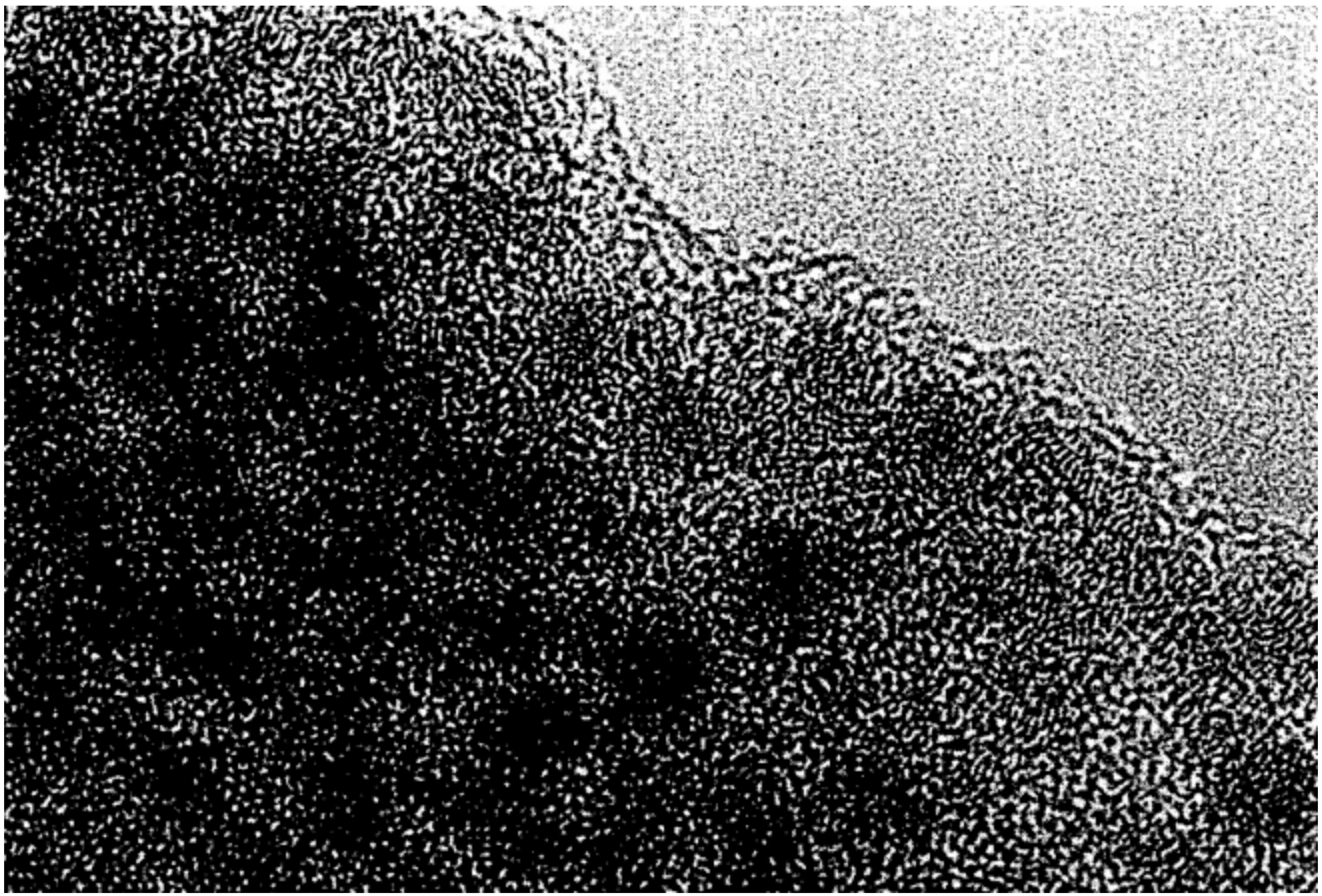

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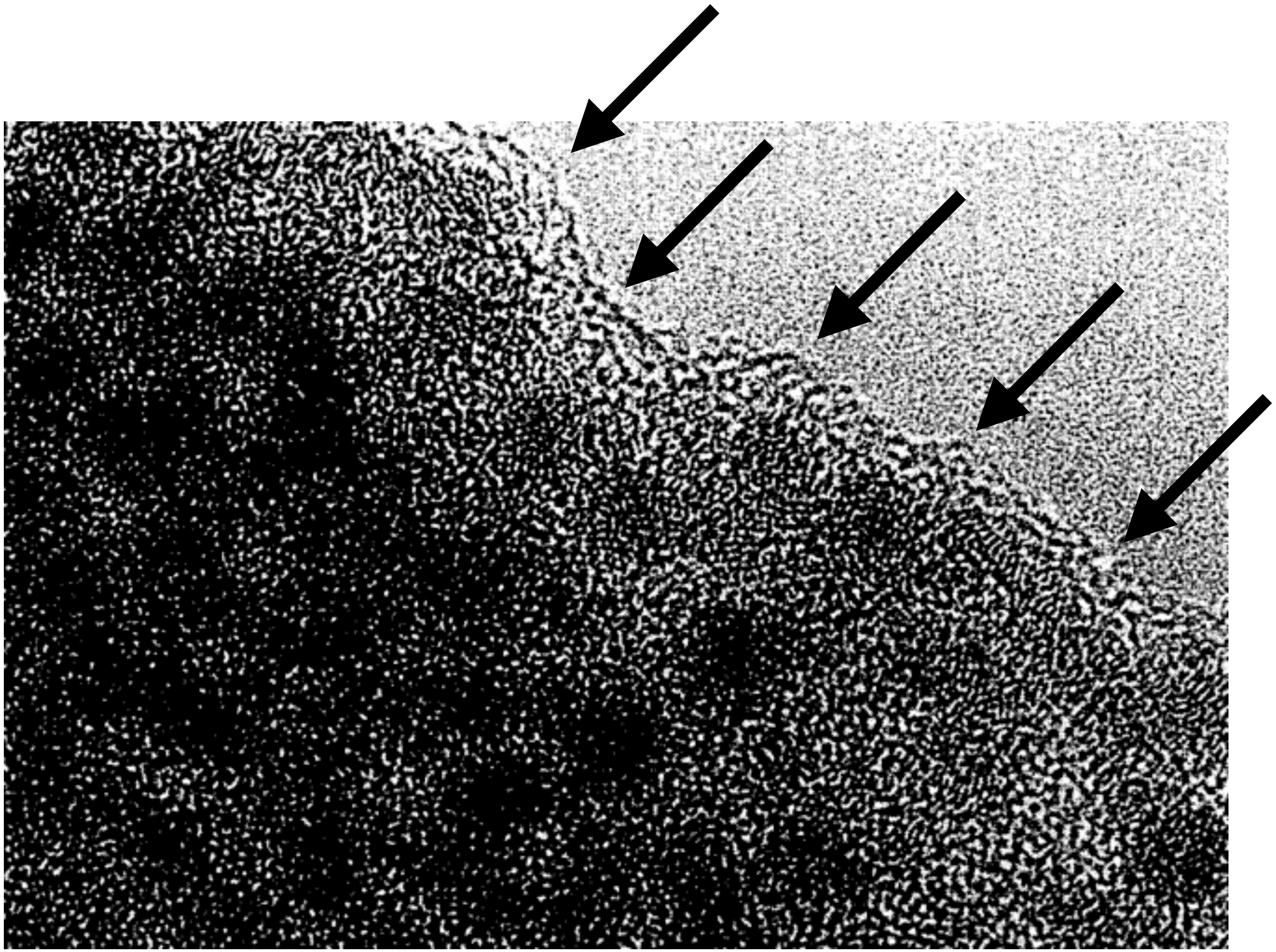
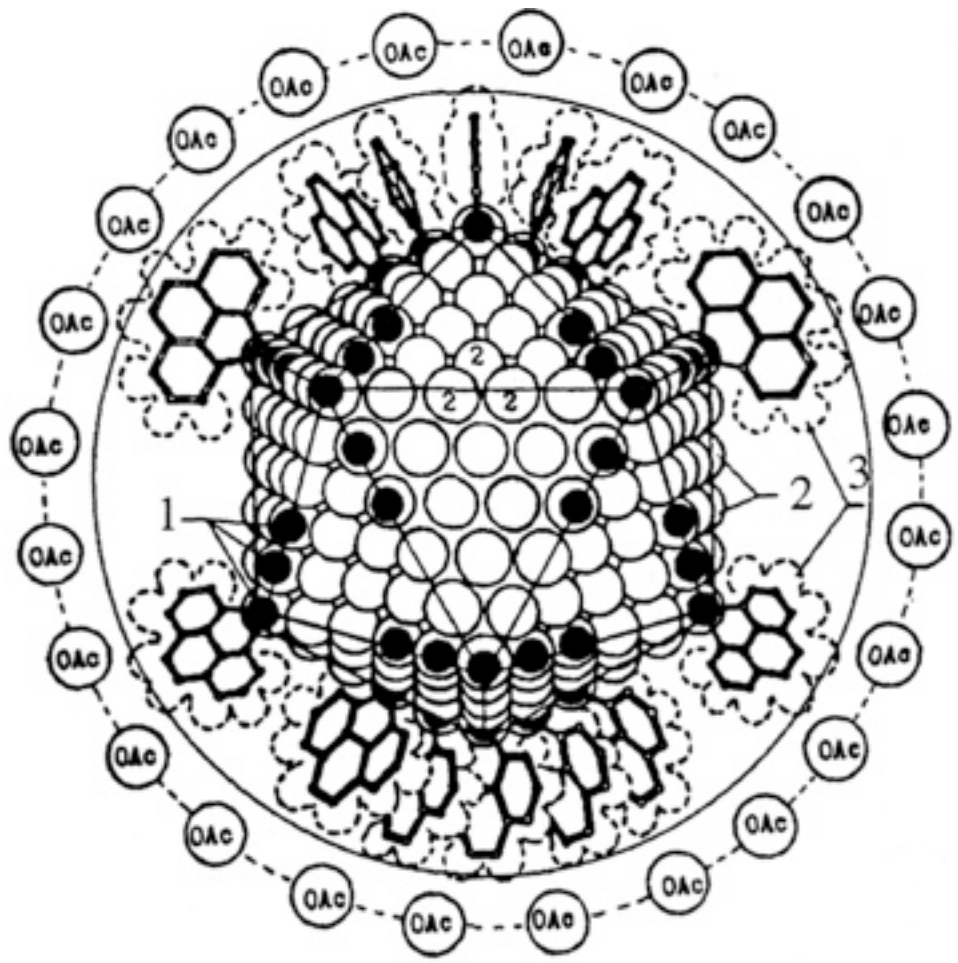


