

# Novel Inorganic Rings and Materials Deposition

Paul O'Brien

Professor of Inorganic Materials  
in the Manchester Materials Science Centre  
and the School of Chemistry,  
University of Manchester,  
Head School of Chemistry.

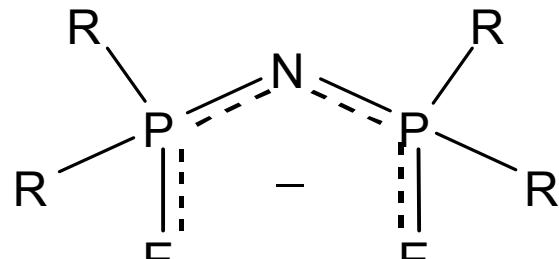
# Plan for the Lecture

*'Using Chemistry to Control Material Deposition: why choose to use a chemical method ?'*

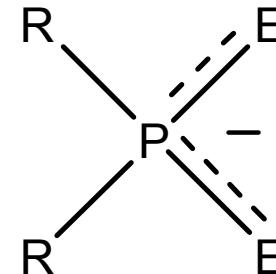
- **Introduction- the inorganic ring systems we have studied**
- Dichalcogenoimidodiphosphinates
- An Introduction to CVD
- Dithio and Diseleno-phosphinates
- New routes to selenohosphinates
- CIGS systems
- Shapes of nanoparticles

# Ligands

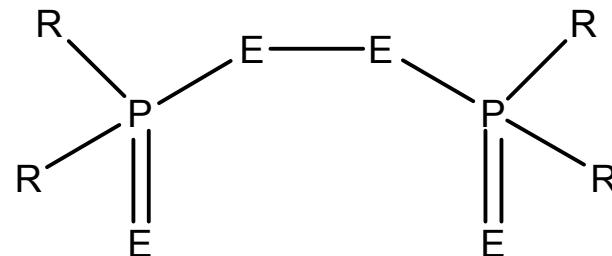
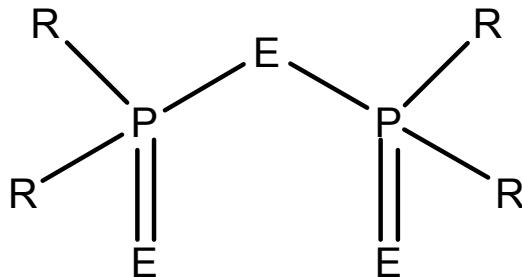
- Dichalcogenoimidodiphosphinates
- Dichalcogenophosphinates



R =  $\text{^iPr}$ ; E = S, Se, Te



R =  $\text{^iPr}$ , Ph,  $\text{^tBu}$ ; E = S, Se



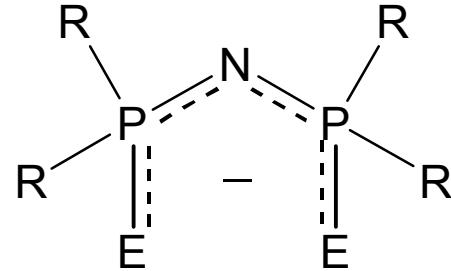
R =  $\text{^iPr}$ , Ph ; E = Se

# Plan for the Lecture

*'Using Chemistry to Control Material Deposition: why choose to use a chemical method ?'*

- **Introduction- the inorganic ring systems we have studied**
- **Dihalcogenoimidodiphosphinates**
- An Introduction to CVD
- Dithio and Diseleno-phosphinates
- New routes to selenohosphinates
- CIGS systems
- Shapes of nanoparticles

# Dichalcogenoimidodiphosphinate Ligands



1 E = O

2 E = S

3 E = Se

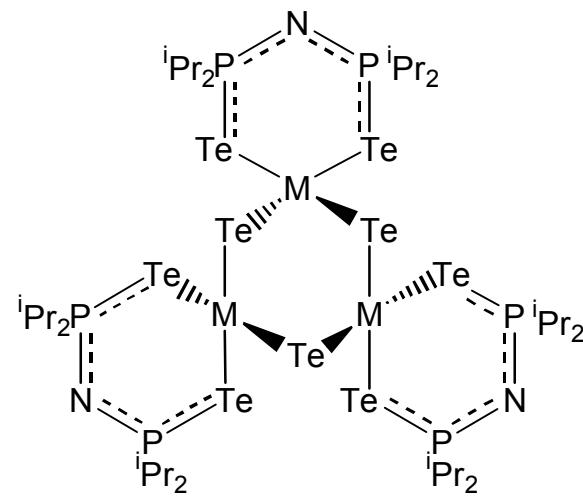
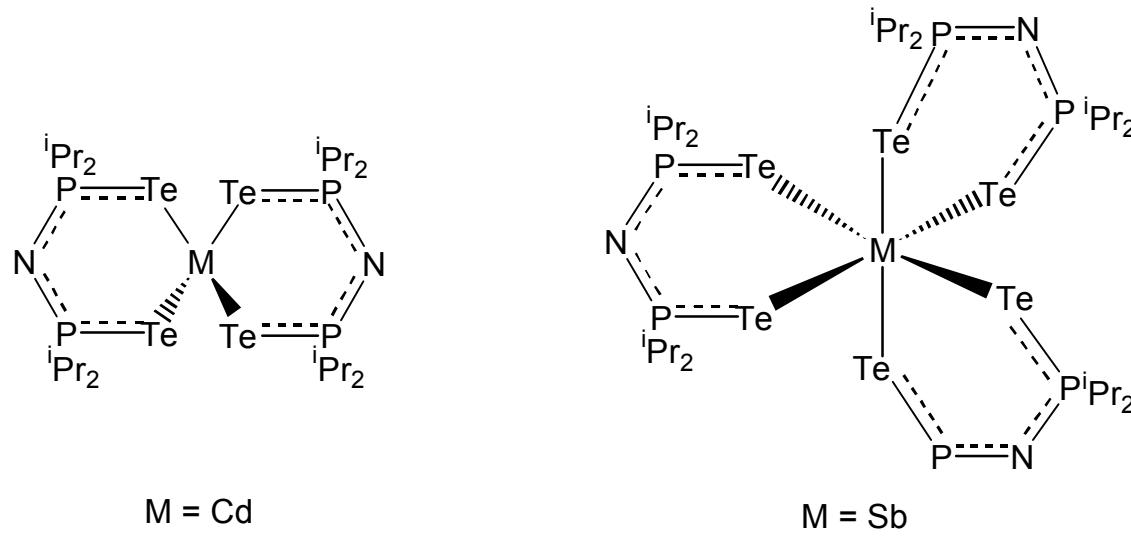
4 E = Te

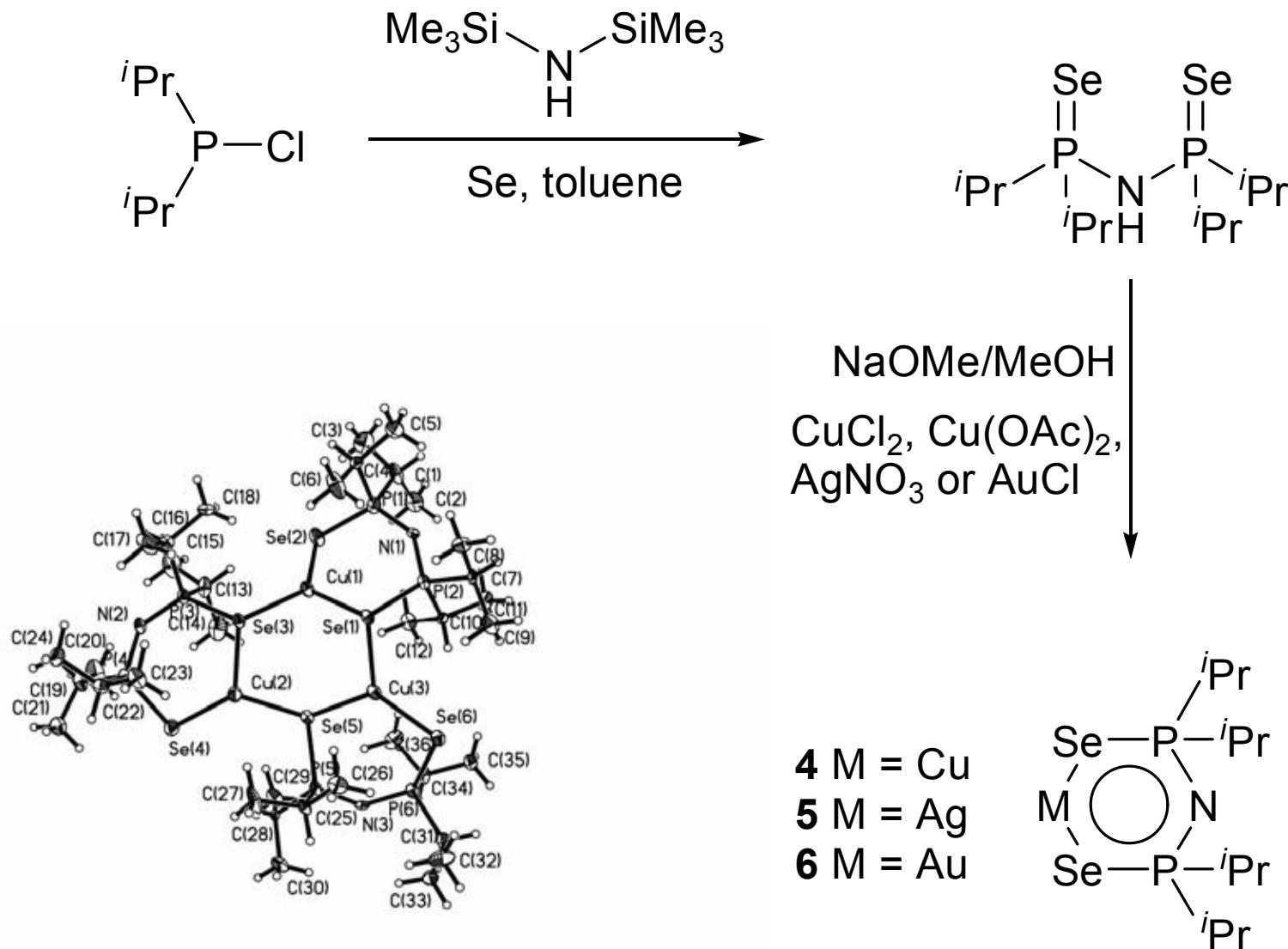
a R = Ph

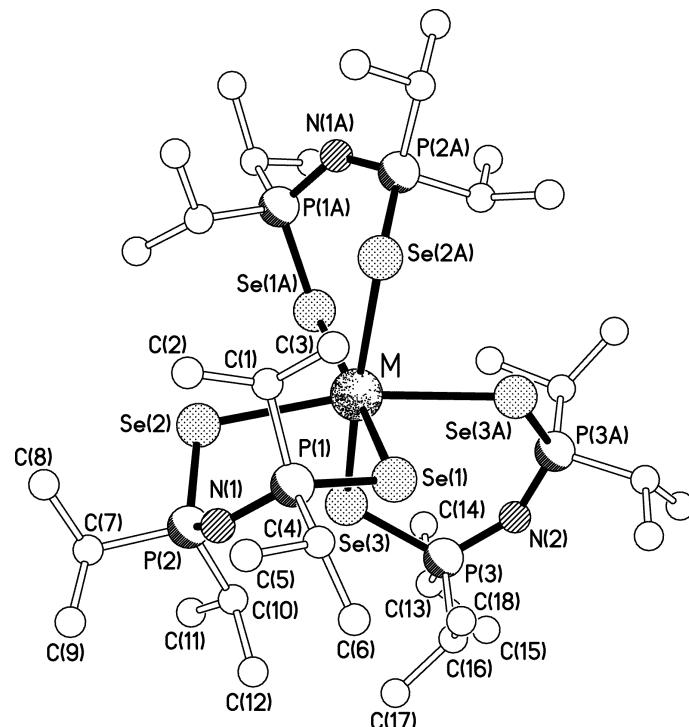
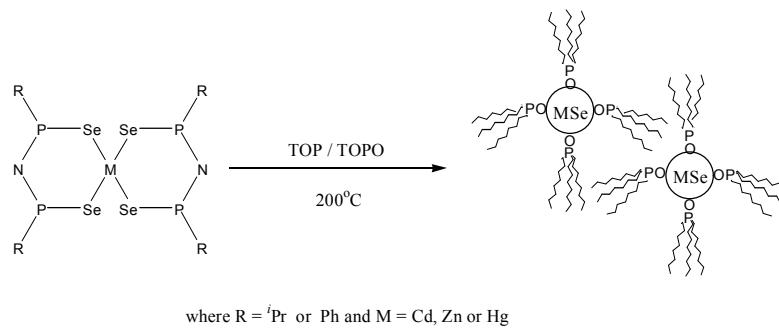
b R = <sup>i</sup>Pr



- a) A. Schmidpeter, H. Groeger, Z. Anorg. Allg. Chem. 1966, 345, 106.
- b) G. G. Briand, T. Chivers and M. Parvez, Angew. Chem. Int. Ed., 2002, 41, 3468.
- c) M. Ellermann, M. Schtz, F. W. Heinemann, M. Moll, Z. Anorg. Allg. Chem. 1998, 624, 257.
- d) D. Cupertino, D. J. Birdsall, A. M. Z. Slawin, J. D. Woollins, Inorg. Chim. Acta, 290, 1, 1999.

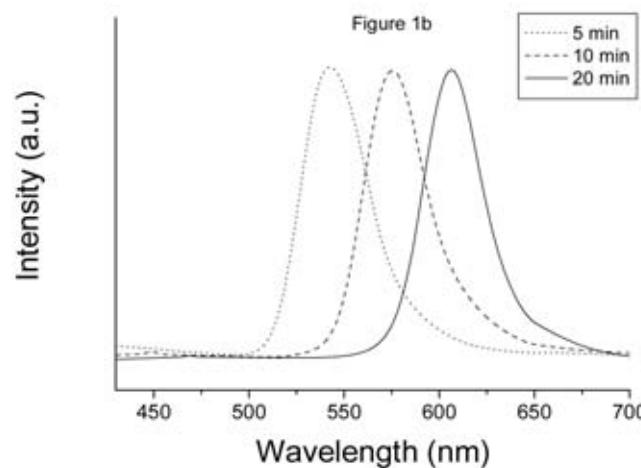






D.J.Crouch, P. O'Brien, M.A.Malik, P.J.Skabara and S.P. Wright, *Chem. Comm.*, 2003 1454.

- Efficient synthesis of “air-stable” M [N(SePR<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (yields 95-99%).
- Reaction can be scaled up (~25g) without loss to quality/yield.
- “Dot” synthesis is convenient and efficient.



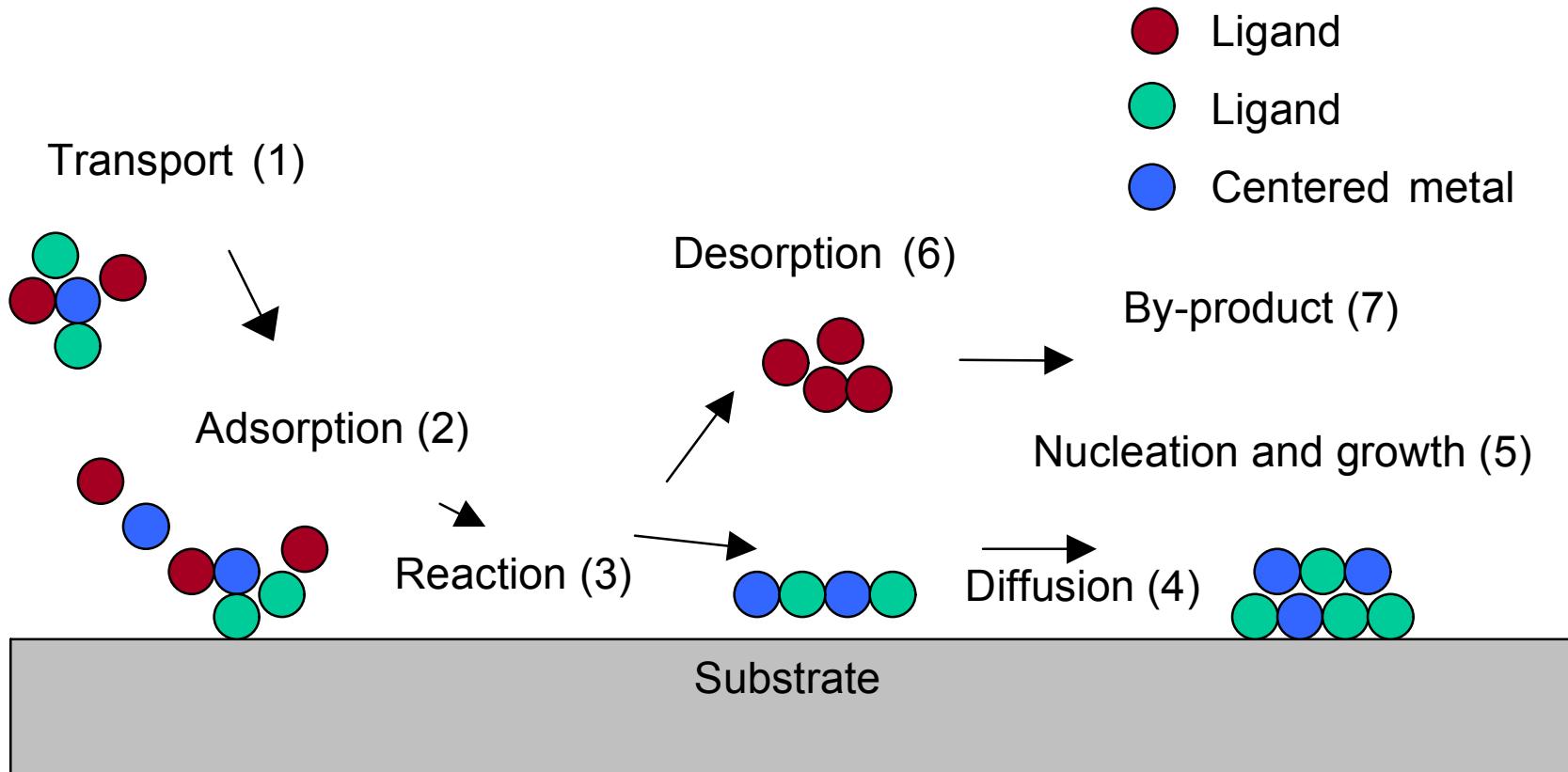
## PL of CdSe by Thermolysis of Cd[N(SeP*i*Pr<sub>2</sub>)<sub>2</sub>]<sub>2</sub>