$Pd_{561}L_{60}(OAc)_{180}$

Characterization



TEM data shows 3 kinds of Pd:

1) **majority of Pd are in FCC environment**
2) **Distorted five-fold axis indicates icosahedral**
3) **Low symmetry sites were identified**

$Pd_{561}L_{60}(OAc)_{180}$

Characterization

TEM data shows 3 kinds of Pd:

1) **majority of Pd are in FCC environment**
2) **Distorted five-fold axis indicates icosahedral**
3) **Low symmetry sites were identified**

↓

The Pd_{540} accounts for only the first and second kind
So there are more than 540 Pd atoms

↓

Supported by other microscopy and element analysis
The formula was deducted to be $Pd_{570\pm30}L_{63\pm3}(OAc)_{190\pm10}$

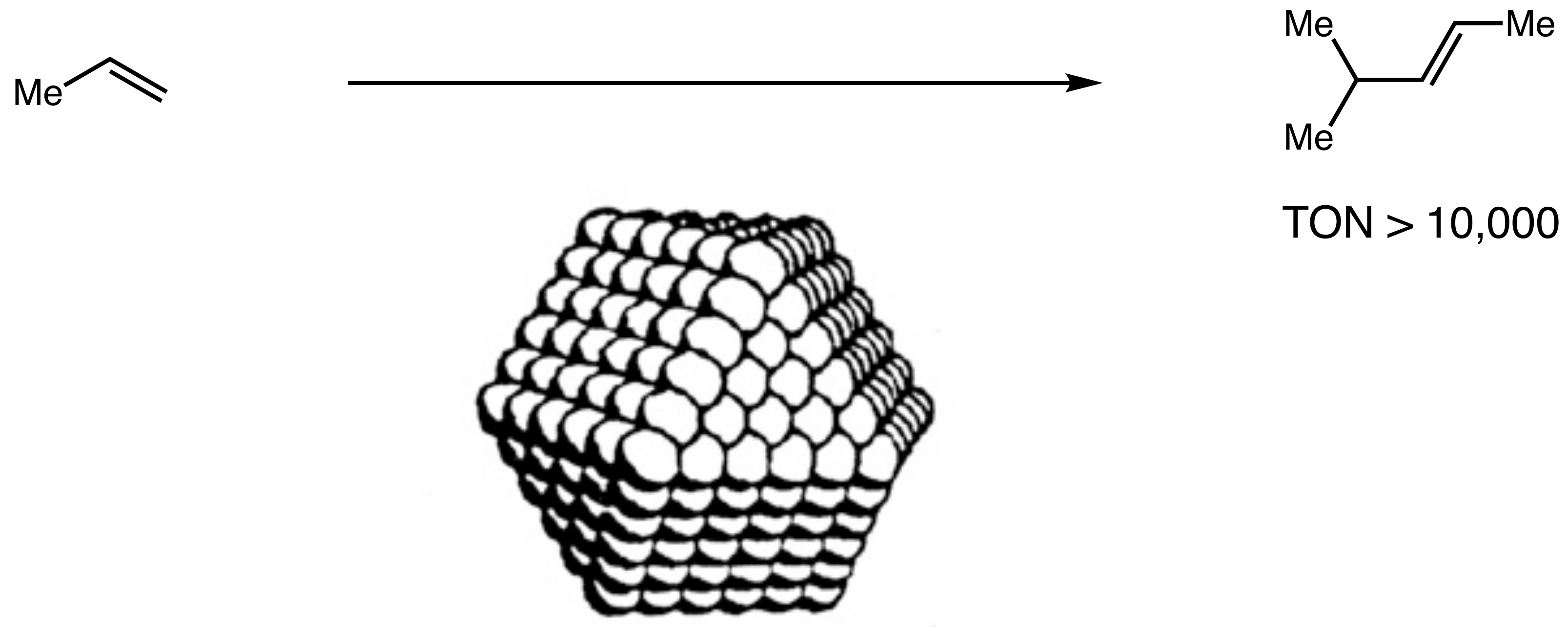
↓

The magic number 561 was suspected to be the result of averaging the ensemble of clusters in different sizes