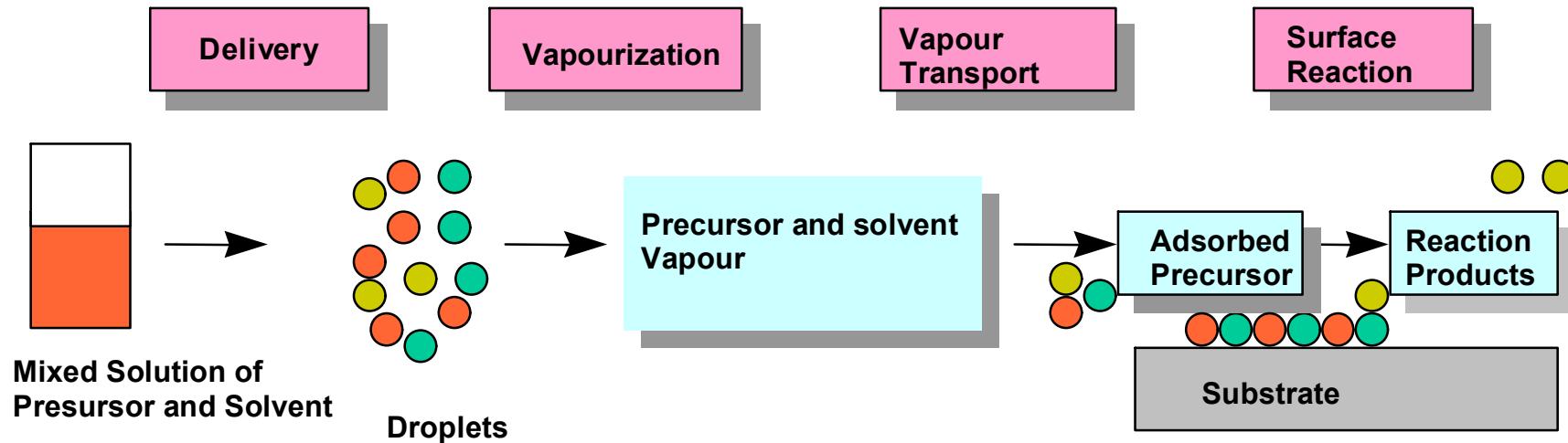
# Plan for the Lecture

*'Using Chemistry to Control Material Deposition: why choose to use a chemical method ?'*

- **Introduction- the inorganic ring systems we have studied**
- **Dihalogenoimidodiphosphinates**
- **An Introduction to CVD**
- Dithio and Diseleno-phosphinates
- New routes to selenohosphinates
- CIGS systems
- Shapes of nanoparticles

# The CVD Process





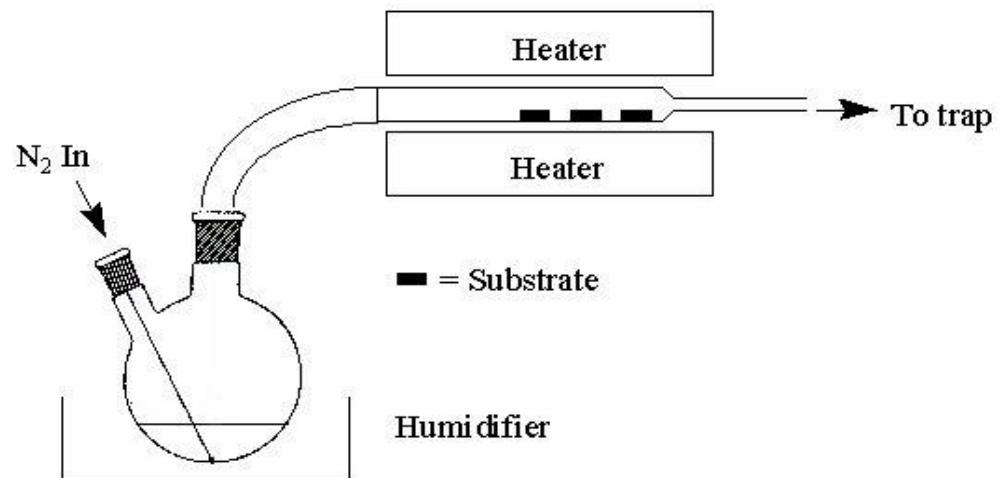
(1)

(2)

(3)

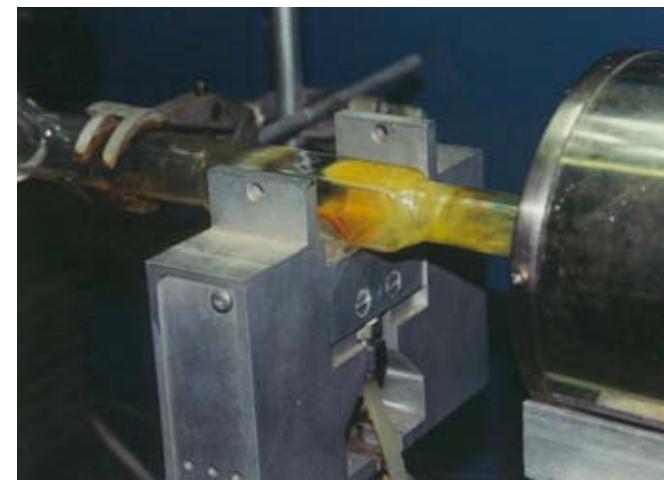
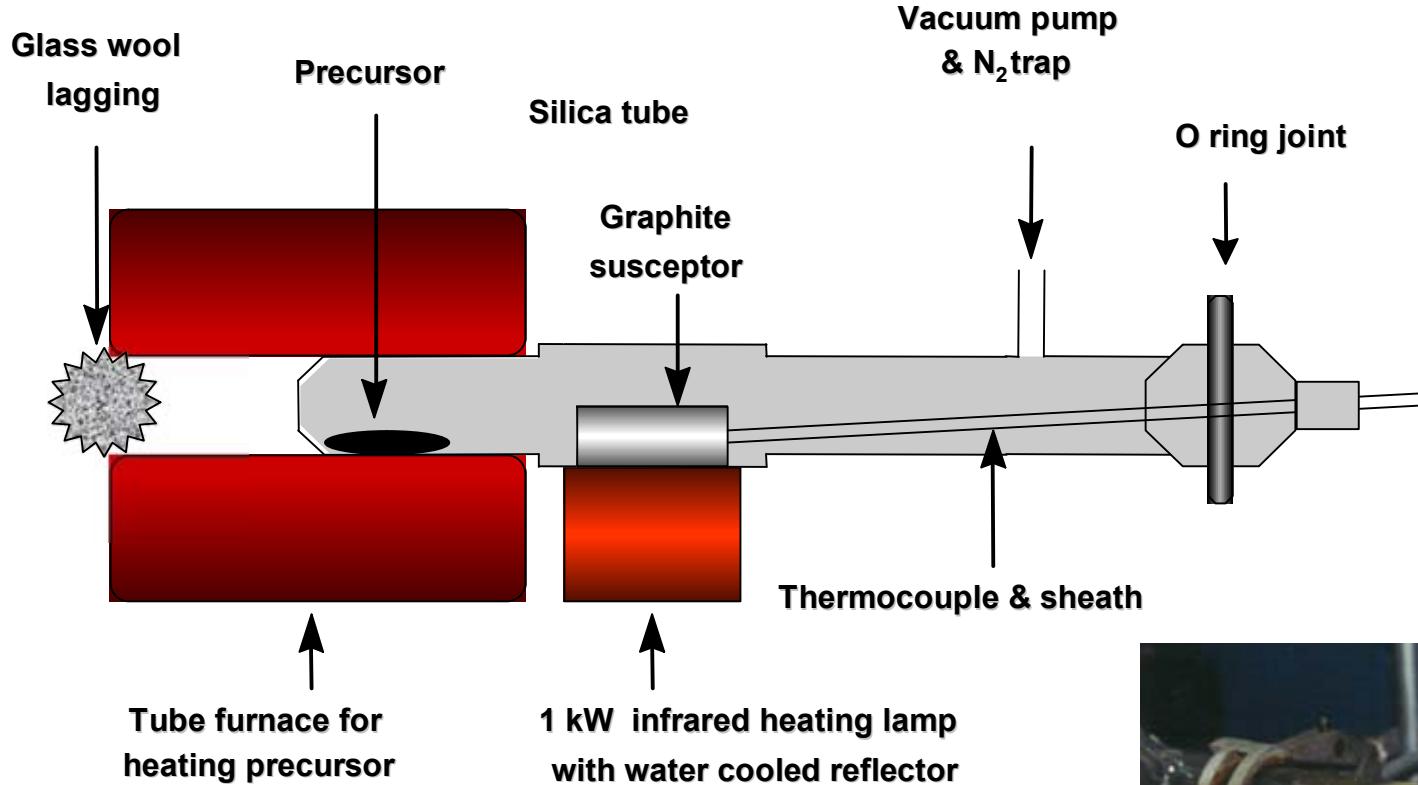
(4)

AACVD KIT



# The AA-CVD Process

# Low-pressure CVD

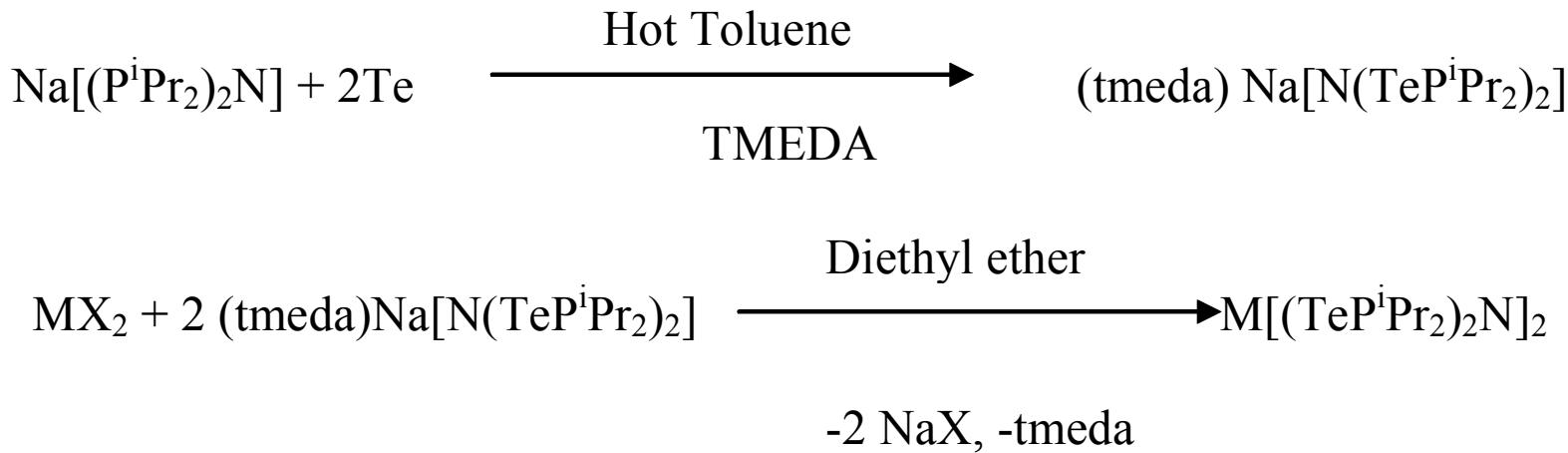


# What makes for a good precursor?

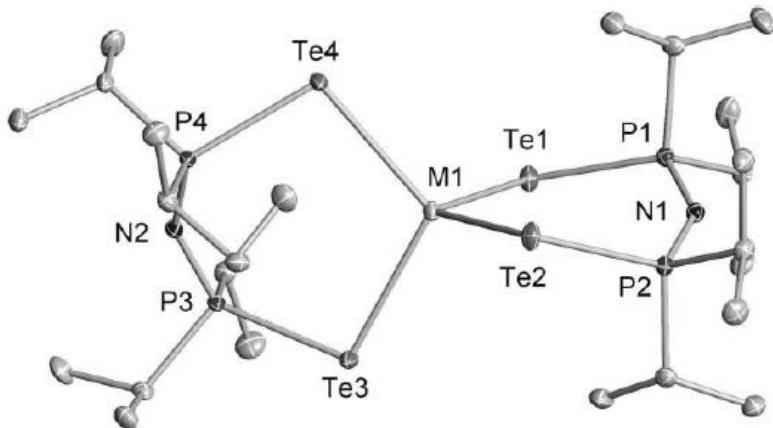
- Volatility
- Clean decomposition
- Stability under delivery conditions
- Compatibility with other precursors
- Freedom from adventitious impurities

## Conventional route

- Highly toxic and/or oxygen or moisture sensitive gases e.g.  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ ,  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{SiH}_4$  etc.
- Environment and safety conditions: particularly important for industrial processes.



$\text{M} = \text{Cd}$  (**1**),  $\text{X} = \text{I}$ ;  $\text{M} = \text{Hg}$  (**2**),  $\text{X} = \text{Cl}$ , tmeda = tetramethylethanediamine

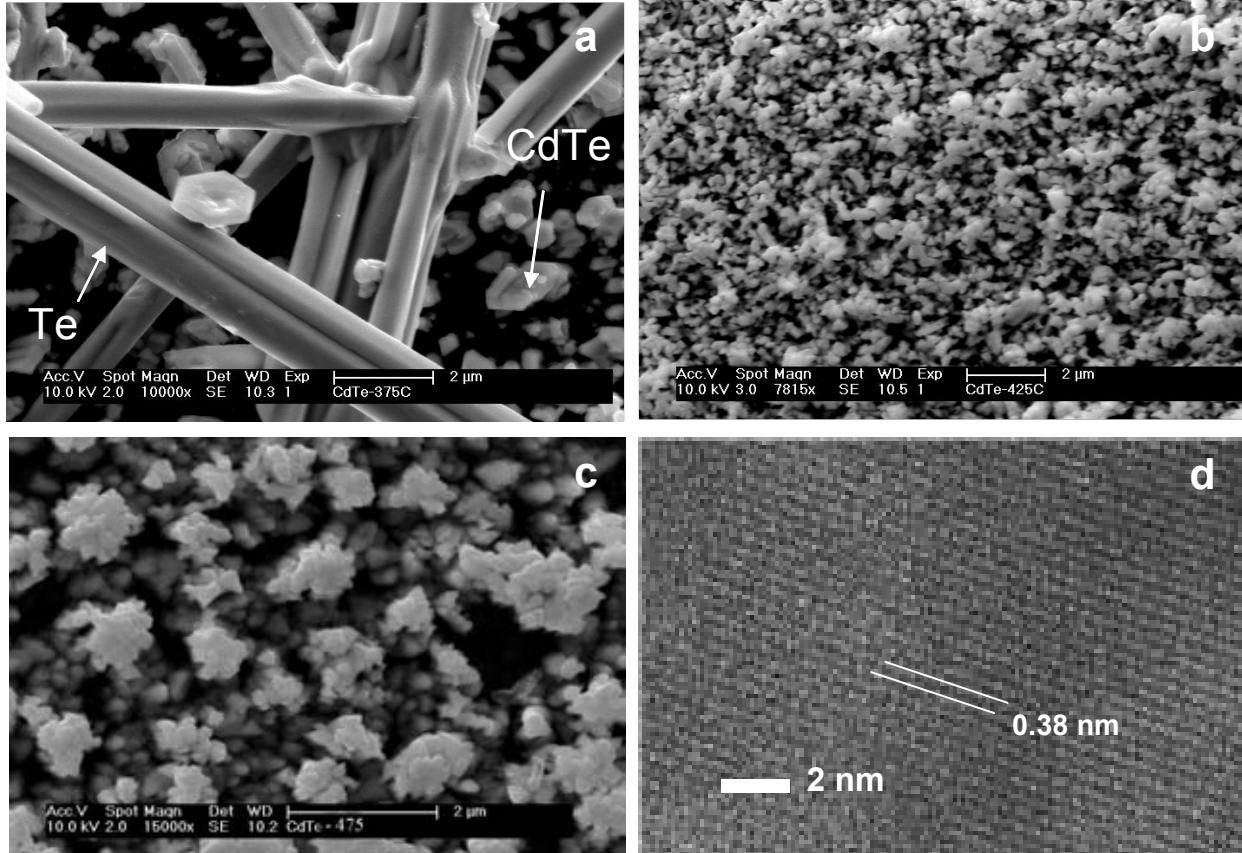


**Fig. 1** Thermal ellipsoid plot (30% probability) of the structure of **2a** ( $\text{M} = \text{Zn}$ ), **2b** ( $\text{M} = \text{Cd}$ ) and **2c** ( $\text{M} = \text{Hg}$ ). Hydrogen atoms have been omitted for clarity.

**Synthesis and structures of  $\text{M}[\text{N}(\text{TeP}^{\text{i}}\text{Pr}_2)_2-\text{Te},\text{Te}']_n$  ( $n = 2$ ,  $\text{M} = \text{Zn}, \text{Cd}, \text{Hg}; n = 3, \text{M} = \text{Sb}, \text{Bi}$ ): the first ditelluroimidodiphosphinato p- and d-block metal complexes**

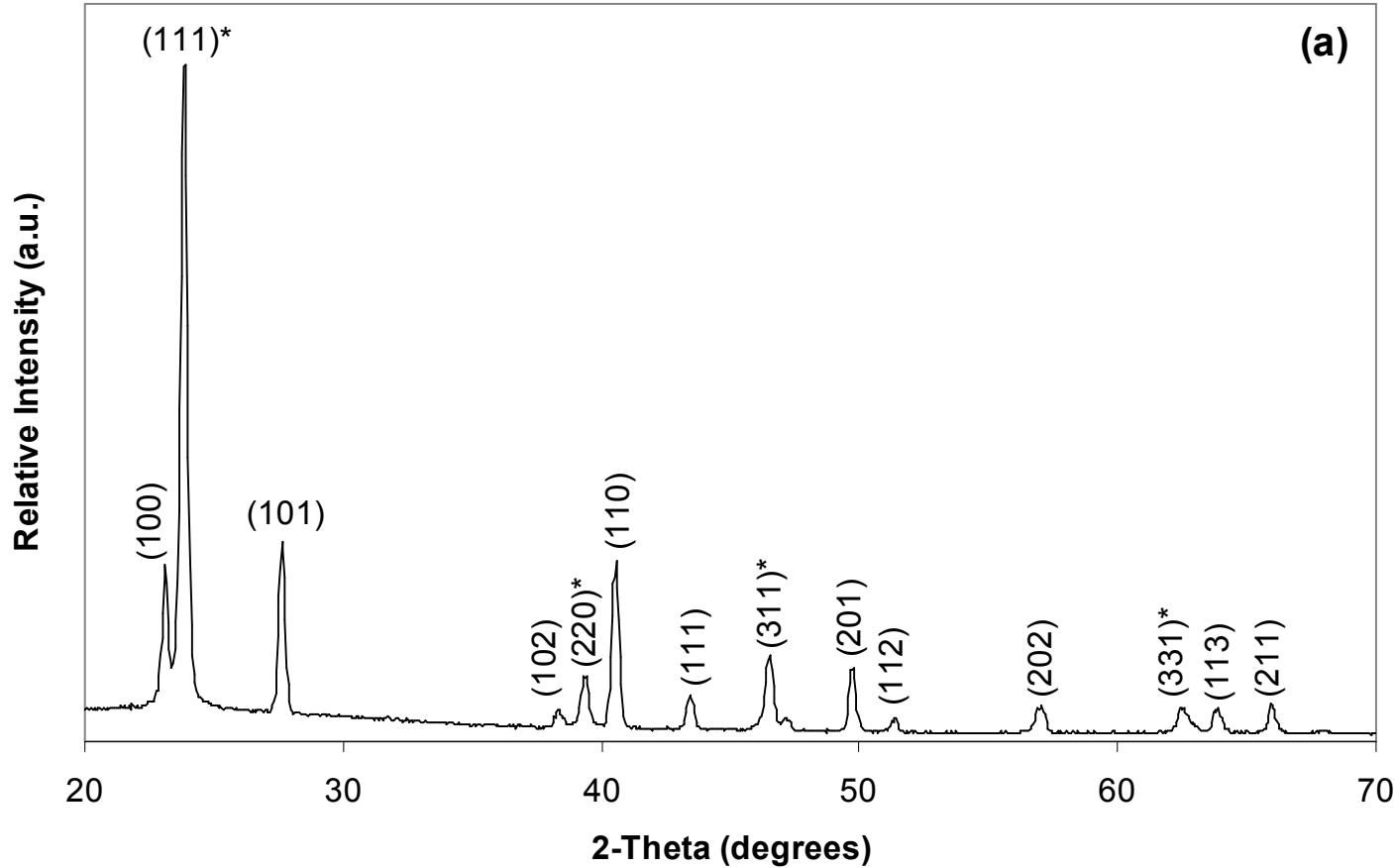
Tristram Chivers,\* Dana J. Eisler and Jamie S. Ritch

Department of Chemistry, University of Calgary, Calgary, AB, Canada T2N 1N4.  
E-mail: chivers@ucalgary.ca; Fax: (+1)403-289-9488; Tel: (+1)403-220-5741

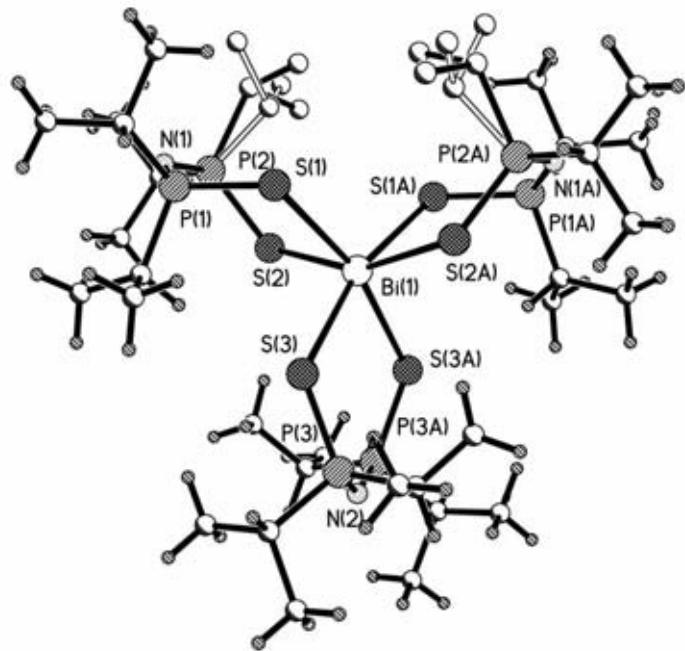


SEM of (a) CdTe and Te deposited at 375°C;

CdTe deposited at (b) 425°C, (c) 475°C; (d) HRTEM of film deposited at 475°C.



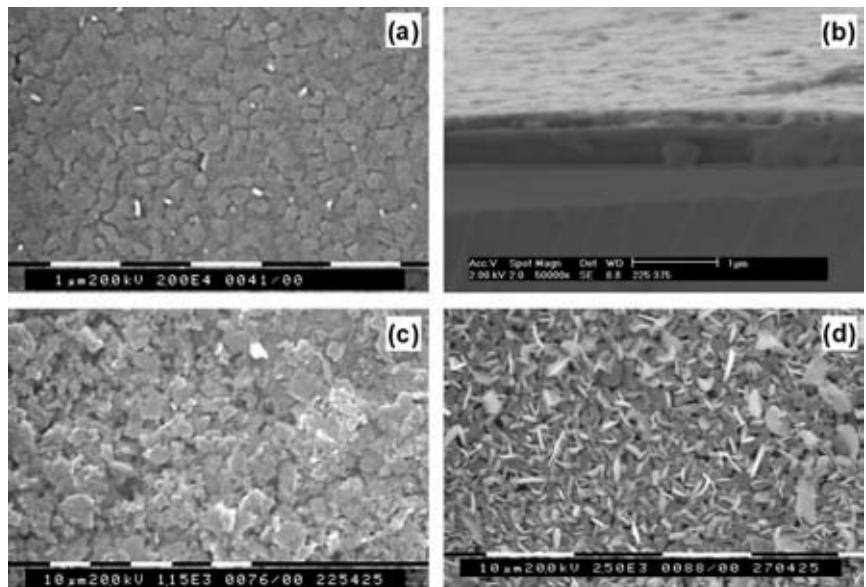
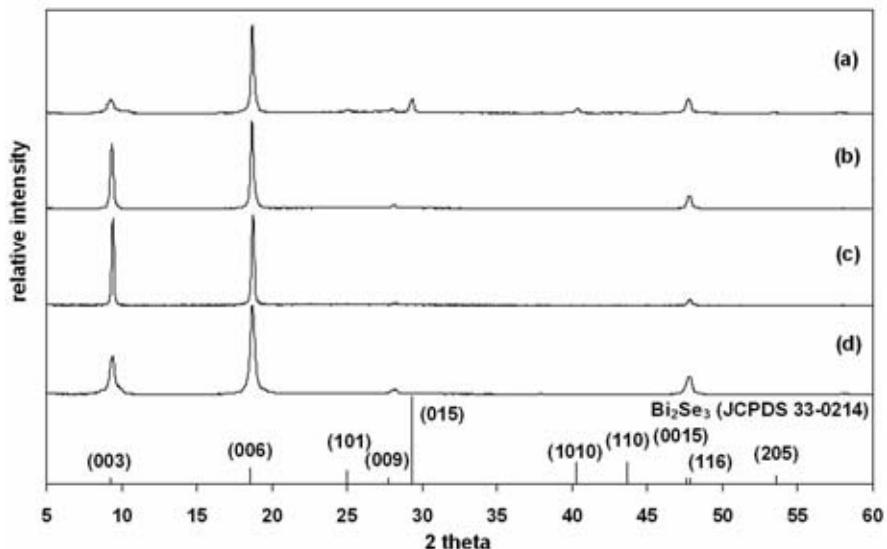
Cubic CdTe marked with asterisk and Hexagonal Te film

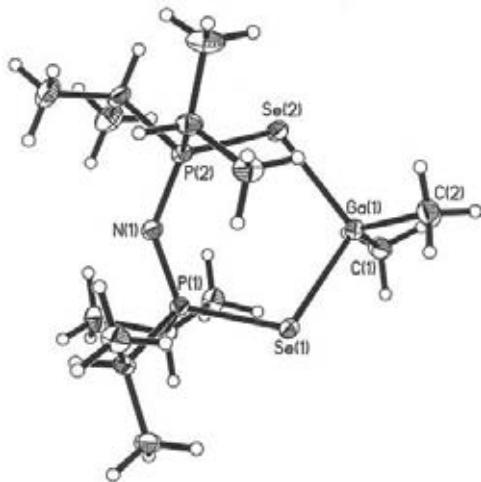


films grown by LP-MOCVD of

$\text{Bi}[(\text{SeP}(\text{Pr})_2)_2\text{N}]_3$  at

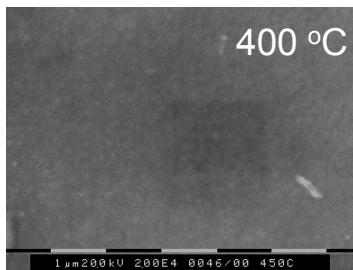
- (a)  $T_{\text{prec}} = 275^\circ\text{C}$ ,  $T_{\text{subs}} = 425^\circ\text{C}$ ,
- (b)  $T_{\text{prec}} = 225^\circ\text{C}$ ,  $T_{\text{subs}} = 425^\circ\text{C}$ ,
- (c)  $T_{\text{prec}} = 225^\circ\text{C}$ ,  $T_{\text{subs}} = 400^\circ\text{C}$ ,
- (d)  $T_{\text{prec}} = 225^\circ\text{C}$ ,  $T_{\text{subs}} = 375^\circ\text{C}$ .



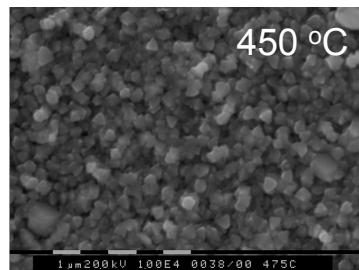


$\xrightarrow{\text{LP-MOCVD}}$   
 $\text{Pre Temp} = 185^\circ\text{C}$

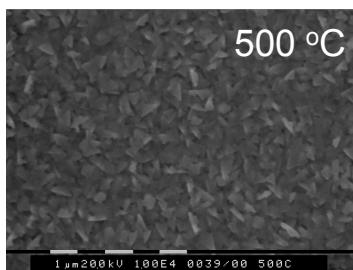
**Cubic  $\text{Ga}_2\text{Se}_3$**



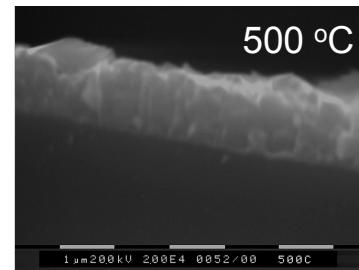
$400^\circ\text{C}$



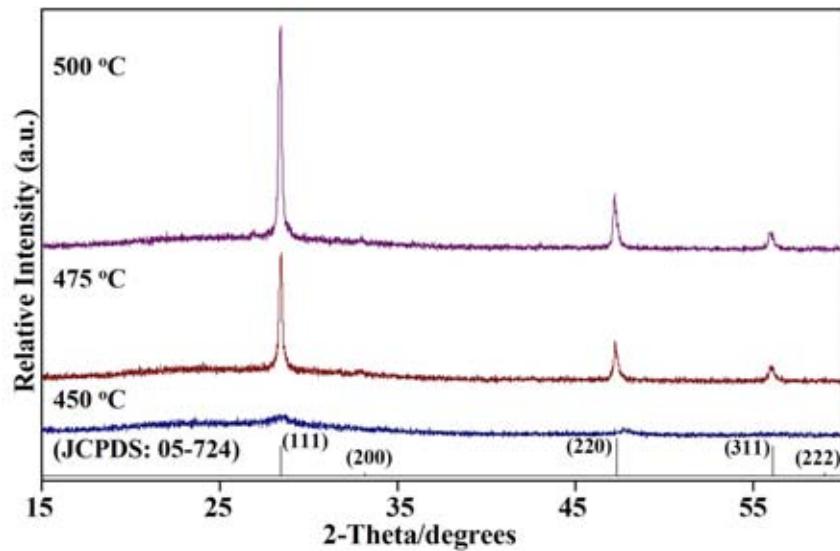
$450^\circ\text{C}$



$500^\circ\text{C}$

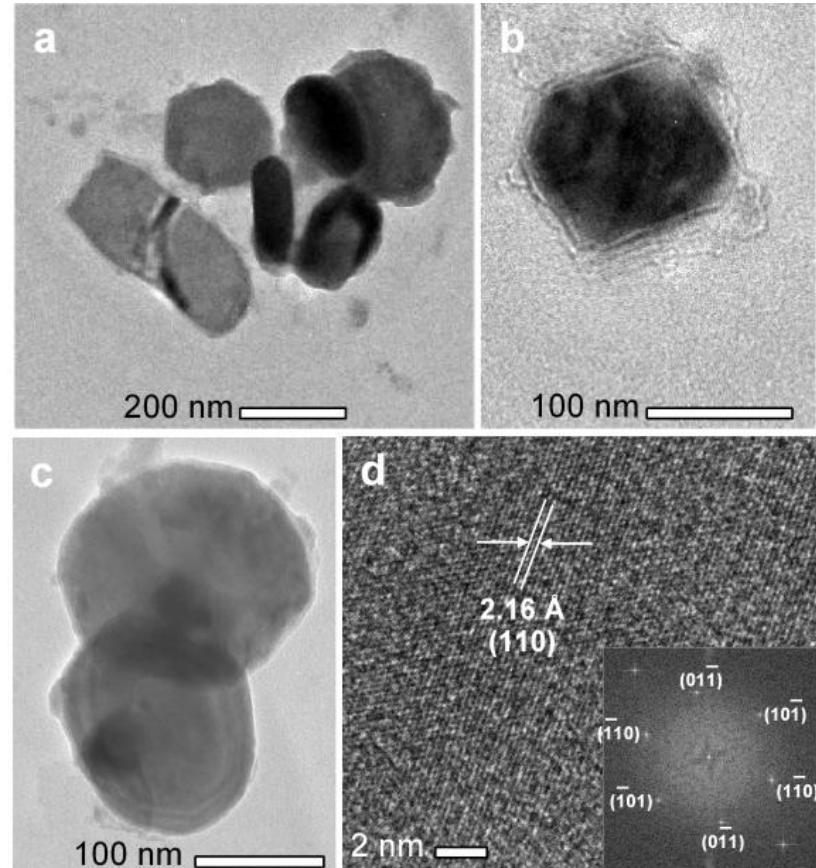
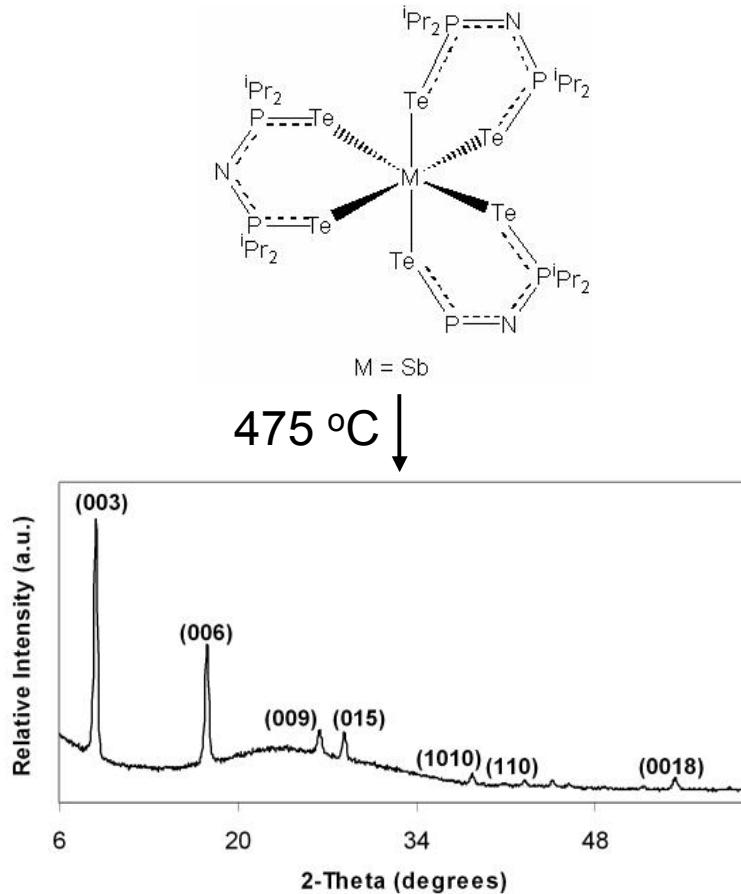


$500^\circ\text{C}$

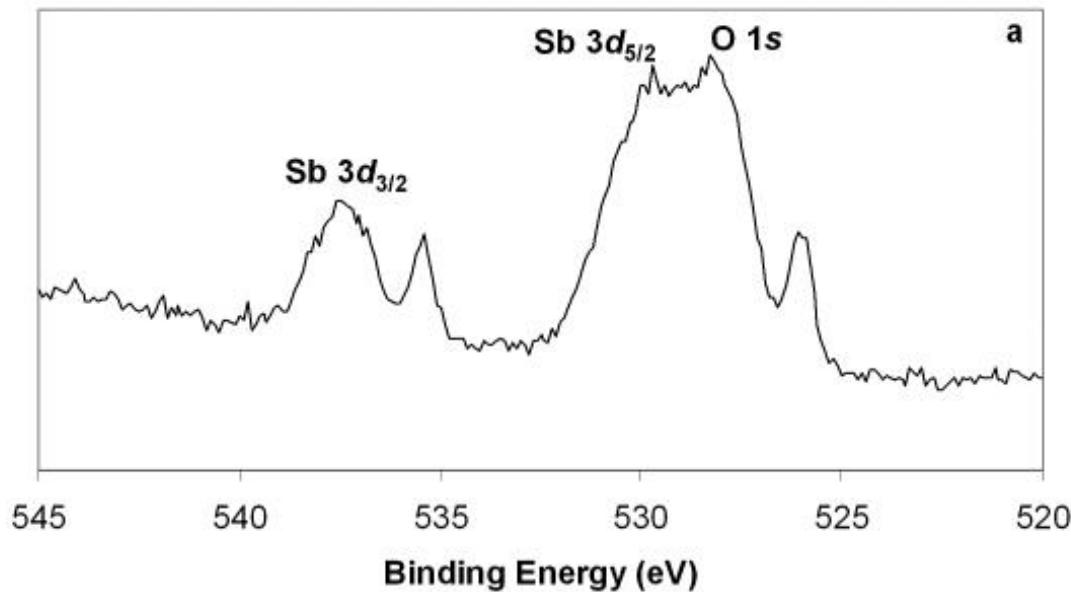


# AACVD studies of Sb[(TeP*i*Pr<sub>2</sub>)<sub>2</sub>N]<sub>3</sub>

- pXRD of rhombohedral Sb<sub>2</sub>Te<sub>3</sub> thin films at 475 °C with a dynamic argon flow rate of 240 sccm.