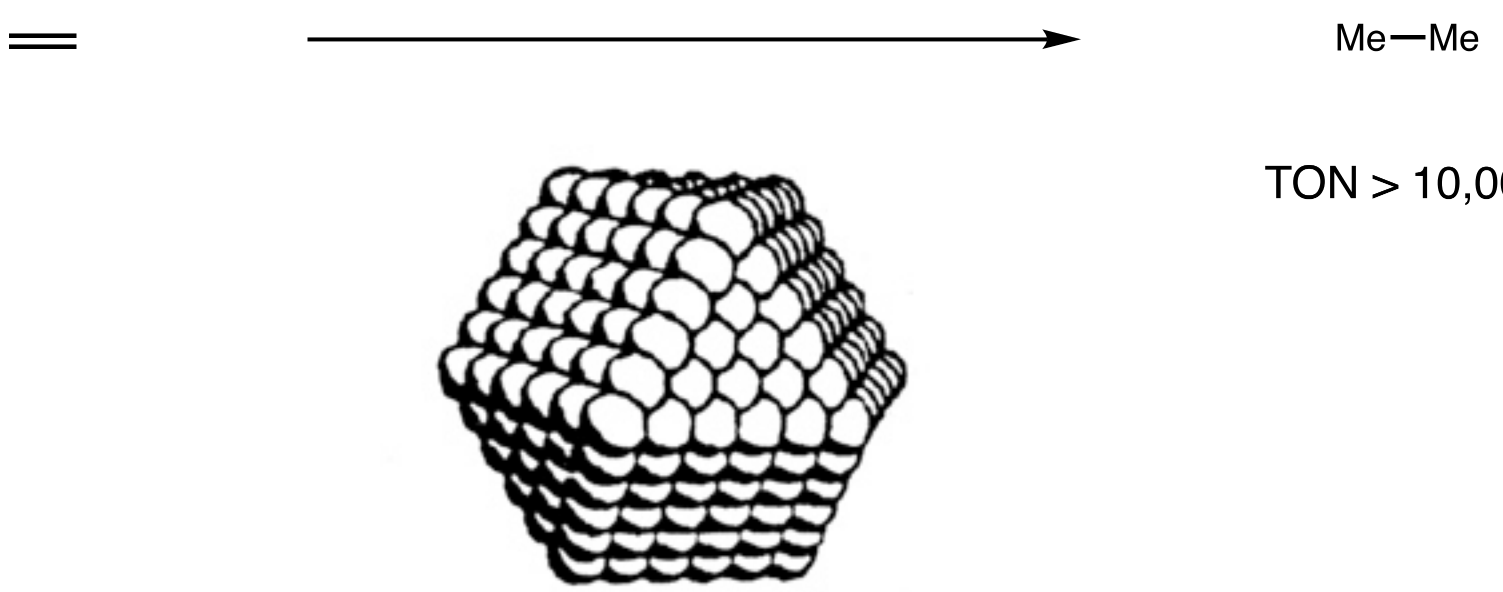
$Pd_{561}L_{60}(OAc)_{180}$

Heterogeneous catalysis

The Pd-561 is significantly more competent as a catalyst

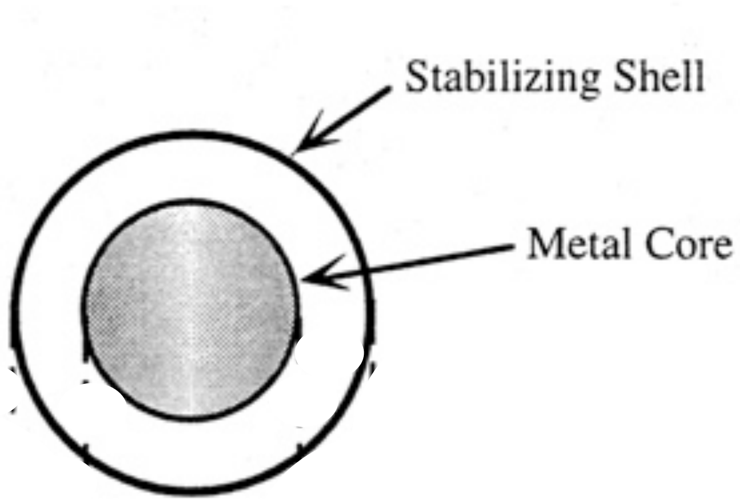


TON > 10,000



TON > 10,000

Can we add stability by other means?

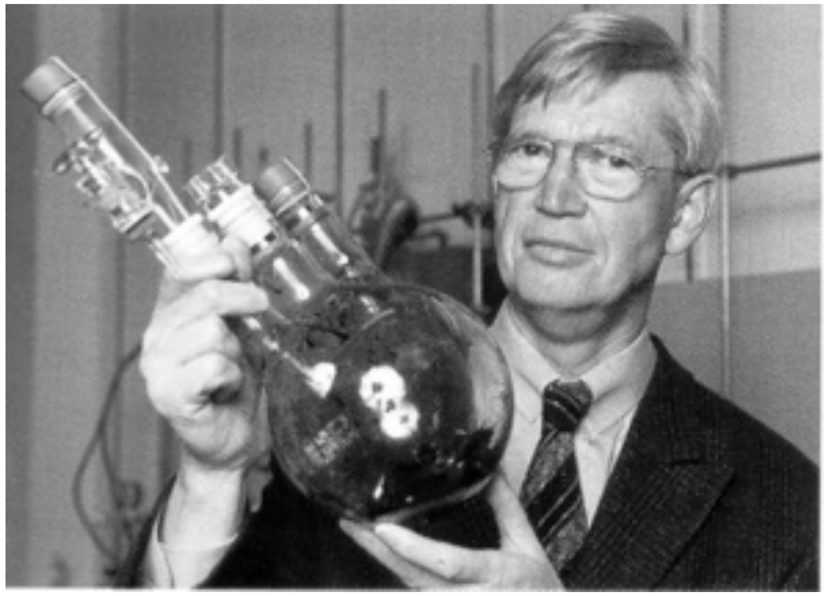


Case study III:
Stablize by ethers
Bö nnemann's nanocluster systems

Case study IV:
Stablize by inorganic
Polyoxoanion- and tetrabutylammonium-stabilized transition-metal nanoclusters

Bönnemann's nanocluster systems

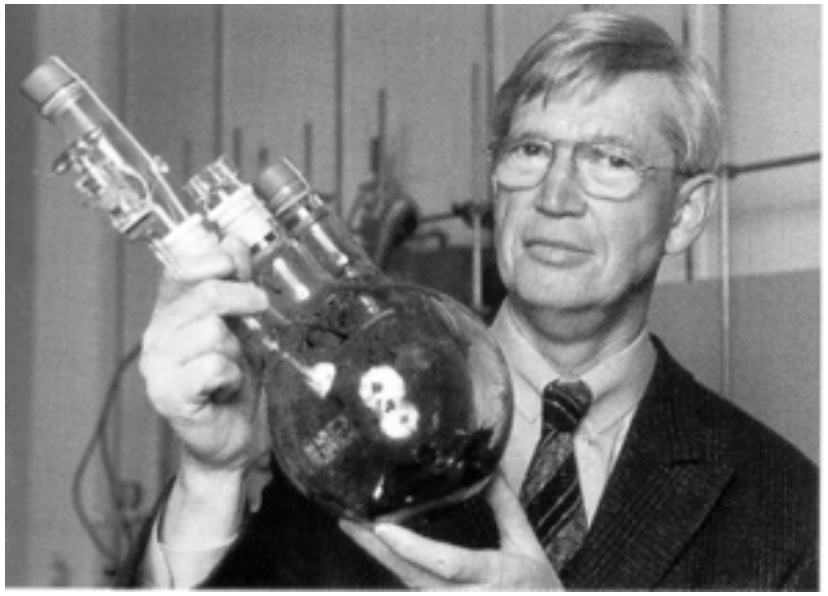
Synthesis

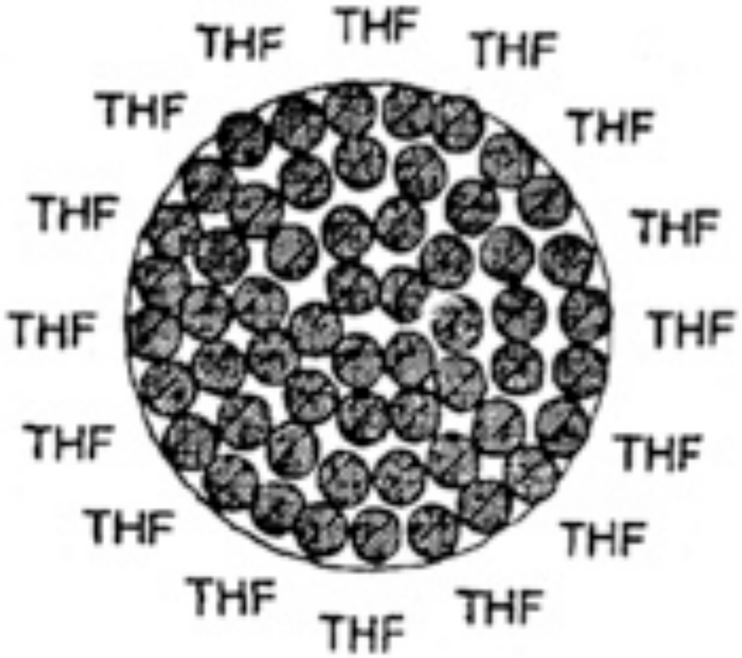


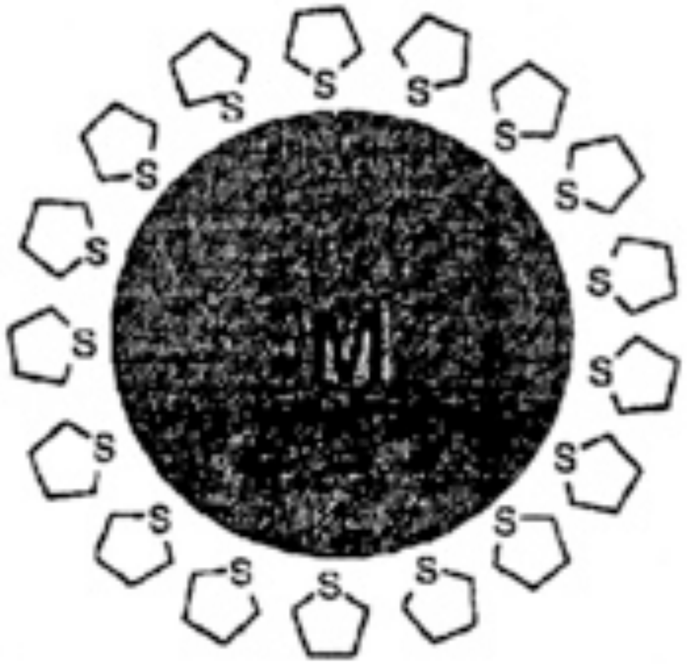
Frémont, P. d.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

Bö nnemann's nanocluster systems

Synthesis







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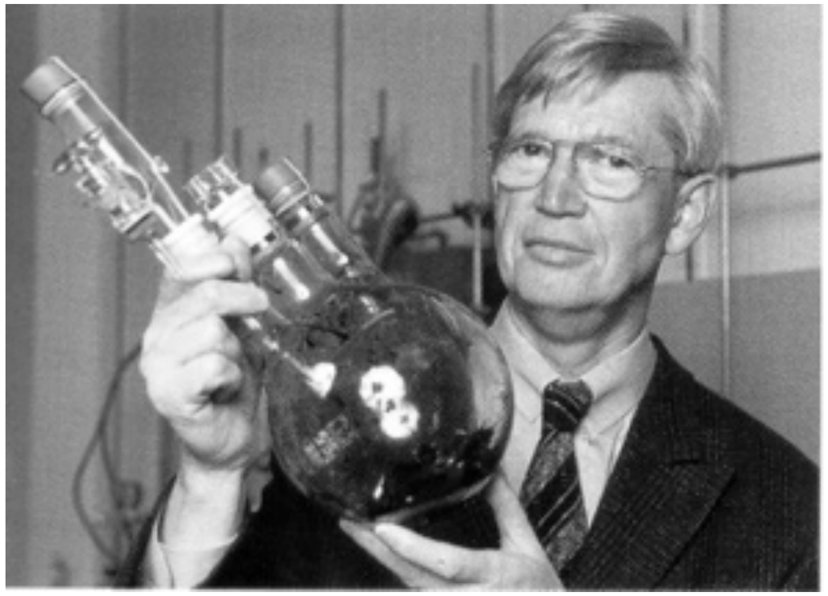
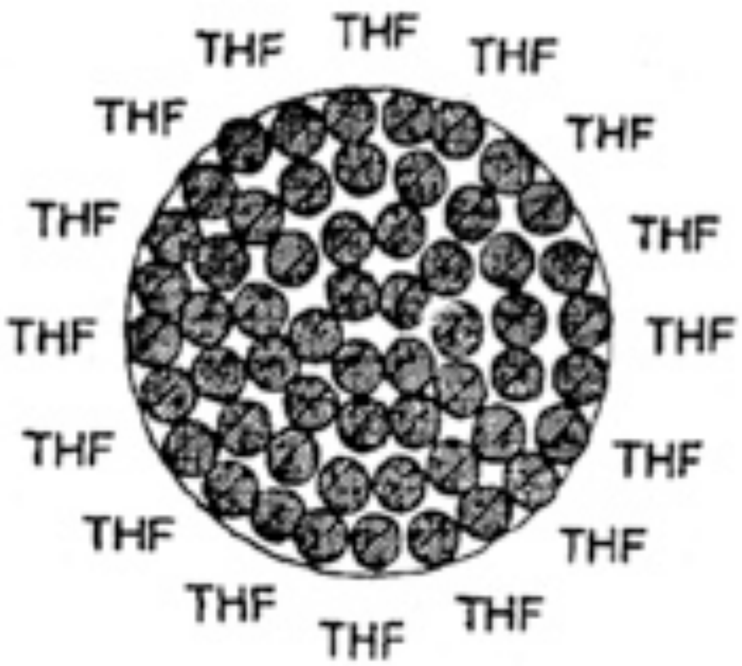
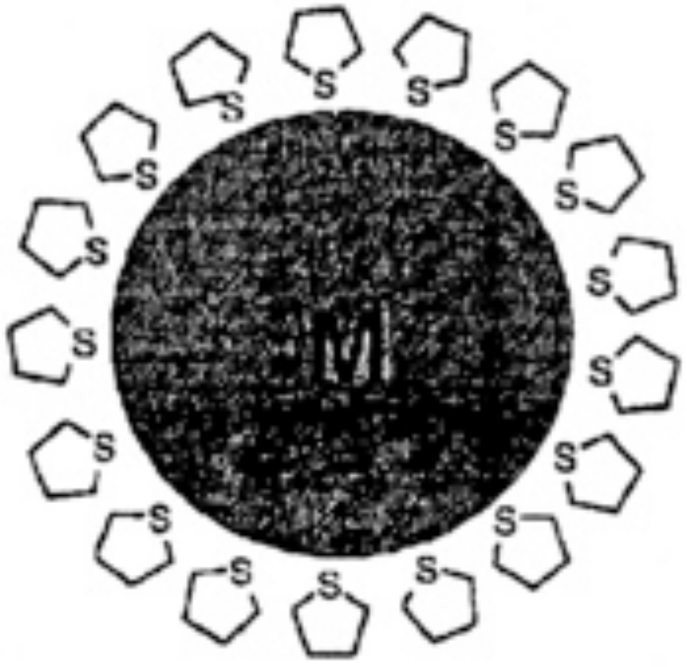
Bö nnemann's nanocluster systems

Synthesis







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Bo¨nnemann’s nanocluster systems

Synthesis

$$MX_v \xrightarrow[\text{ether},\ <50\ °C]{vNR_4(HBEt_3)} \text{ether}\cdot M\ (\text{cluster}) + vNR_4X + vBEt_3 + 0.5vH_2$$

Translatable strategy

Cr, Co, Mo, etc can all be made as stable cluster solutions

Ether is rather important for stability

Participate out under H_2 makes it ineffective catalyst

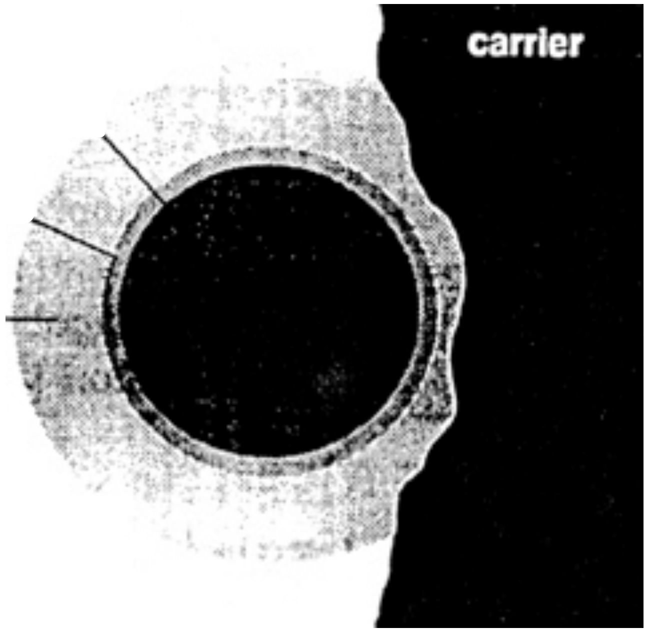
Frémont, P. d.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

Can we fix that?