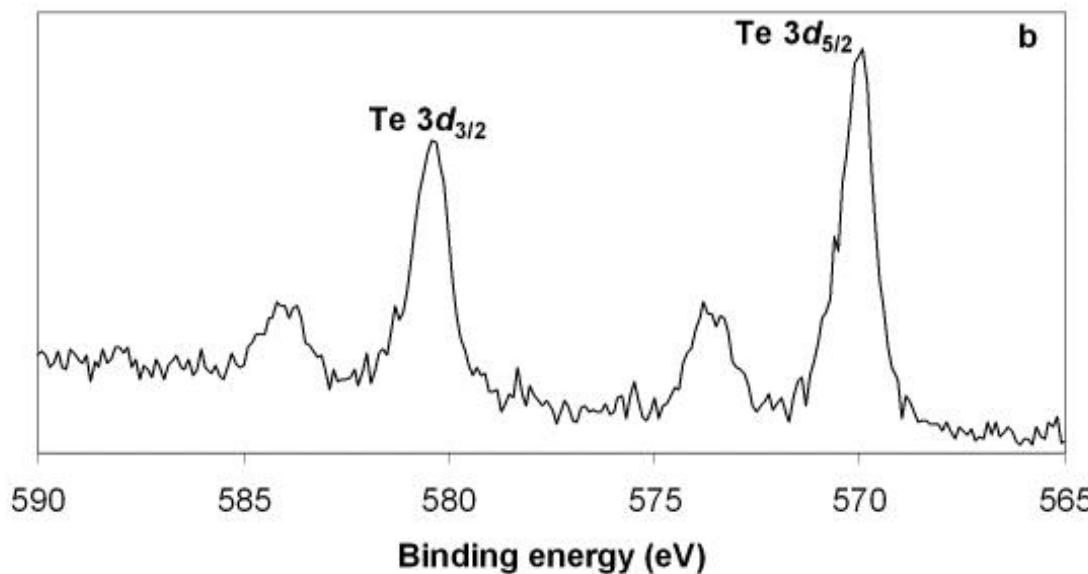


S. S. Garje, D. J. Eisler, J. S. Ritch, M. Afzaal, P. O'Brien, and T. Chivers, *J. Am. Chem. Soc.*, 2006, 128, 3120.



Relatively Intensity (a.u.)

a

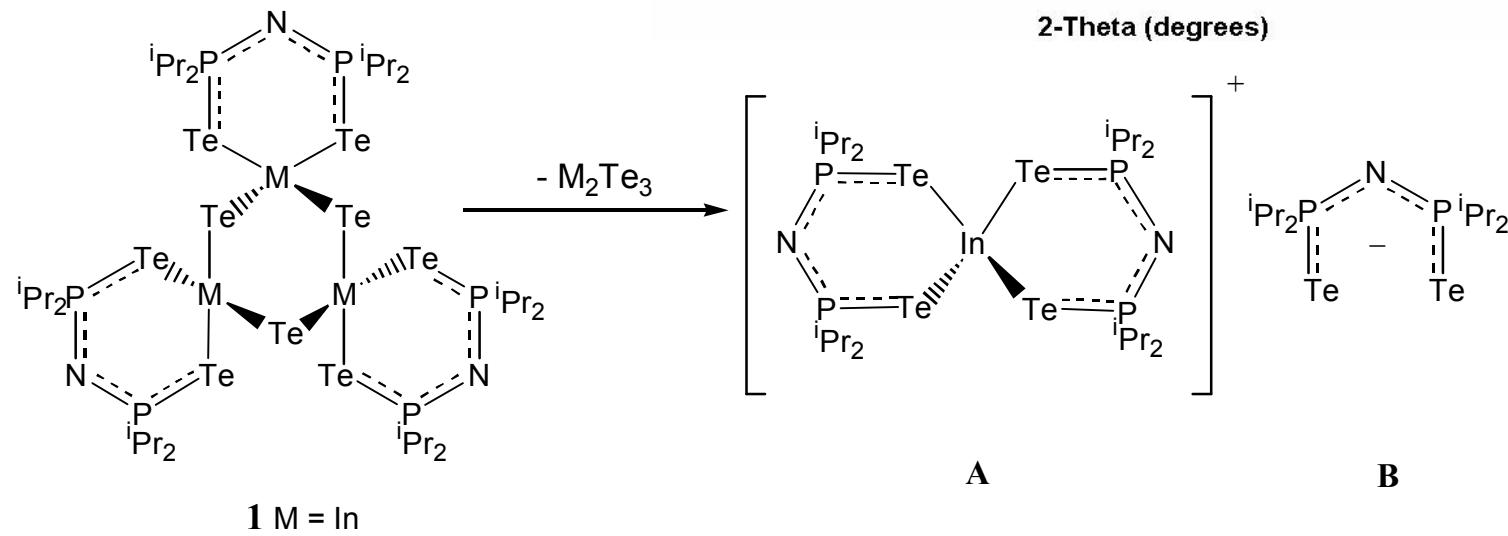
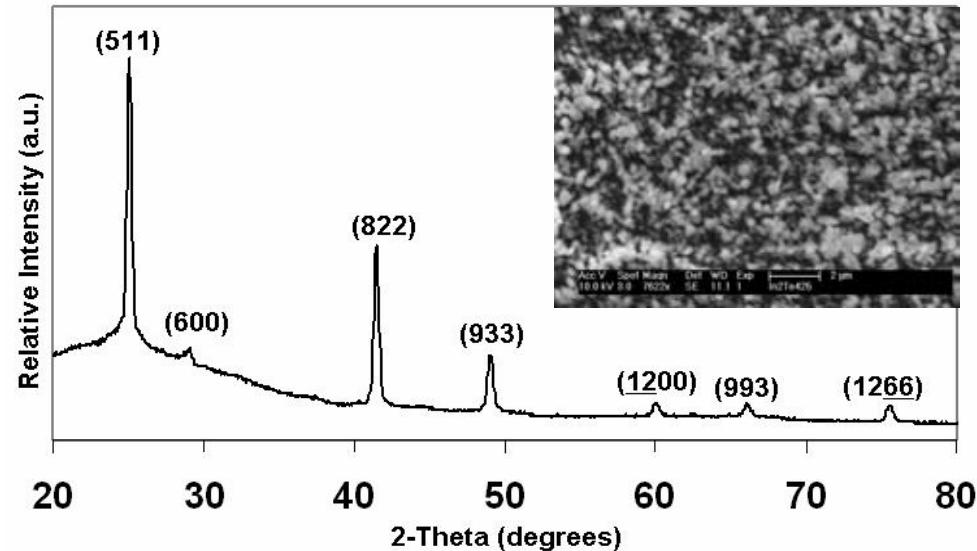


Relative Intensity (a.u.)

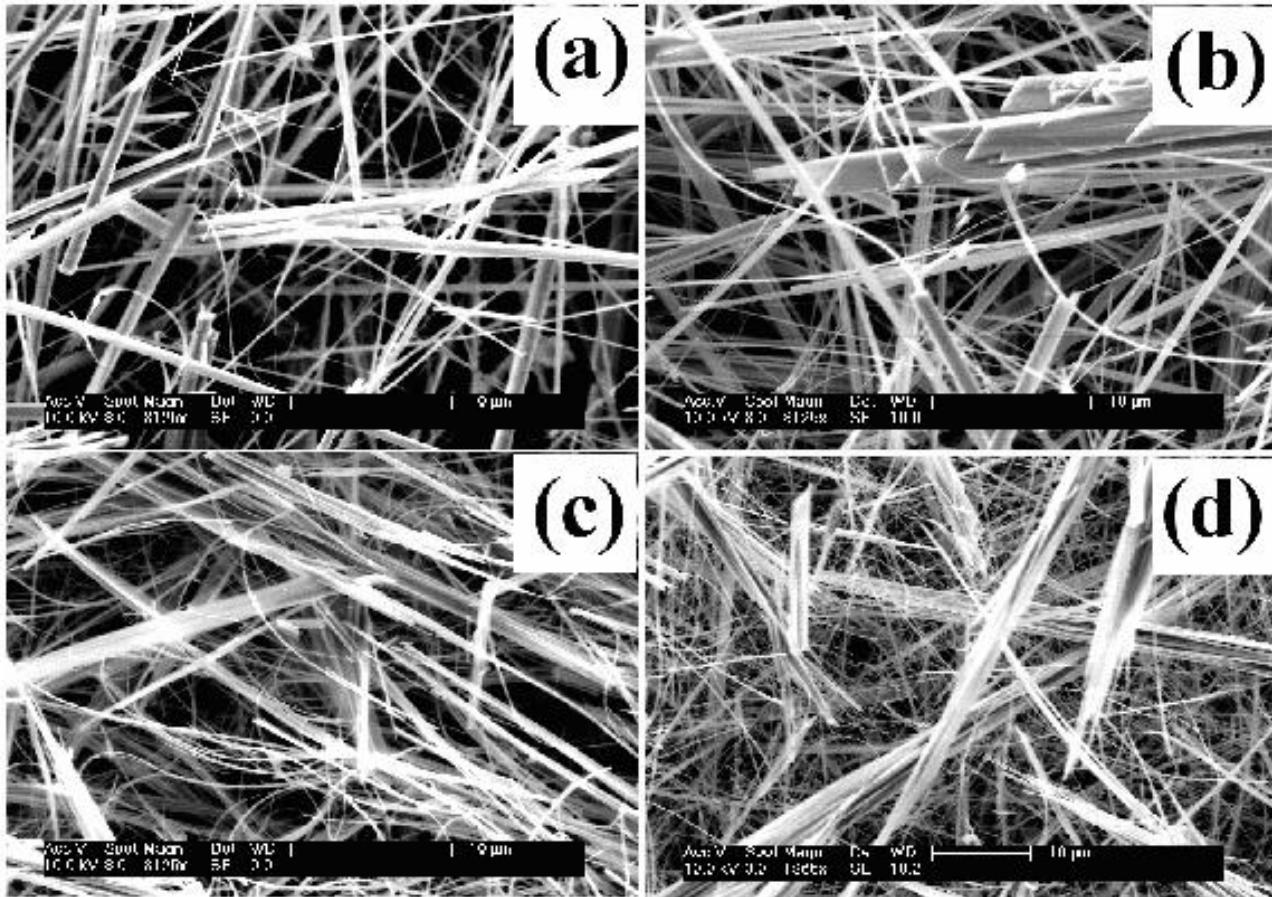
b

# AACVD from $\{\text{In}(\mu\text{-Te})[\text{N}(\text{iPr}_2\text{PTe})_2]\}_3$

- pXRD of cubic  $\text{In}_2\text{Te}_3$  thin films at 425 °C with a dynamic argon flow rate of 240 sccm.



S. S. Garje, M. Capsey, M. Afzaal, P. O'Brien, and T. Chivers, *J. Mater. Chem.* submitted.



Micrograph of rhombohedral  $\text{Sb}_2\text{Se}_3$  grown on glass at  
(a) 400 °C (b) 425 °C (c) 450 °C (d) 475 °C from  
(b)  $[\text{Sb}(\text{Se}_2\text{P}^{\prime}\text{Pr}_2)_3]$  with an Ar flow rate of 180 sccm

# Plan for the Lecture

*'Using Chemistry to Control Material Deposition: why choose to use a chemical method ?'*

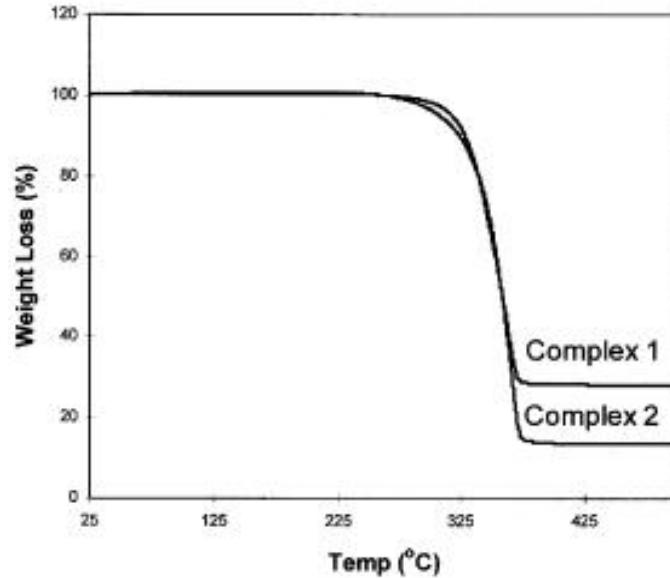
- **Introduction- the inorganic ring systems we have studied**
- **Dihalogenoimidodiphosphinates**
- **An Introduction to CVD**
- **Dithio and Diseleno-phosphinates**
- New routes to selenohosphinates
- CIGS systems
- Shapes of nanoparticles

# Synthesis of dithiophosphinates

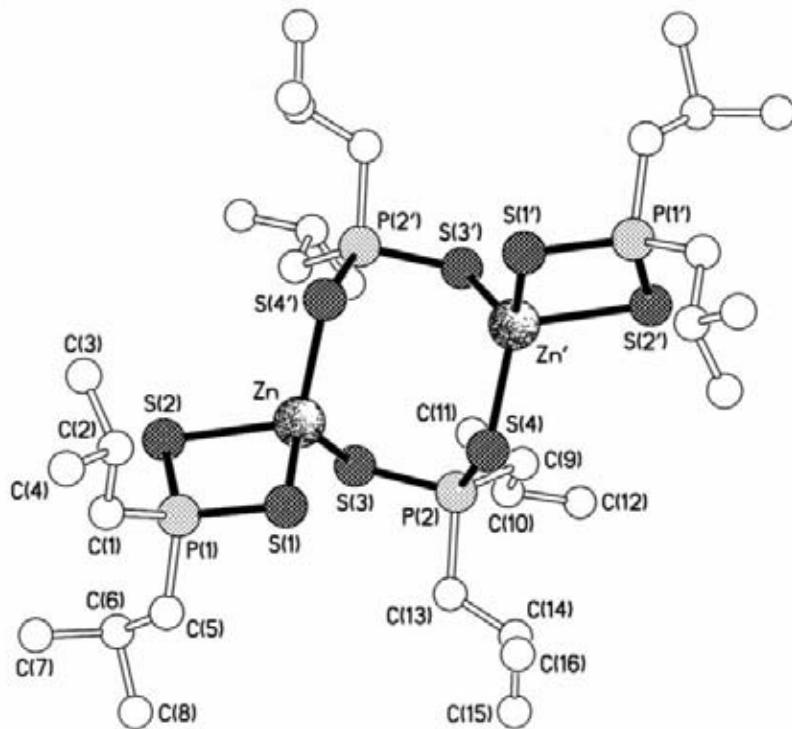
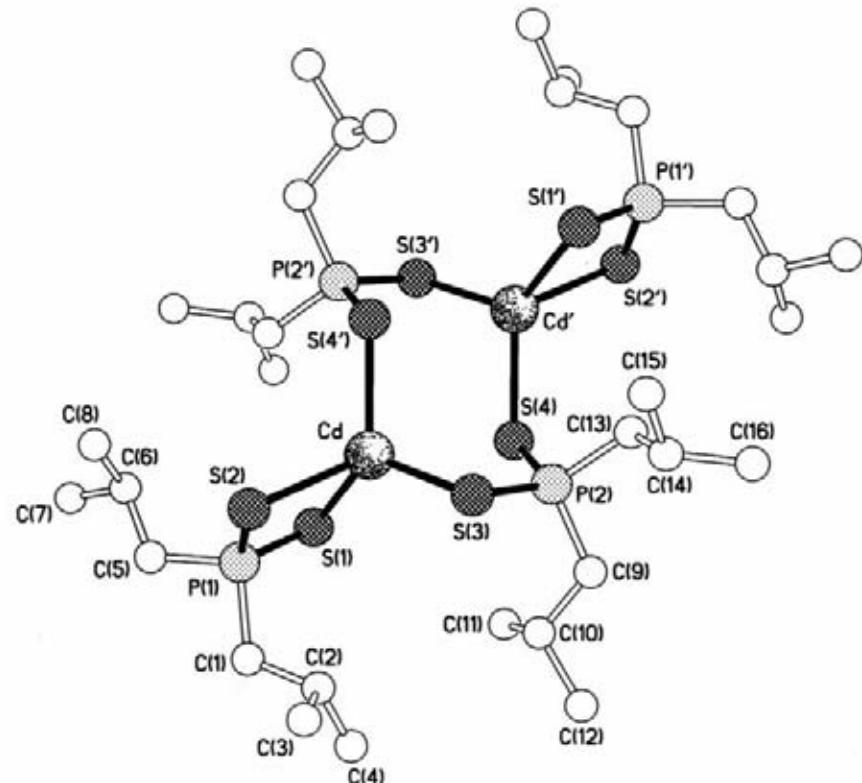


R = Et, Bu; M = Zn, Cd

TGA profile of  $[\text{Cd}(\text{S}_2\text{P}^i\text{Bu}_2)_2]$  (**1**)  
and  $[\text{Zn}(\text{S}_2\text{P}^i\text{Bu}_2)_2]$  (**2**)



- a) Y. Takahashi, R. Yuki, M. Sugiura, S. Motojima, K. Sugiyama, J. Cryst. Growth 50, 1980 491.  
b) C. Byrom, M.A. Malik, P. O'Brien, A.J.P. White, D.J. Williams, Polyhedron, 19, 2000, 211.