Importance of support

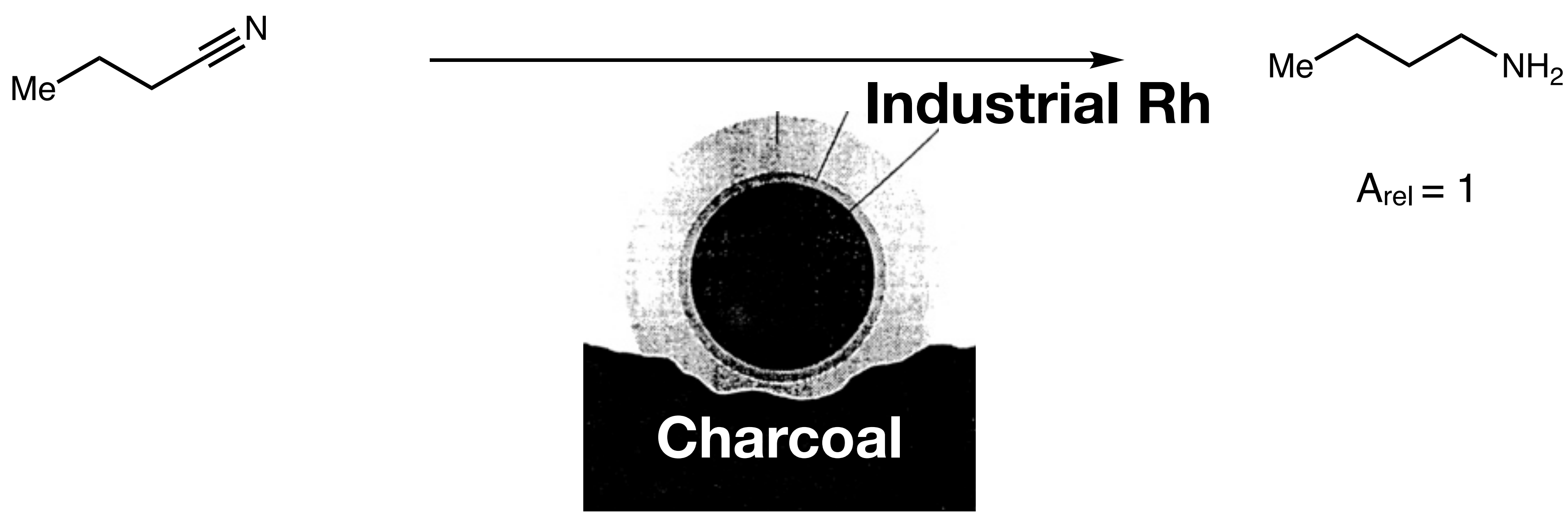
Support materials

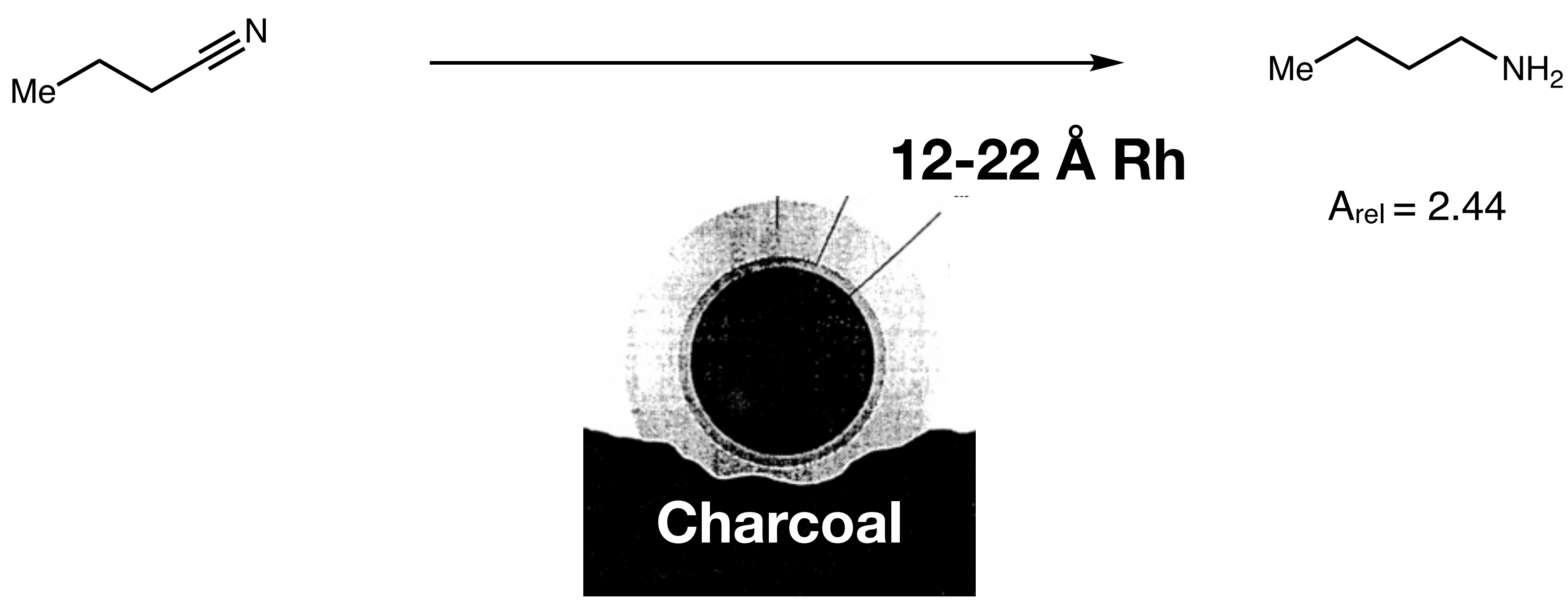
Dipping support in Cluster solutions



SMCs

SMCs play important role in heterogeneous catalysis

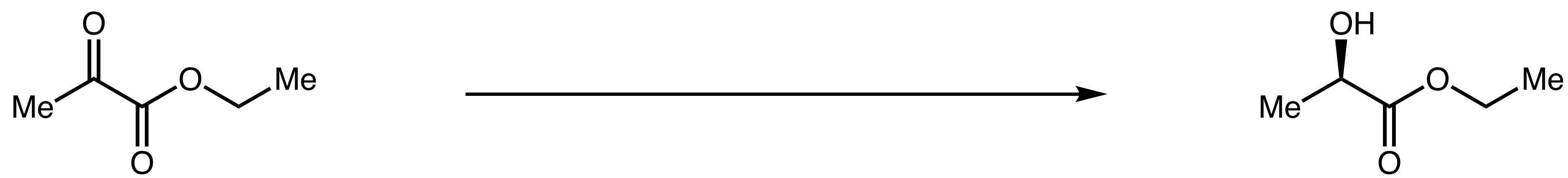




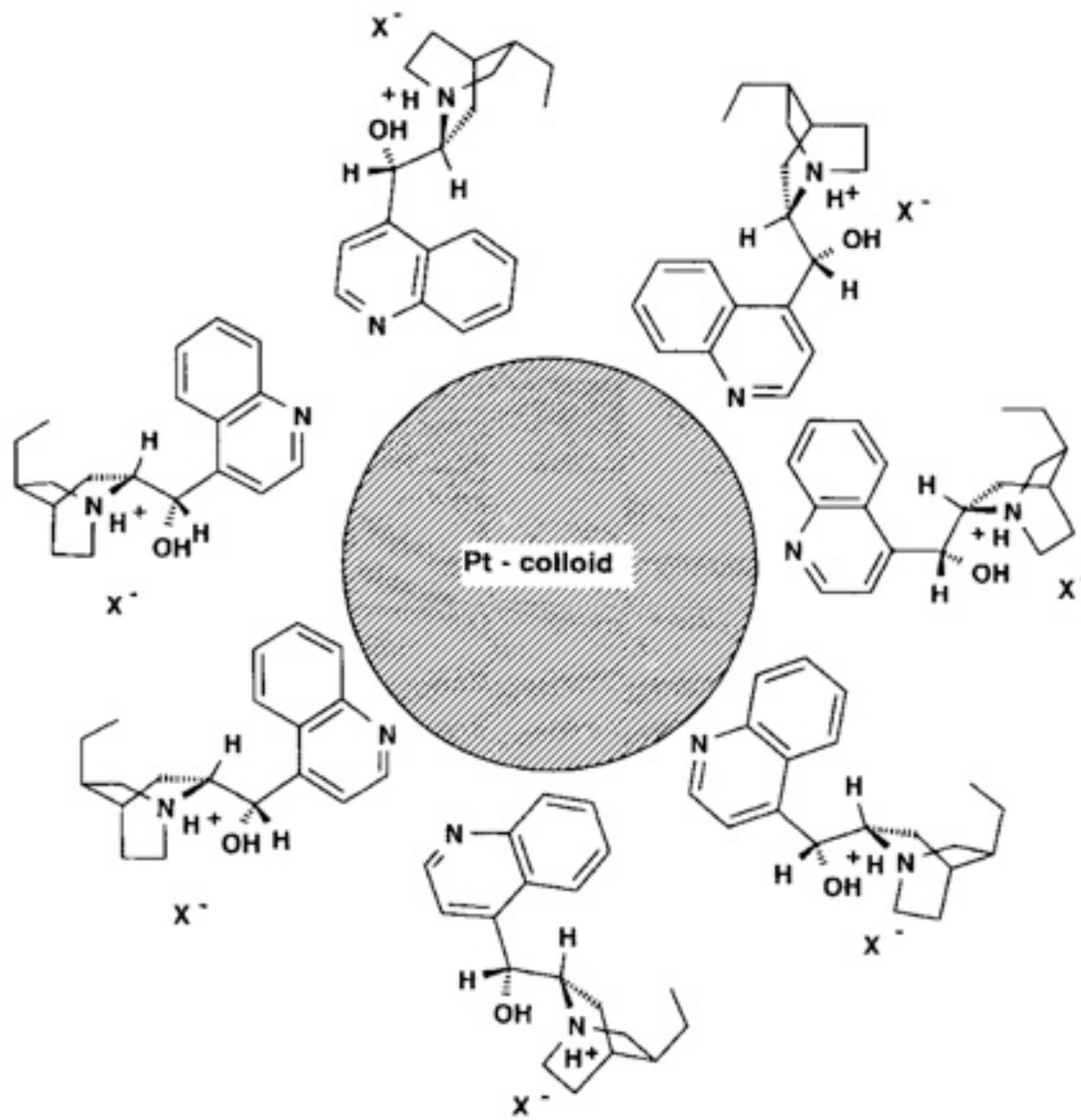
Supported clusters

Heterogeneous catalysis

By using chiral NR_4X in the synthesis asymmetric catalyst can be obtained



Up to 92% ee



Polyoxoanion- and tetrabutylammonium-stabilized transition-metal nanoclusters

Synthesis

Frémont, P. d.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

Polyoxoanion- and tetrabutylammonium-stabilized transition-metal nanoclusters