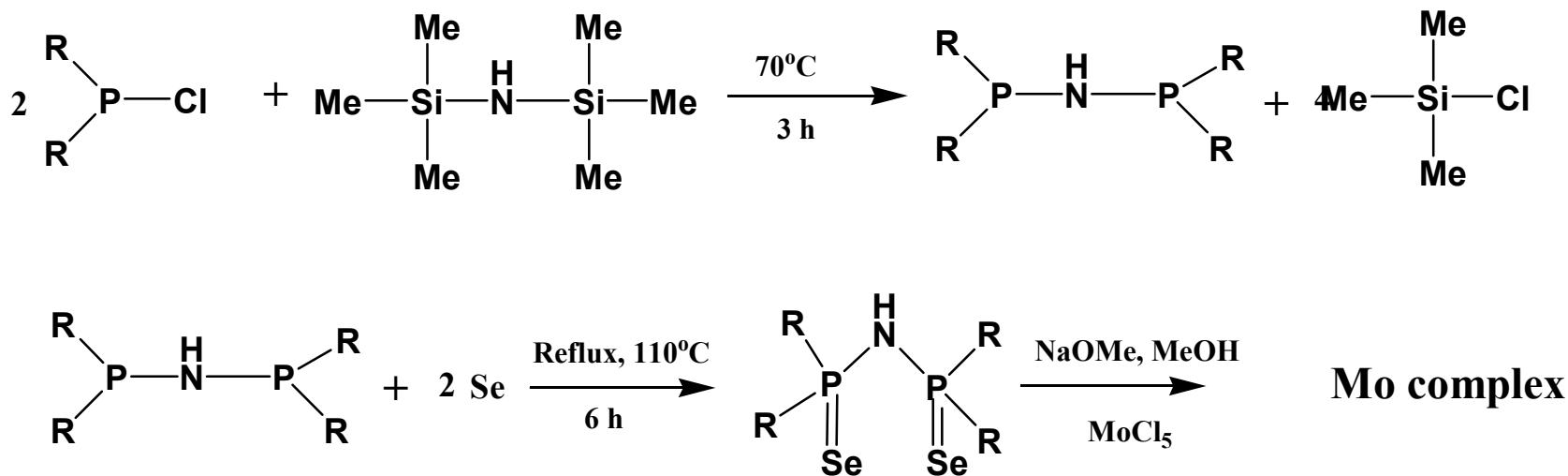
X-ray structure  $[\text{Zn}(\text{S}_2\text{P}'\text{Bu}_2)_2]$ X-ray structure  $[\text{Cd}(\text{S}_2\text{P}'\text{Bu}_2)_2]$

# Plan for the Lecture

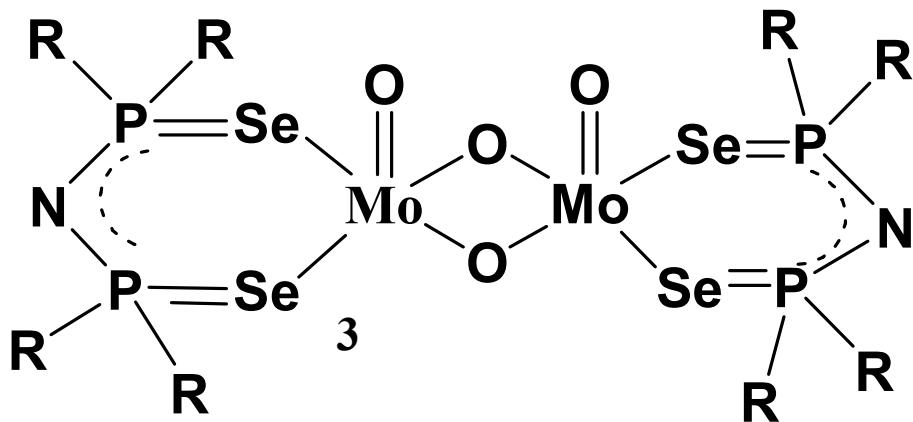
*'Using Chemistry to Control Material Deposition: why choose to use a chemical method ?'*

- **Introduction- the inorganic ring systems we have studied**
- **Dihalcogenoimidodiphosphinates**
- **An Introduction to CVD**
- **Dithio and Diseleno-phosphinates**
- **New routes to selenophosphinates**
- **CIGS systems**
- **Shapes of nanoparticles**

# A Serendipitous Synthesis of Diselenophosphinates



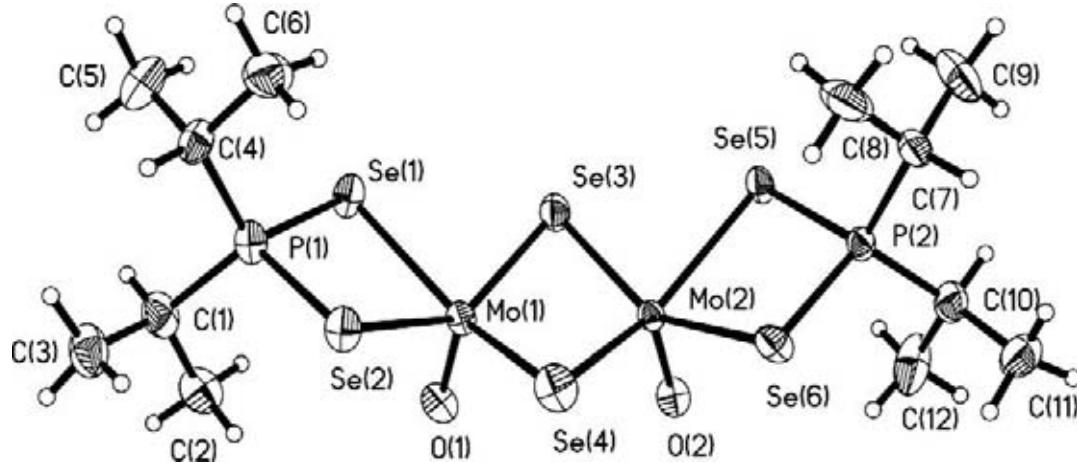
R = iPr



$\text{R} = \text{^IPr}$

Expected Product

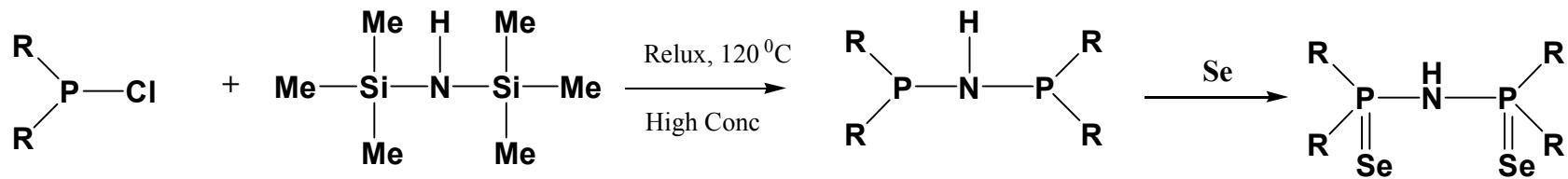
**HOWEVER!**



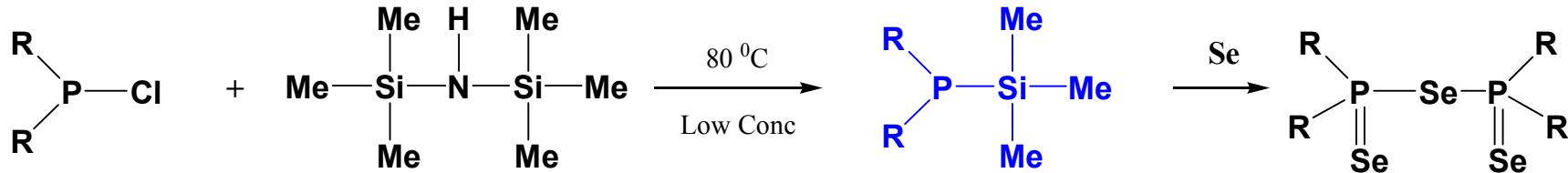
Obtained Product

# Possible Mechanism?

Main Product



By-Product

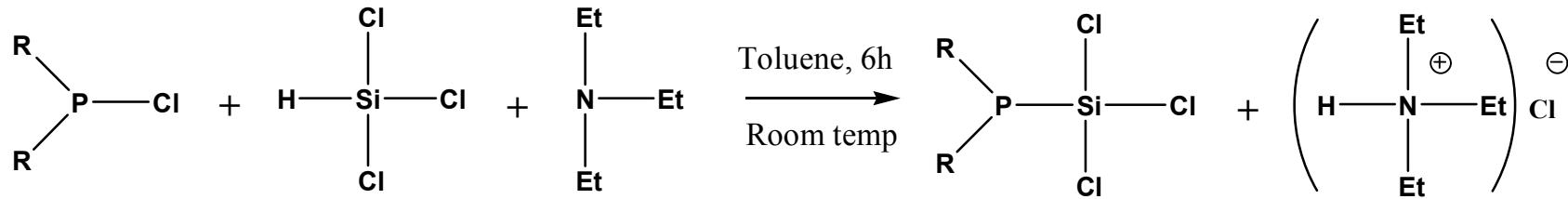


$\text{R} = \text{iPr, Ph}$

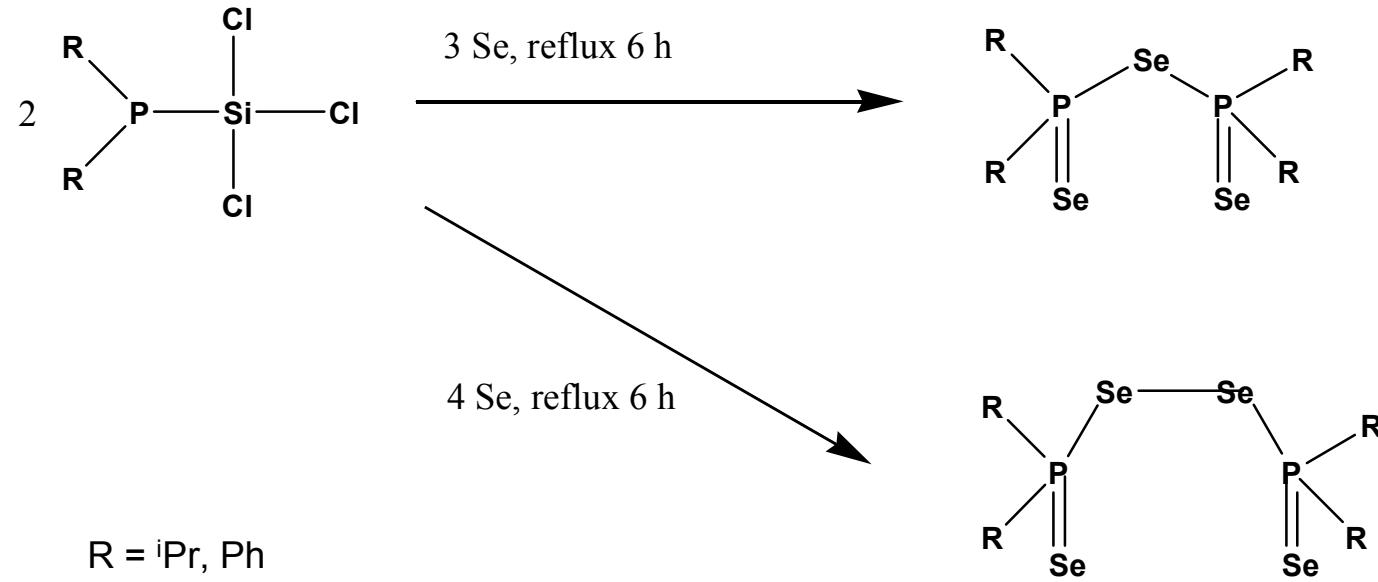
Inserting of Se into P-Si bond of the intermediate  $\text{R}_2\text{PSi}(\text{Me})_3$  ?

# Novel Synthetic Route to Se Phosphinates

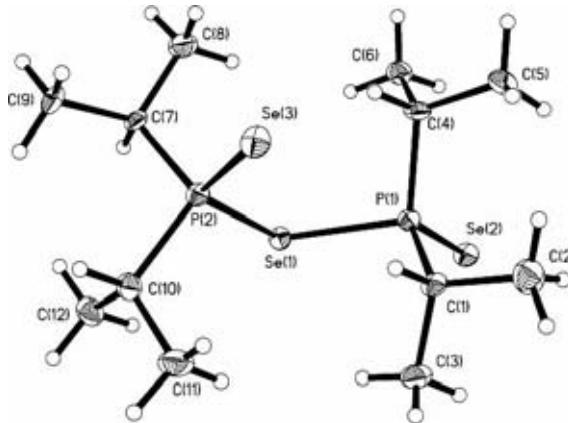
## Step 1: Making the intermediate



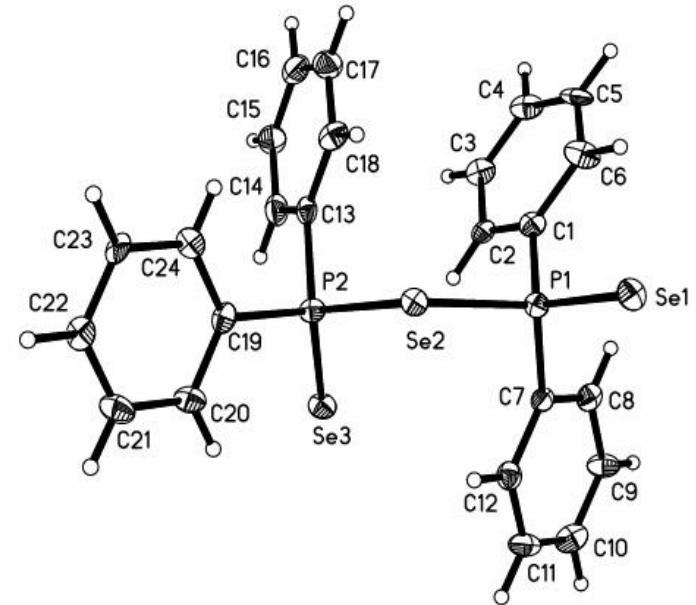
## Step 2: Inserting Se



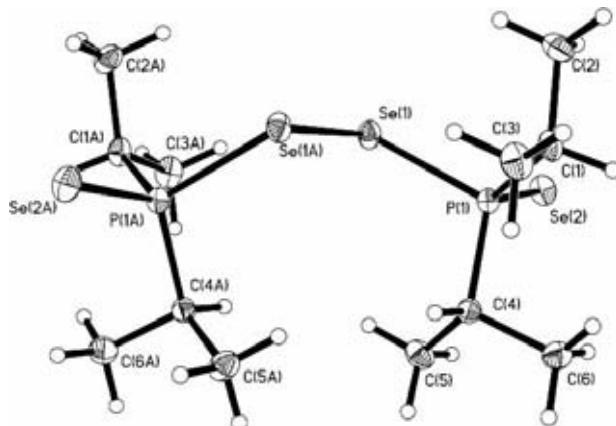
# X-ray Crystal Structures



$(i\text{Pr}_2\text{PSe})_2\text{Se}$

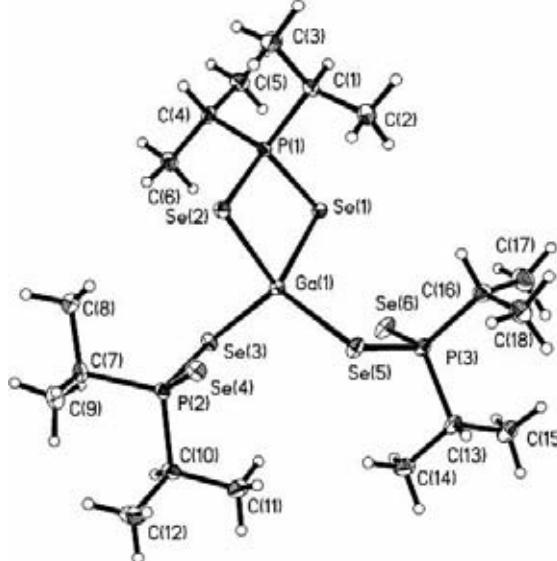
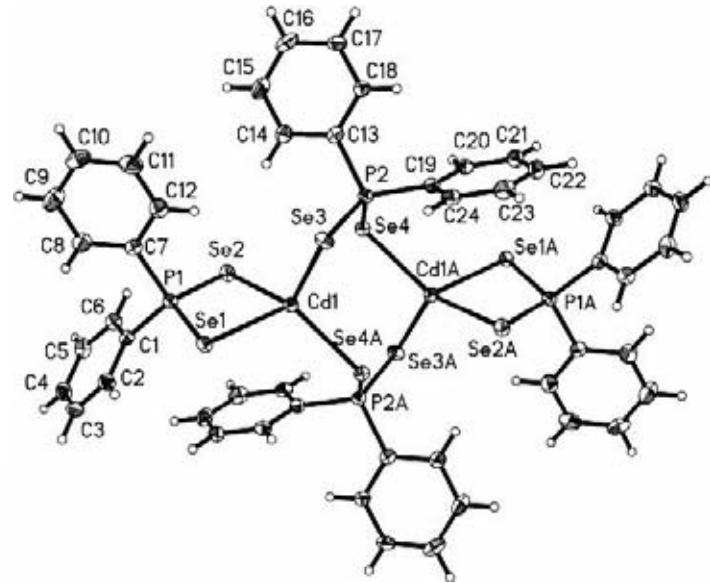
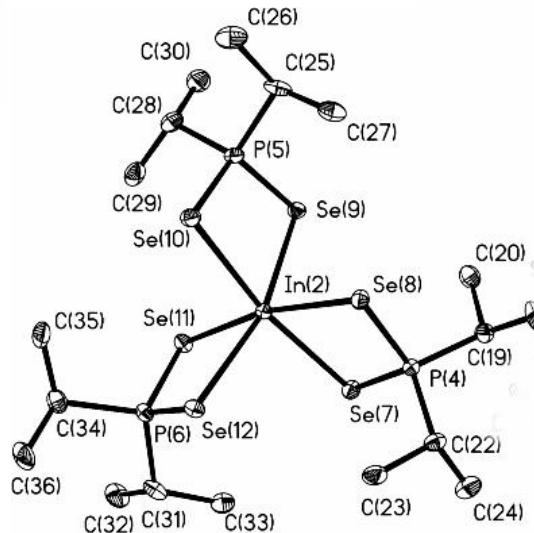


$(\text{Ph}_2\text{PSe})_2\text{Se}$



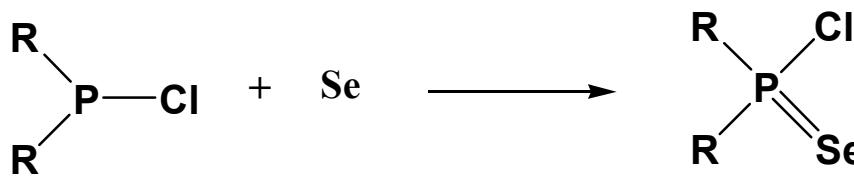
$(i\text{Pr}_2\text{PSe})_2\text{Se}_2$

# Inorganic complexes

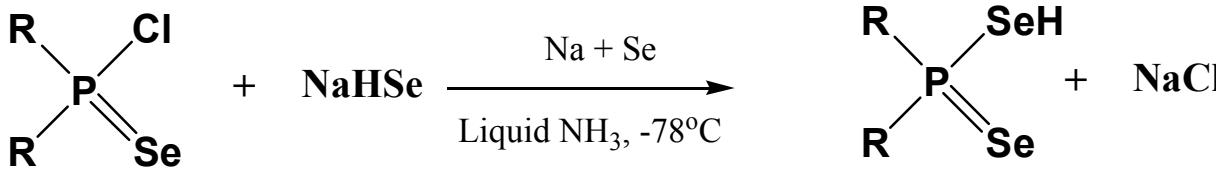
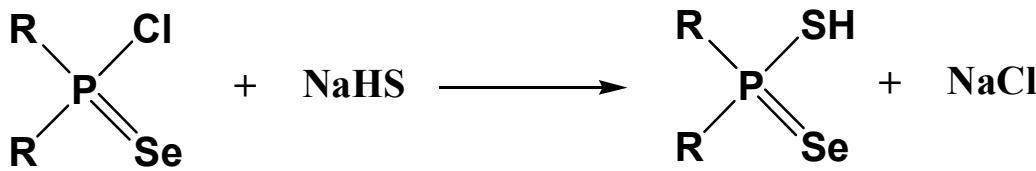
[Ga(*i*Pr<sub>2</sub>PSe<sub>2</sub>)<sub>3</sub>][Cd<sub>2</sub>(Ph<sub>2</sub>PSe<sub>2</sub>)<sub>4</sub>][In(*i*Pr<sub>2</sub>PSe<sub>2</sub>)<sub>3</sub>]

# DIALKYLDICHALCOGENOPHOSPHINATES

## Previous Work



Not-reproducible with  
added difficulty of  
using  $\text{NaHSe}$

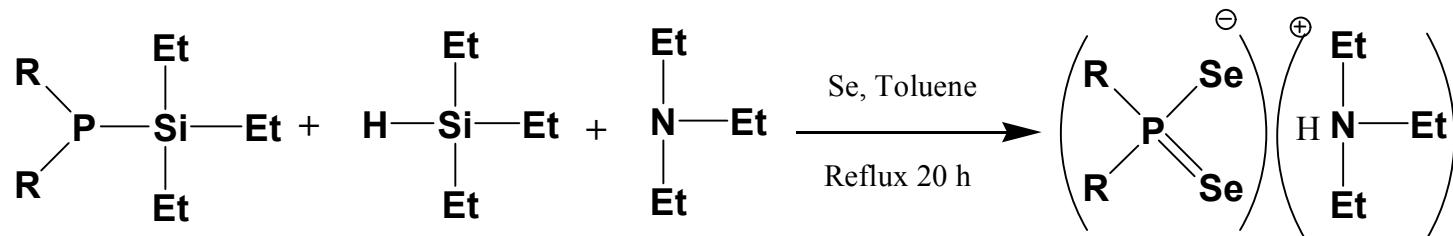
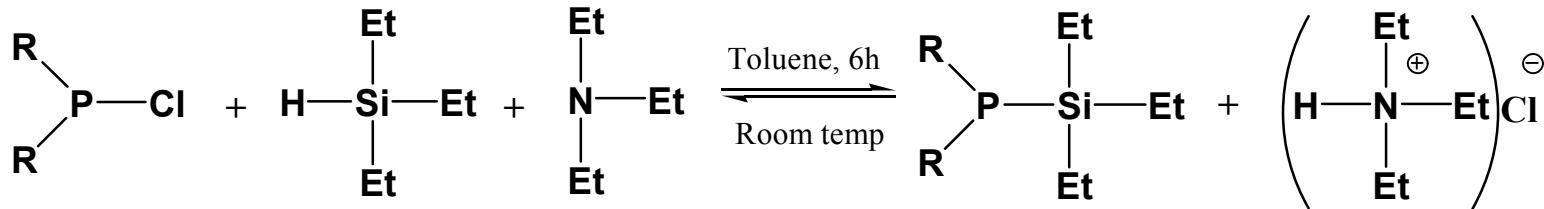


Unstable, never isolated, used *in situ* to make metal complexes, no solid state characterization

References: (a) J. Inorg. Nucl. Chem. 1974, **36**, 472-5; (b) Angw. Chem. 1969, **8**, 89.  
(c) Polyhedron 1991, **10**, 2641.

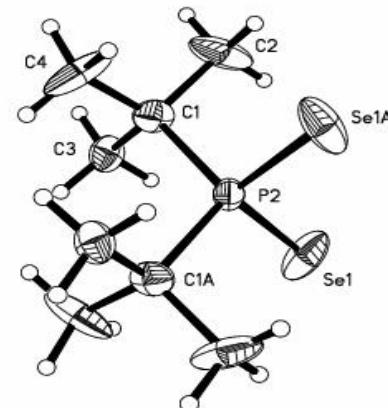
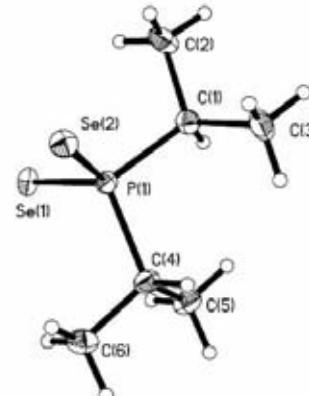
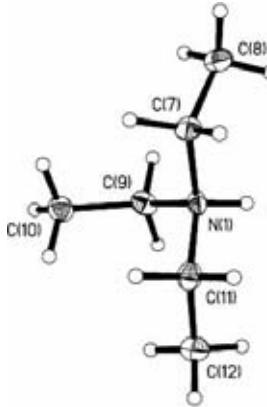
# A New Route to $\text{R}_2\text{PSe}_2$ Ligands

- Alternatively, use excess Lewis Base  $\text{NEt}_3$  to stabilize ionic species e.g.  $[({}^i\text{Pr})_2\text{PSe}_2]^-$
- $\text{HSiCl}_3/\text{NEt}_3$  : did not work due to the formation of  $[\text{HNEt}_3^+][\text{SiCl}_3^-]$
- $\text{HSiEt}_3/\text{NEt}_3$  : worked

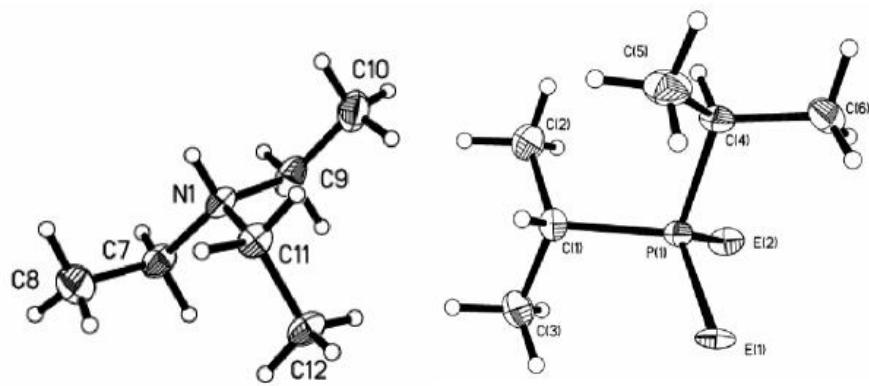
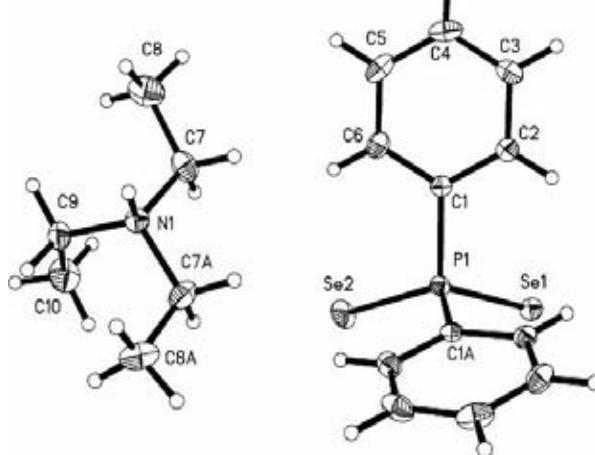


$\text{R} = {}^i\text{Pr, Ph, } {}^t\text{Bu}$

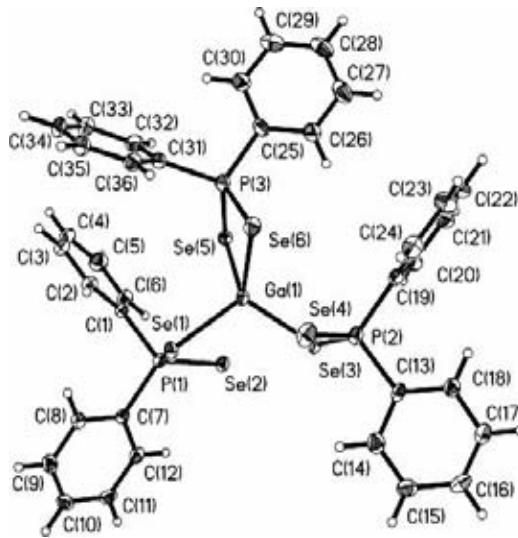
# X-ray Crystal Structures



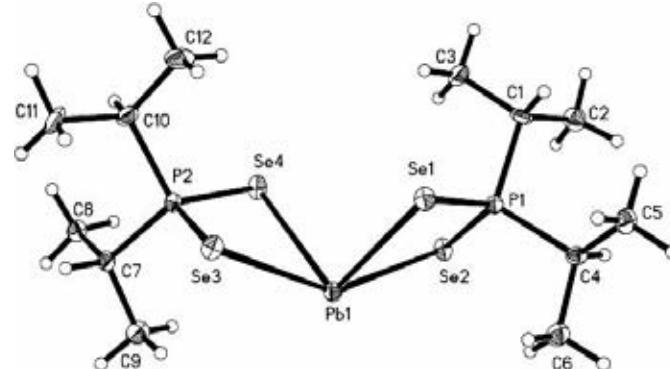
Disorder in the cation hence, not shown



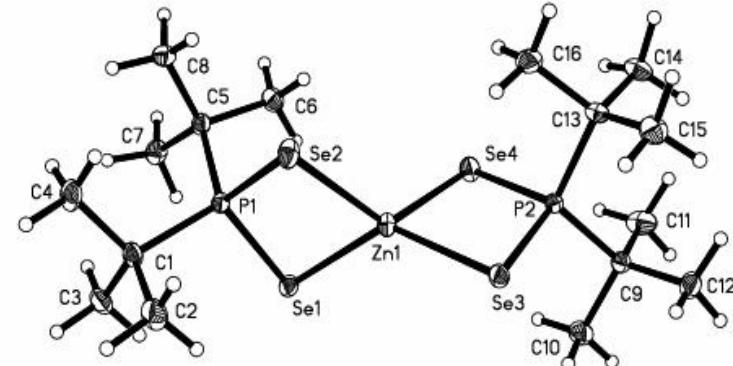
# Inorganic complexes



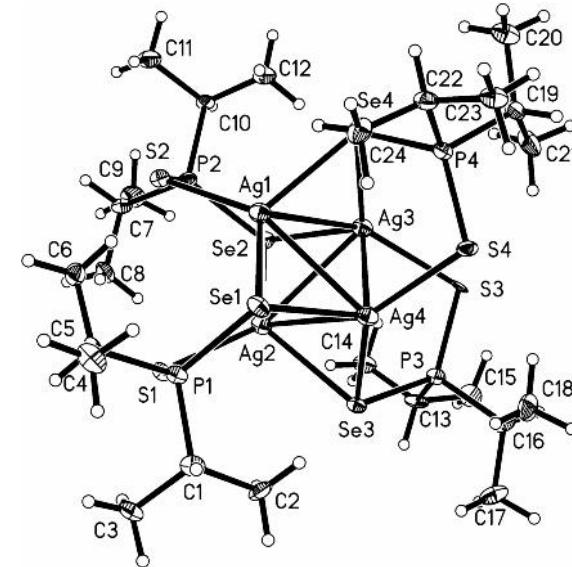
$[\text{Ga}(\text{Ph}_2\text{PSe}_2)_3]$



$[\text{Pb}(\text{Se}_2\text{P}^i\text{Pr}_2)_2]$



$[\text{Zn}(\text{tBu}_2\text{PSe}_2)_2]$



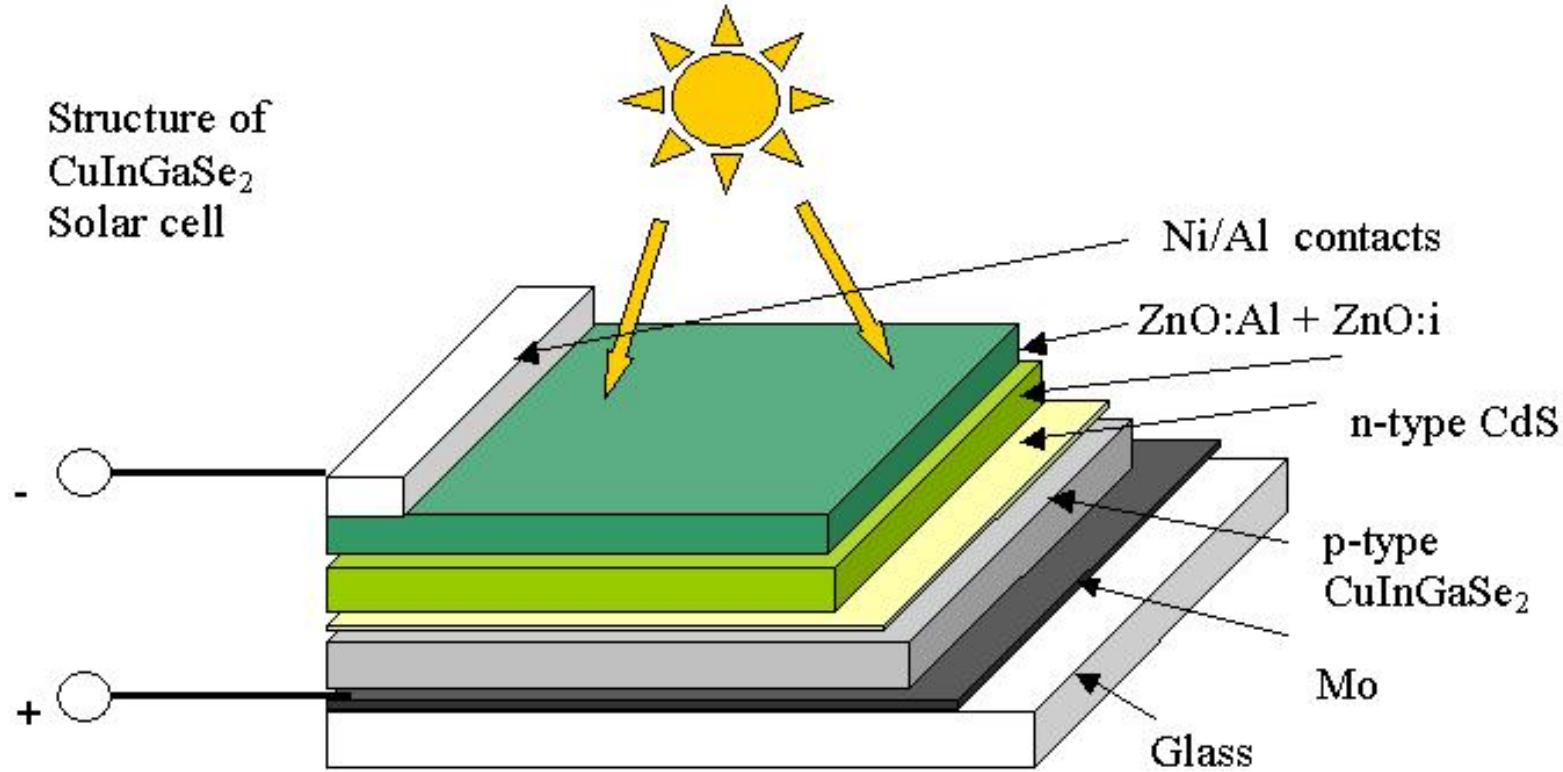
$[\text{Ag}_4(\text{SSeP}^i\text{Pr}_2)_4]$

# Plan for the Lecture

*'Using Chemistry to Control Material Deposition: why choose to use a chemical method ?'*

- **Introduction- the inorganic ring systems we have studied**
- **Dihalcogenoimidodiphosphinates**
- **An Introduction to CVD**
- **Dithio and Diseleno-phosphinates**
- **New routes to selenophosphinates**
- **CIGS systems**
- **Shapes of nanoparticles**

Structure of  
 $\text{CuInGaSe}_2$   
Solar cell

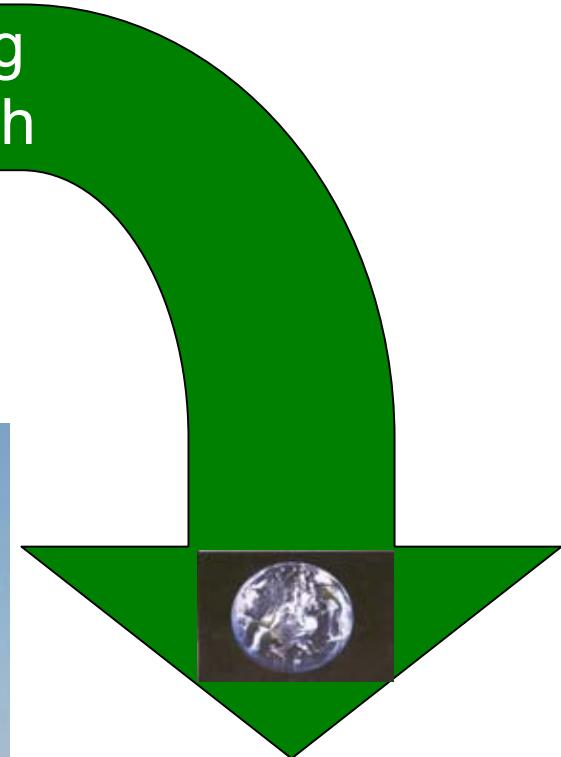


Thin-film solar cells based on CIGS ( $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ ) companies working with CIGS cells include Shell Solar and Würth.

Early Honda CIGS module prototypes had a maximum output of 112 W at dimensions of  $1,367 \times 802 \times 46$  mm.