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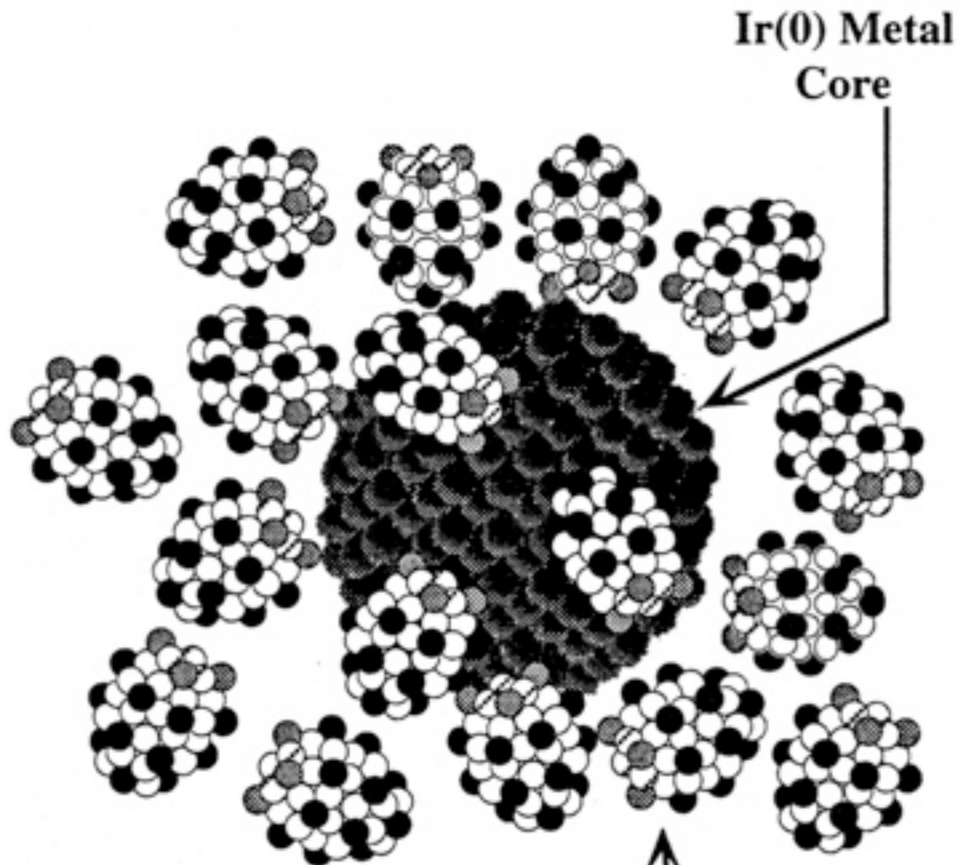

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Polyoxoanion- and tetrabutylammonium-stabilized transition-metal nanoclusters

Synthesis

$$300[(COD)Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-} \xrightarrow{750\ H_2} 300\ COD + Ir(0)_{300}\cdot 300(P_2W_{15}Nb_3O_{62})^{9-} + 300H^+$$

"Clean" metal cluster

Highly catalytically reactive

Counter ion is restricted

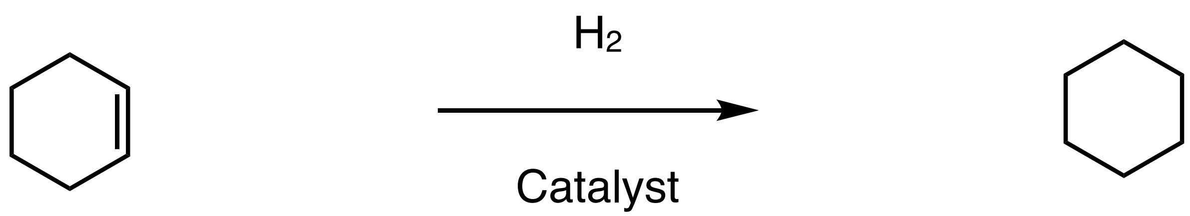
Rigerous air/moisure free synthesis required

Frémont, P. d.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862.