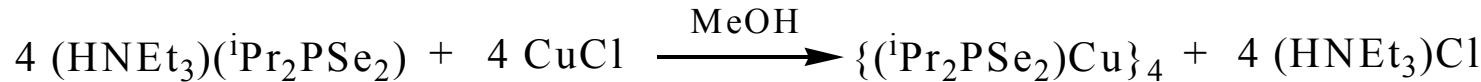


CIGS Coming  
Down to Earth



# Copper complexes

## From CuCl

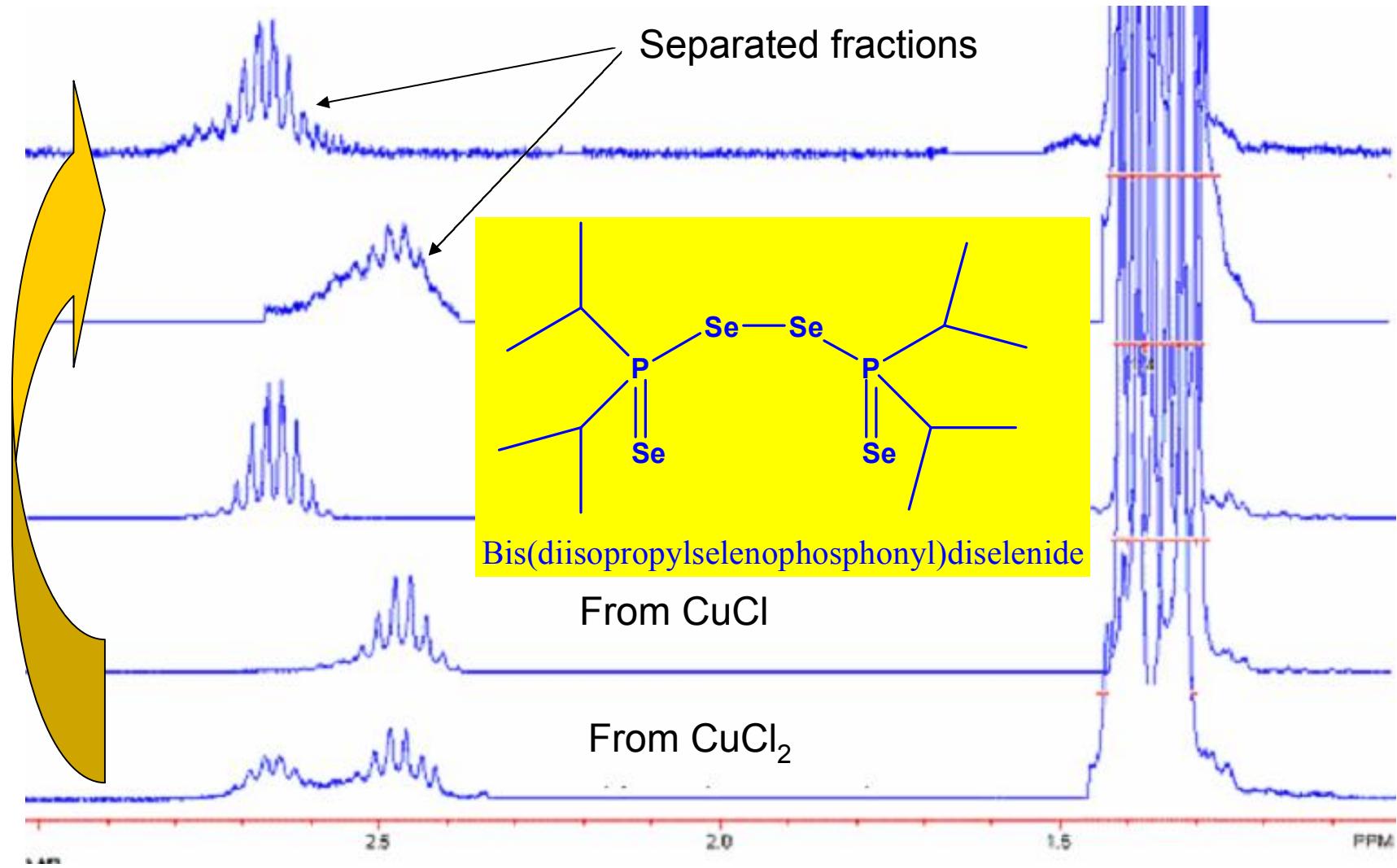


## From CuCl<sub>2</sub>

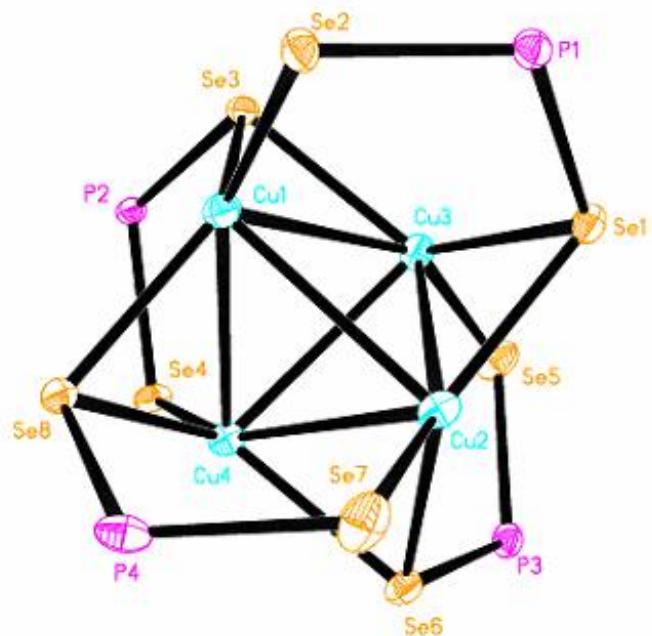
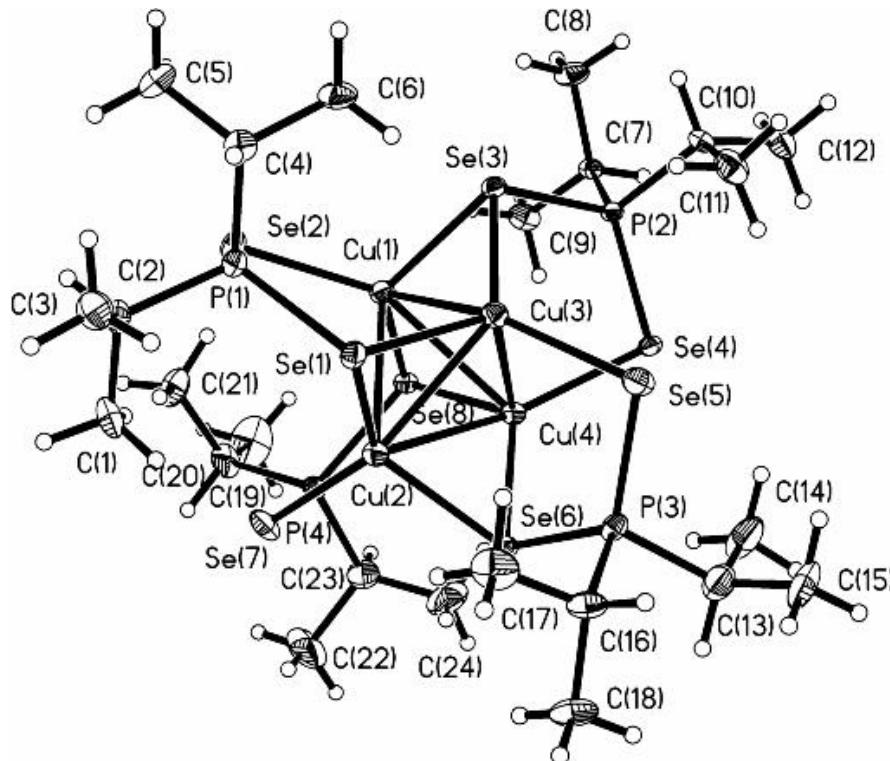


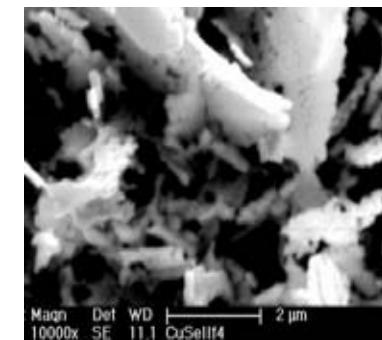
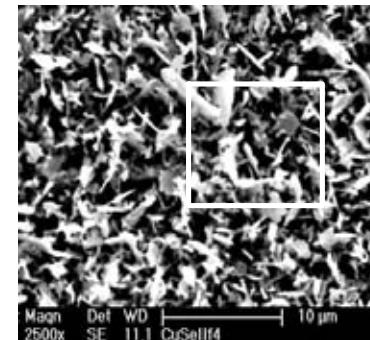
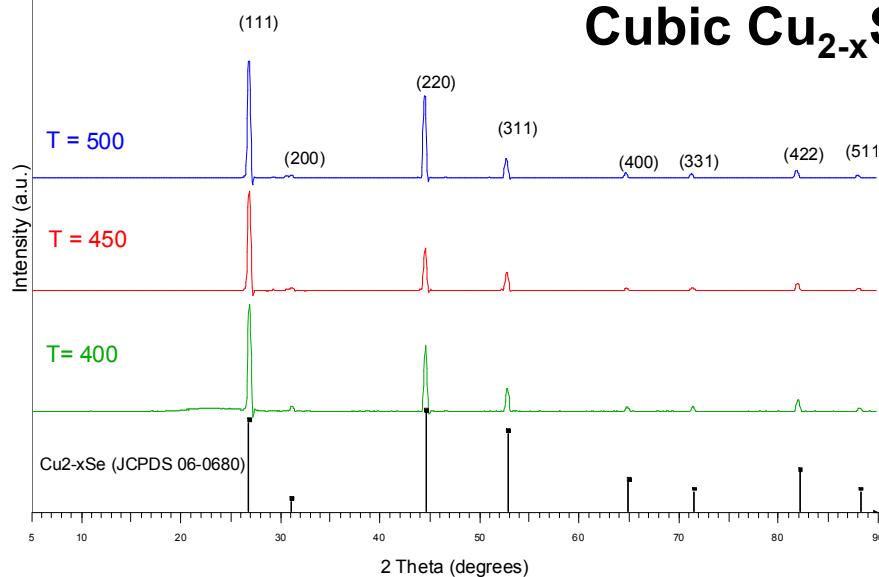
**Cu(II) is reduced to Cu(I) by the ligand**

# NMR of Copper complexes

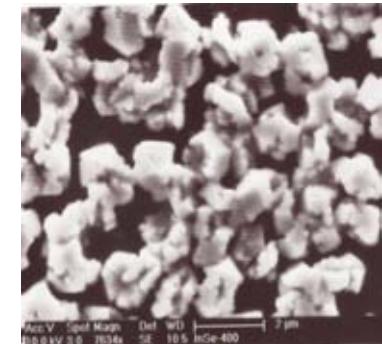
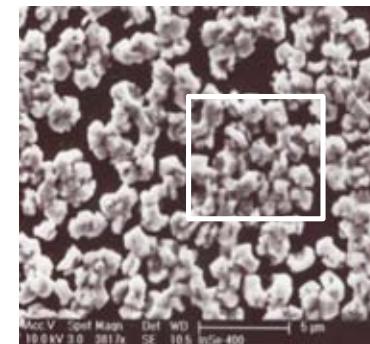
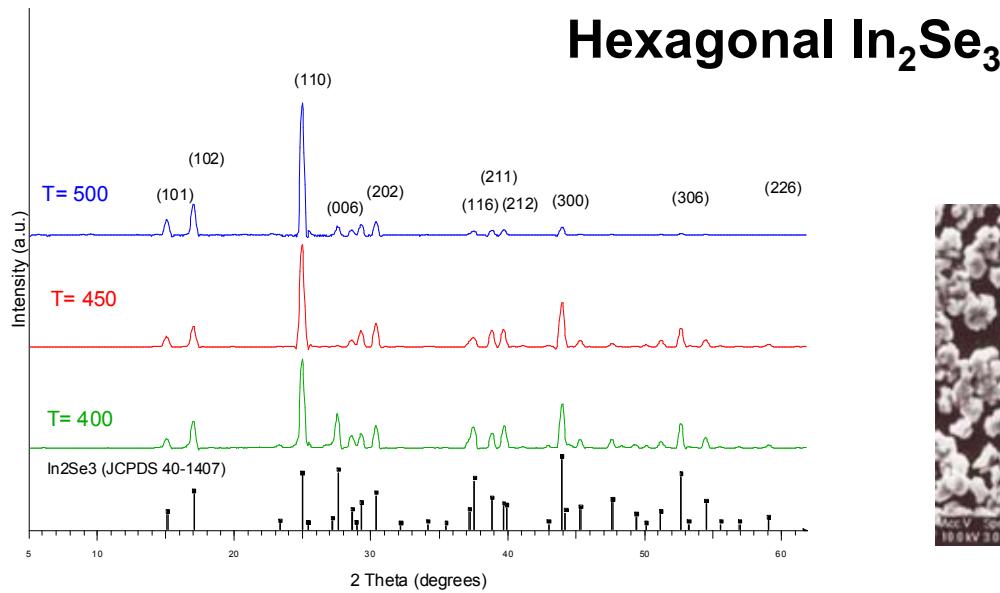


# X-ray Structure of Copper complex



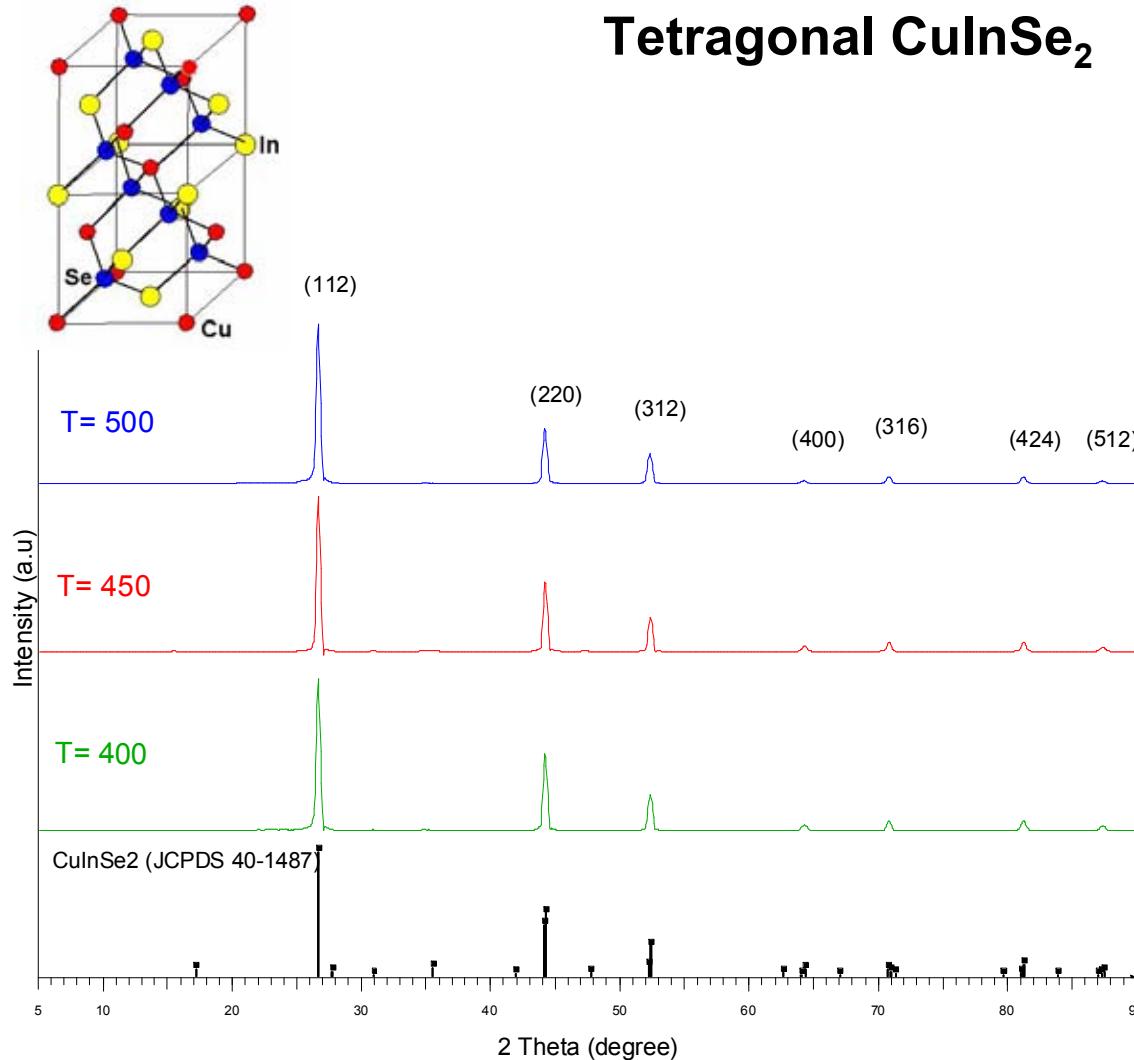


400 °C

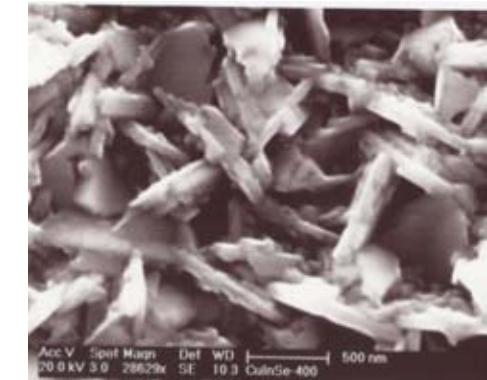
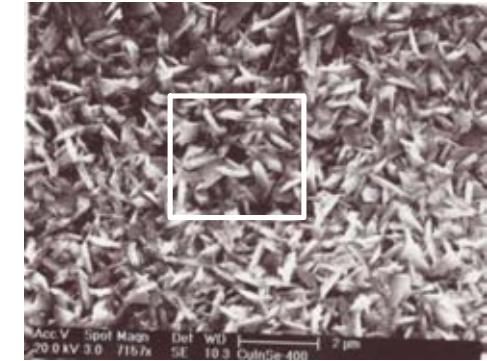


400 °C

**AA-CVD Experiments:** Solvent: toluene; Flow rate: 160 sccm; Time: 90 mins; Substrate: Glass



## Tetragonal CuInSe<sub>2</sub>



400 °C

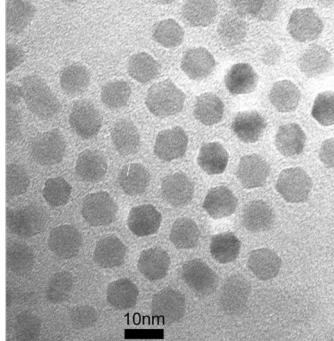
**AA-CVD Experiments:** Solvent: toluene; Flow rate: 160 sccm; Time: 90 mins; Substrate: Glass;  
Stoichiometric Cu:In ratio

# And also Nanoparticles

## Nanoco's Technology



High resolution electron microscope  
Image of single QD (5nm across)