Iridium based hydrogenation catalysts

Very interesting observation

$$[(COD)Ir{\cdot}P_2W_{15}Nb_3O_{62}]^{8-} \xrightarrow{H_2} COD + Catalyst + 300H^+$$



TON > 1500

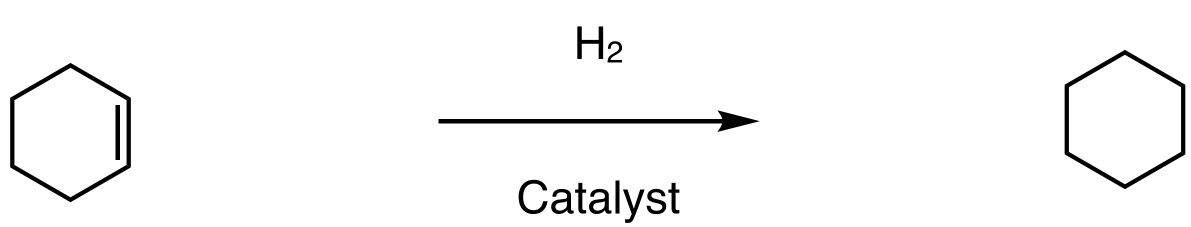
Iridium based hydrogenation catalysts

Very interesting observation

$$[(COD)Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-} \xrightarrow{H_2} COD + Catalyst + 300H^+$$

- 1 equiv of COD was generated in 10 hrs.
- Hydrogenation of cyclohexane has an induction period ~2 hrs
- After 6 hrs, only 45% of COD was generated but >85% of cyclohexane.

What’s happening here?



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$$[(COD)Ir\cdot P_2W_{15}Nb_3O_{62}]^{8-} \xrightarrow{H_2} COD + Catalyst + 300H^{+}$$

Only a small fraction of active catalyst is enough

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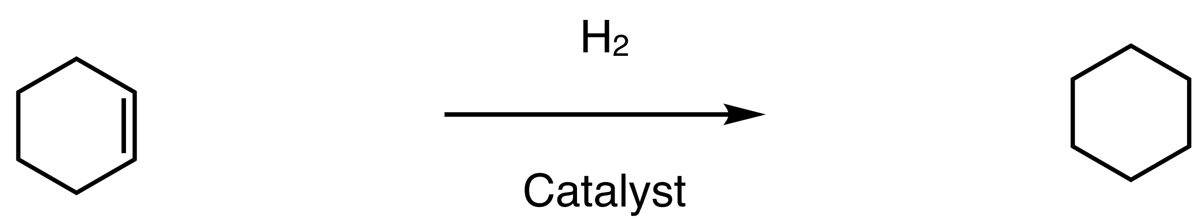

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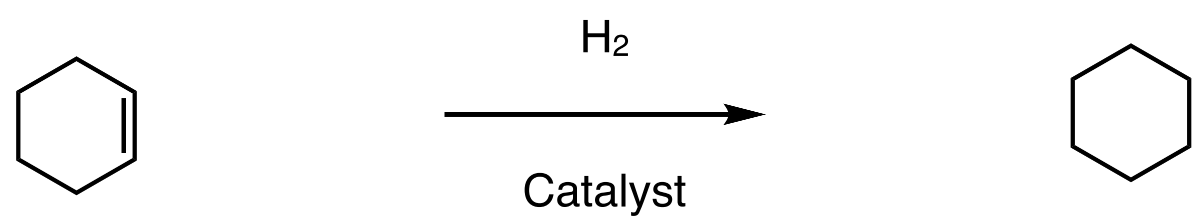
The active catalyst is catalyzing the catalyst formation



TON > 190000

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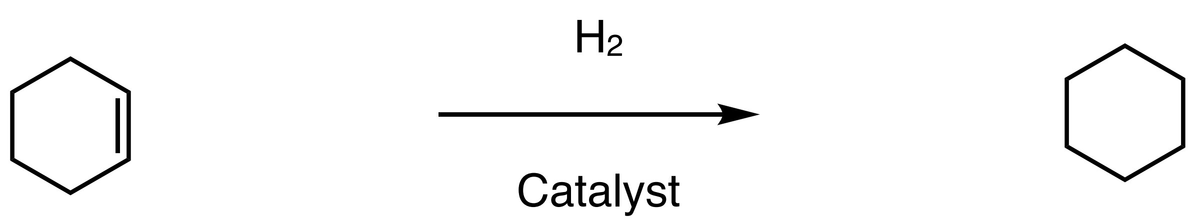


TON > 190000

Iridium based hydrogenation catalysts

Very interesting observation

Iridium based hydrogenation catalysts

Very interesting observation

$$x \left[A \xrightarrow{k_1} B \right]$$

Nucleation

Iridium based hydrogenation catalysts

Very interesting observation

$$x \left[A \xrightarrow{k_1} B \right]$$

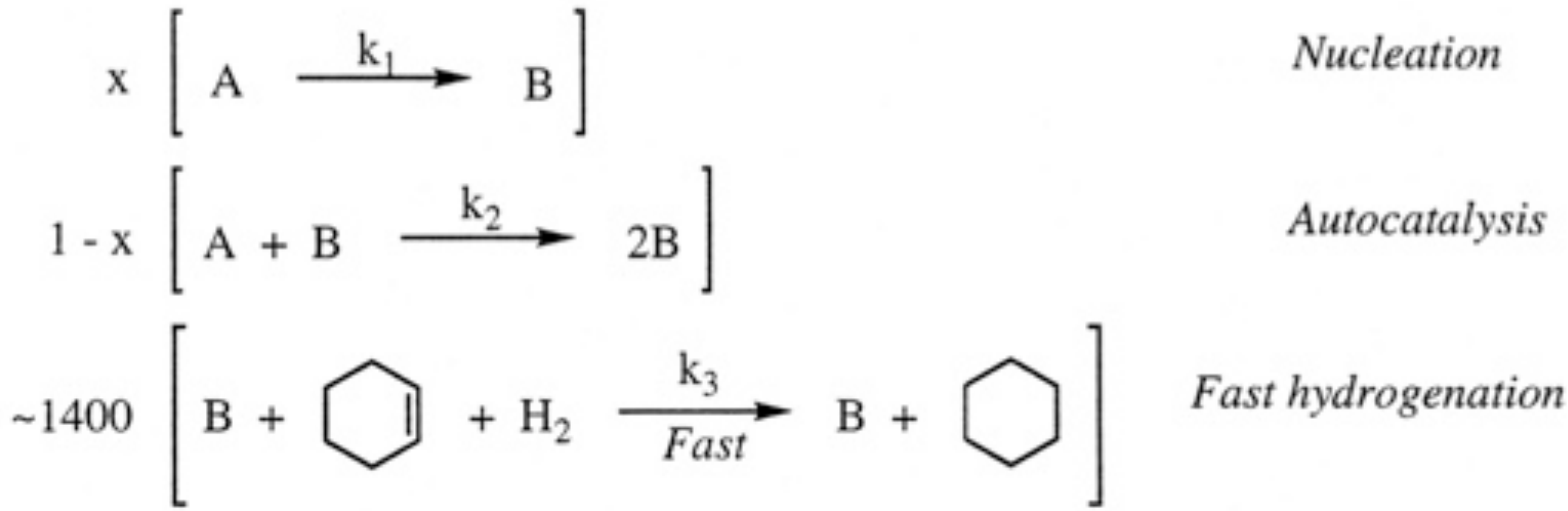
Nucleation

$$1 - x \left[A + B \xrightarrow{k_2} 2B \right]$$

Autocatalysis

Iridium based hydrogenation catalysts

Very interesting observation



Iridium based hydrogenation catalysts

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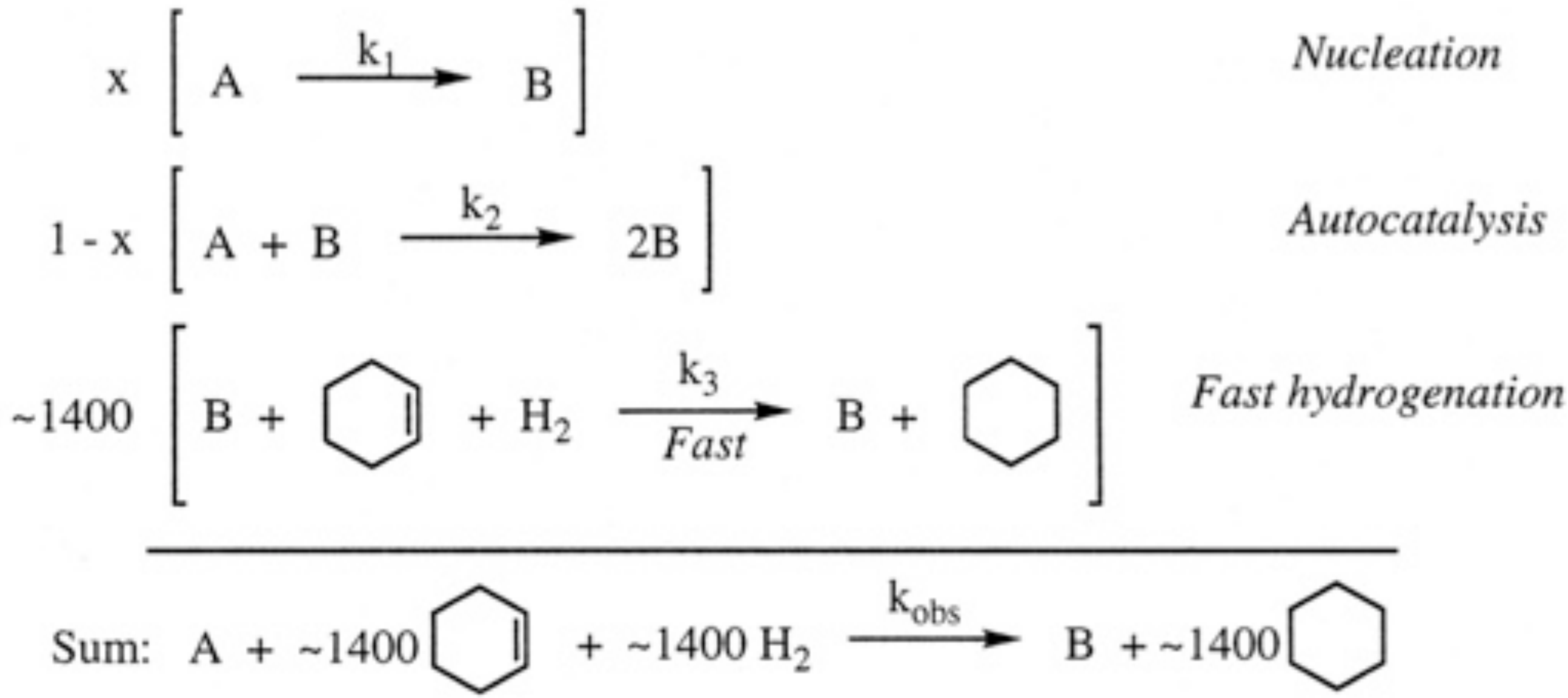
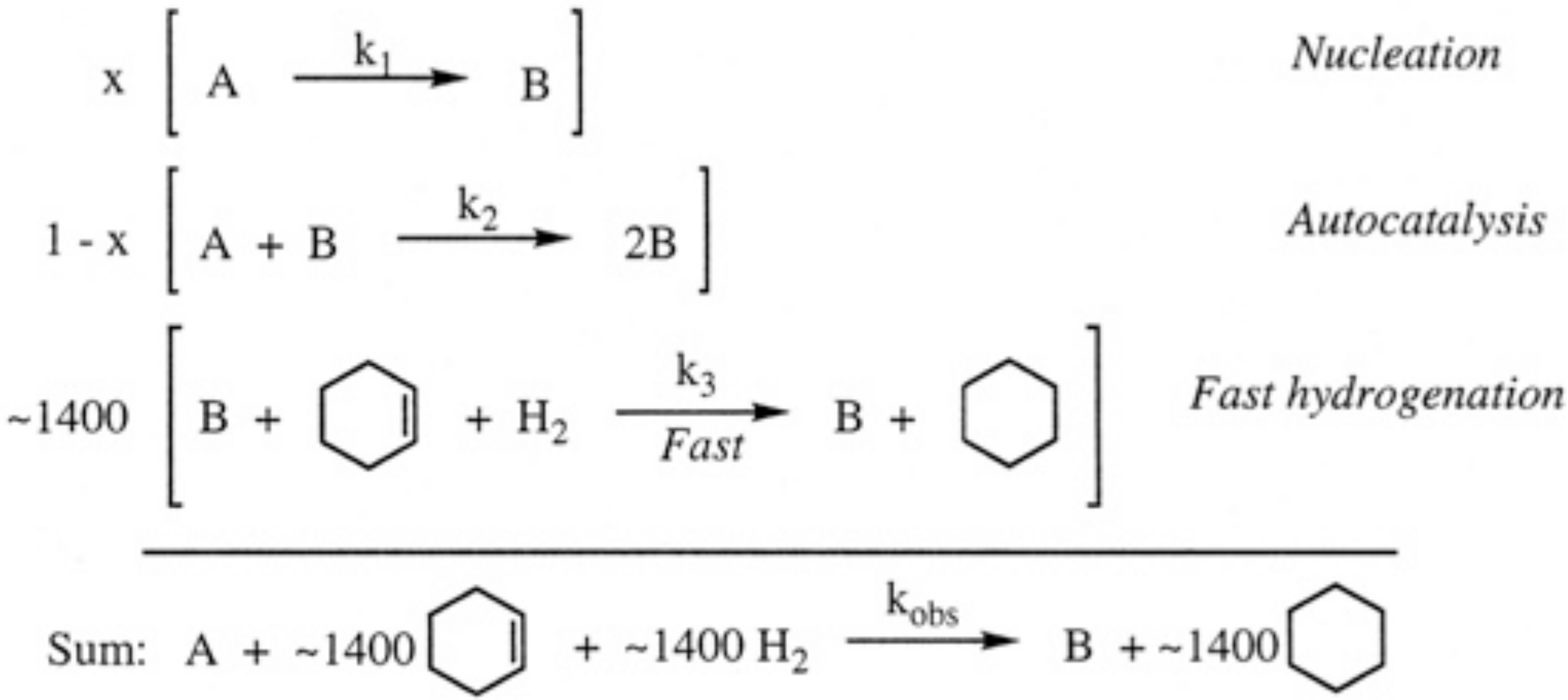


Auto catalysis enables fast turnover after induction period

Iridium based hydrogenation catalysts

Very interesting observation



Cluster Chemistry

Challenges- 4S

For more active, long-live, and selective catalysis

- Scalability

  -retaining isolability and catalytic activity remains challenging on gram scale synthesis.

- Stability

  -lack of physical chemical understanding lead to not having a general protocol to predict and synthesize stable clusters

- Synthesis

  -poor understanding of cluster formation kinetics needs to be improved to provide chemists with more controlled synthesis of clusters in particular size or shape.

- Single active site heterogeneous catalysts

  - Limiting a cluster to only one single active site to achieve theoretically 100% selectivity is one of the biggest promise of cluster chemistry to catalysis, methods of which to achieve that is still in the air.

Yu, A.; Choi, Y. H.; Tu, M. *Pharmacol Rev* **2020**, *72*, 862.

The yet to be explored chemical space in clusters may have treasures within

Yu, A.; Choi, Y. H.; Tu, M. *Pharmacol Rev* **2020**, *72*, 862.