Electron microscope image showing QD  
In very ordered pattern  
10nm



Dilute solution QD excited by UV light

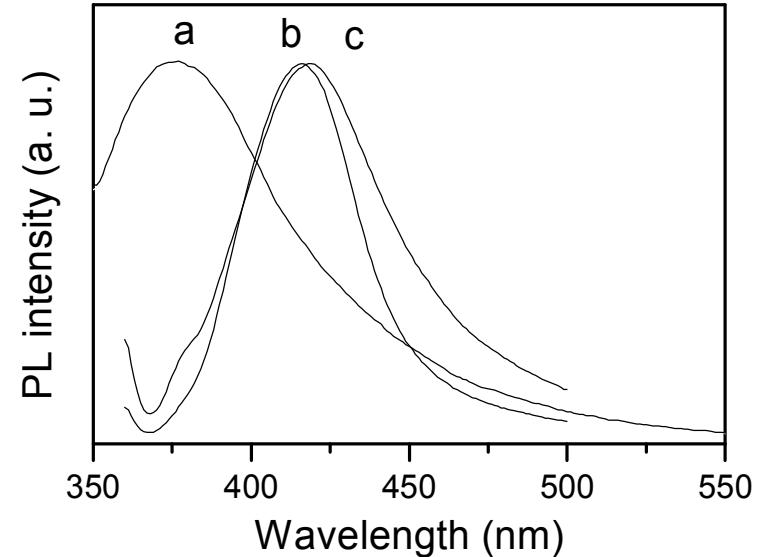
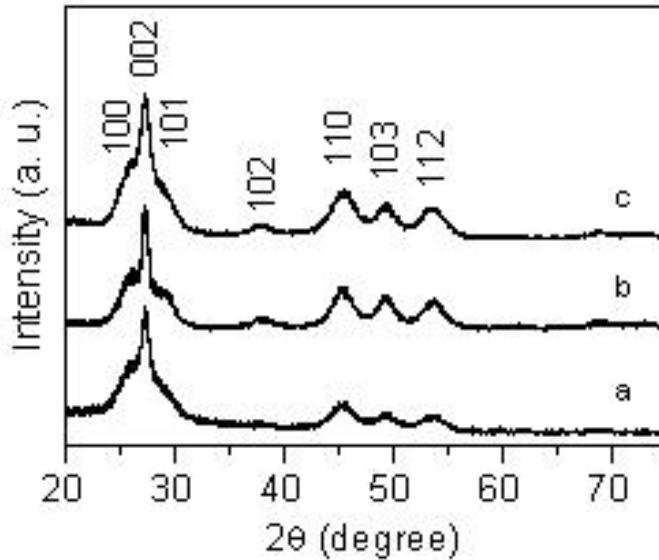


30 grams of 560nm QD. No other company in the world can produce this quantity. Market value in today's bio applications greater than \$10Million. Competitors can only produce 100 milligrams, 300X less material per batch. Nanoco will soon be producing 1 kilo batches



*illuminating the future*

# ZnSe nanoparticles from $[Zn(Se_2P^iPr_2)_2]$



Hexadecylamine (HDA) capped hexagonal ZnSe nanoparticles grown at 300 °C for 30 min from (a) 0.2 g, (b) 0.4 g and (c) 0.6 g of precursor.

## Emission Spectra

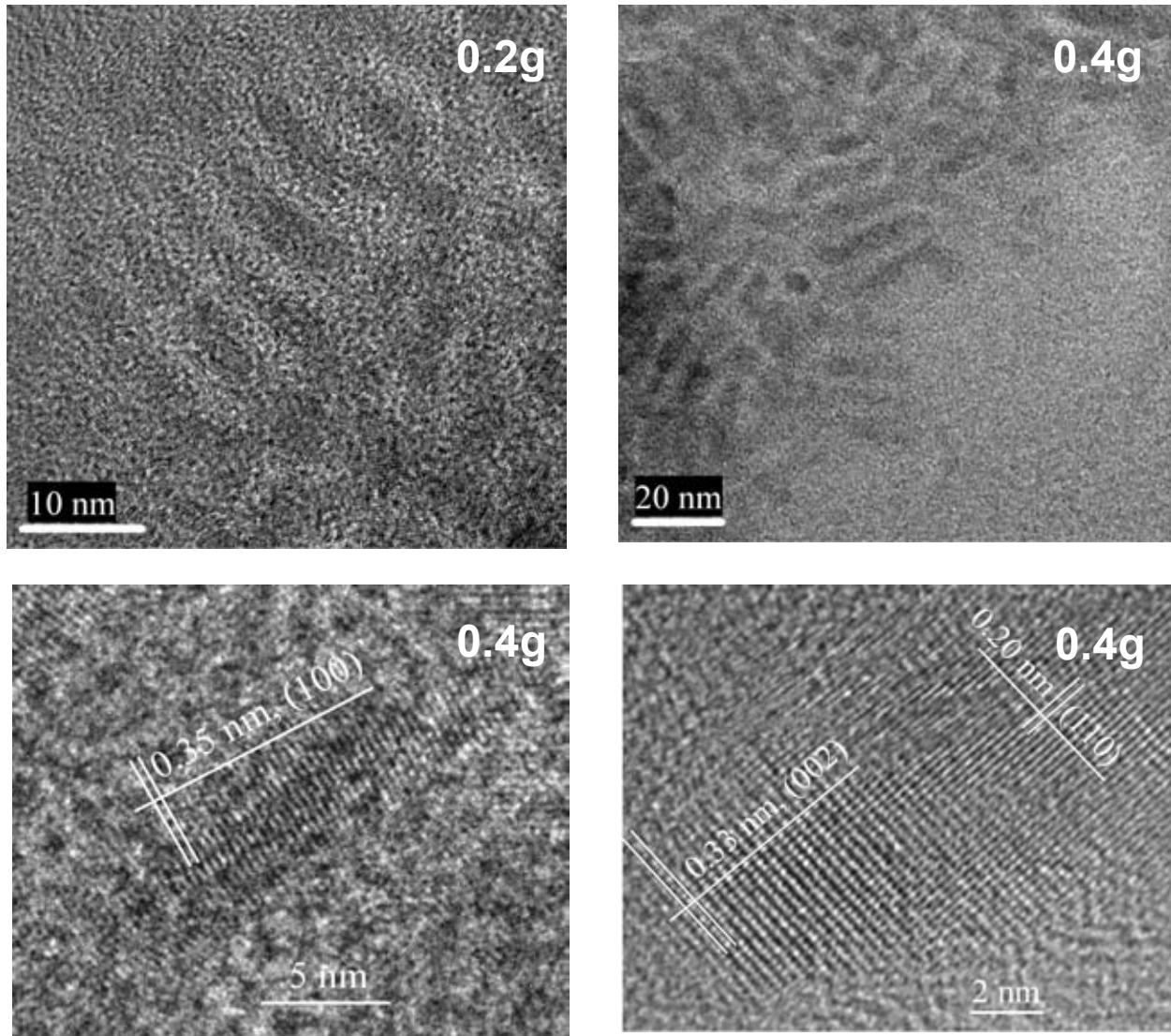
$$a = 375 \text{ nm (3.30 eV)}$$

$$b = 414 \text{ nm (2.99 eV)}$$

$$c = 418 \text{ nm (2.96 eV)}$$

vs.

$$\text{Bulk ZnSe} = 459 \text{ nm (2.79 eV)}$$

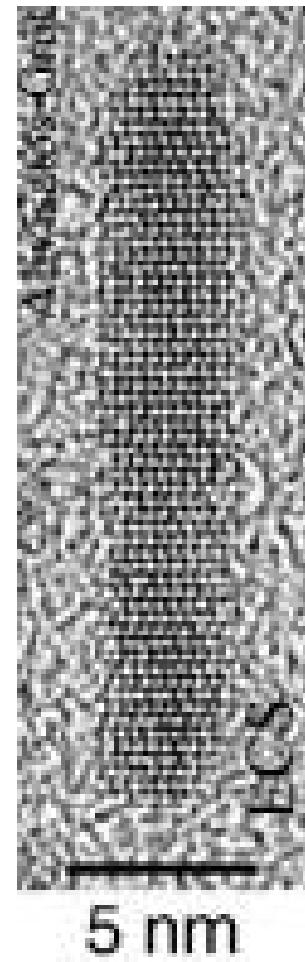
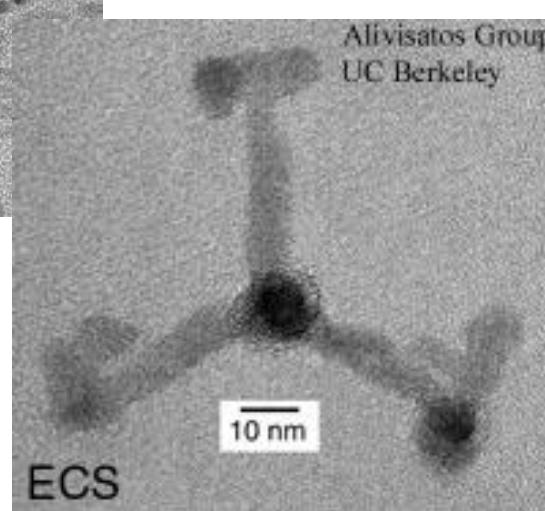
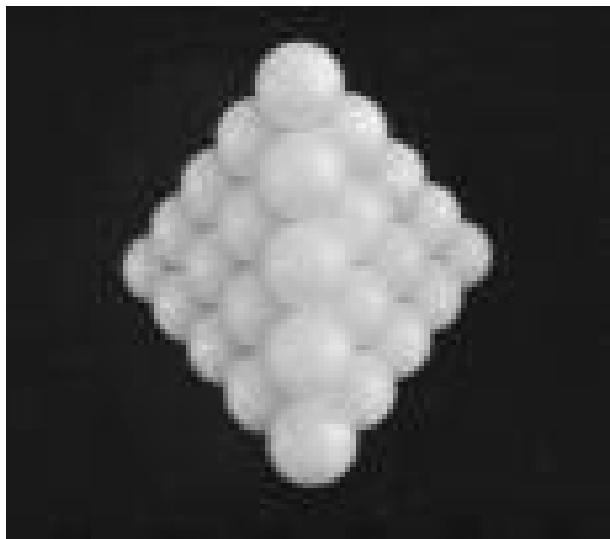
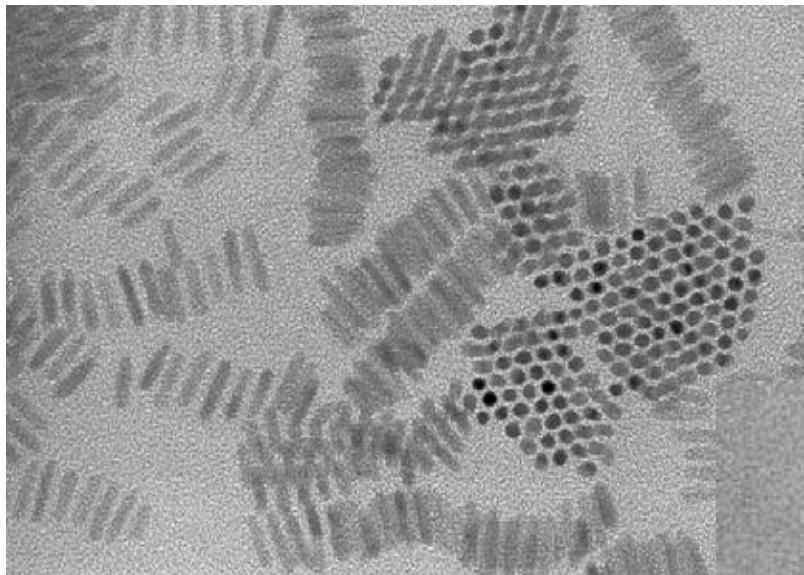


TEM image of ZnSe nanomaterial

# Plan for the Lecture

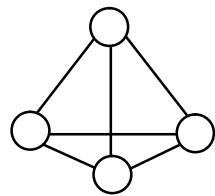
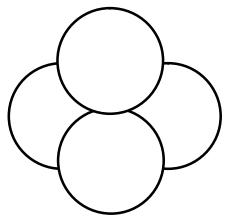
*'Using Chemistry to Control Material Deposition: why choose to use a chemical method ?'*

- **Introduction- the inorganic ring systems we have studied**
- **Dihalcogenoimidodiphosphinates**
- **An Introduction to CVD**
- **Dithio and Diseleno-phosphinates**
- **New routes to selenophosphinates**
- **CIGS systems**
- **Shapes of nanoparticles**



## Tetrahedron

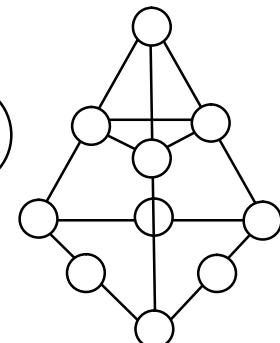
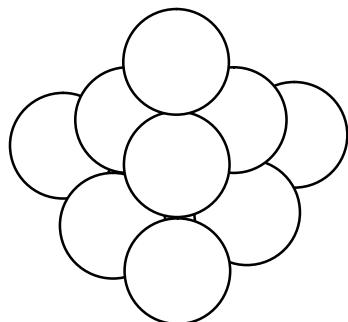
**N = 2**



Total atoms = 4

Surface atoms = 4

**N = 3**

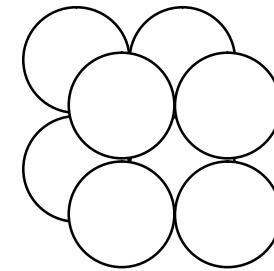
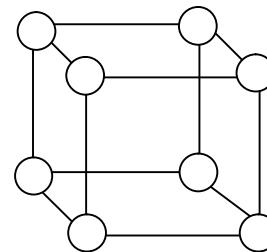


Total atoms = 10

Surface atoms = 10

## Cube

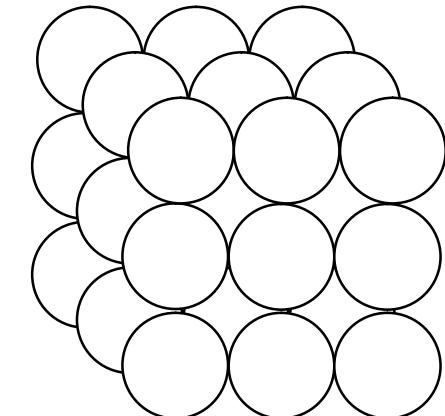
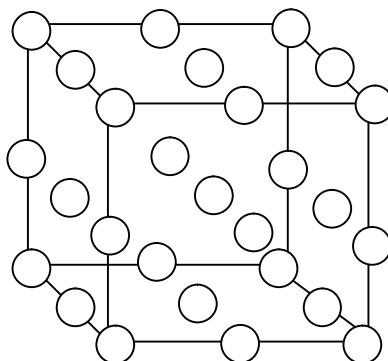
**N = 2**



Total atoms = 8

Surface atoms = 8

**N = 3**



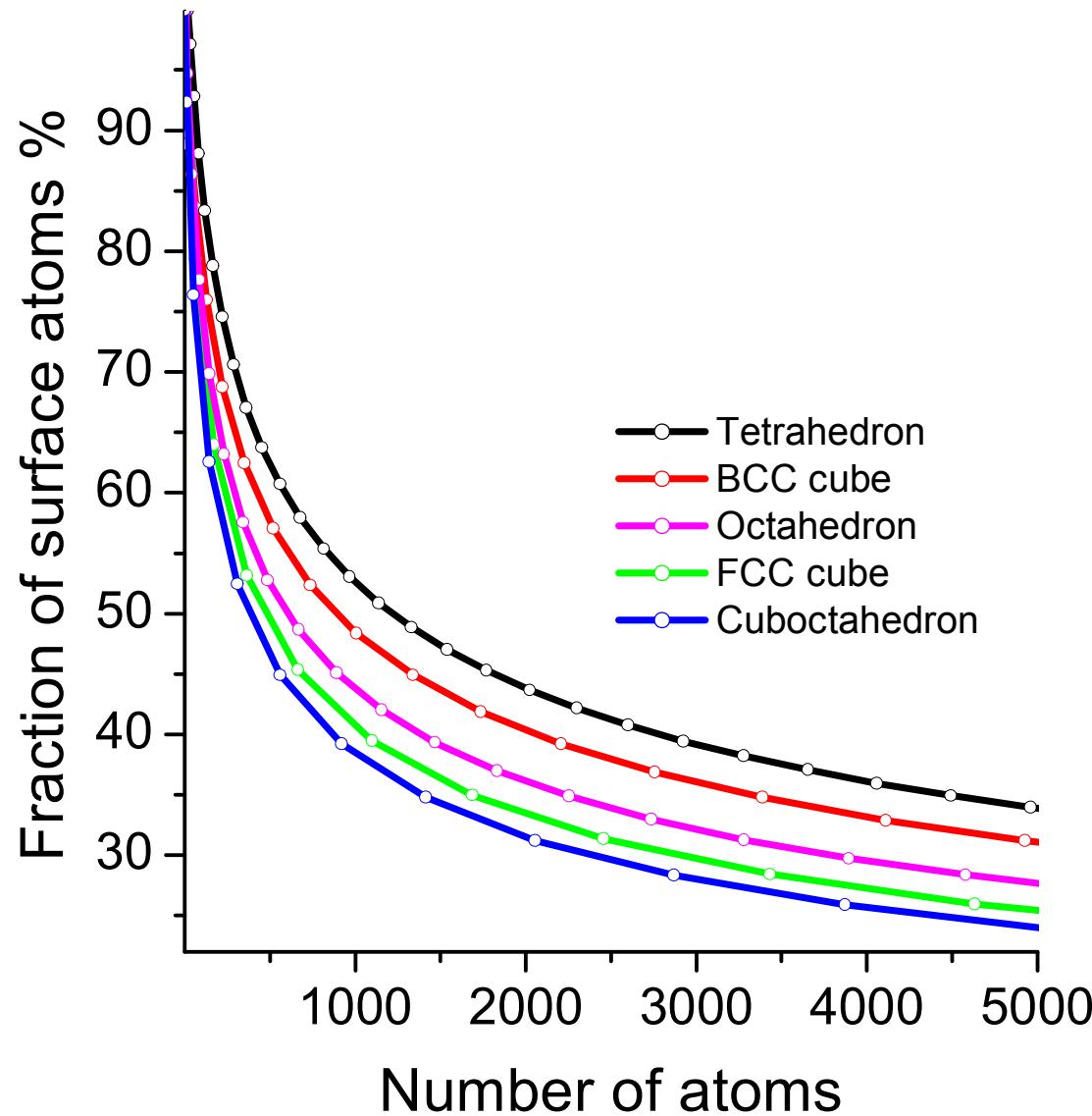
Total atoms = 27

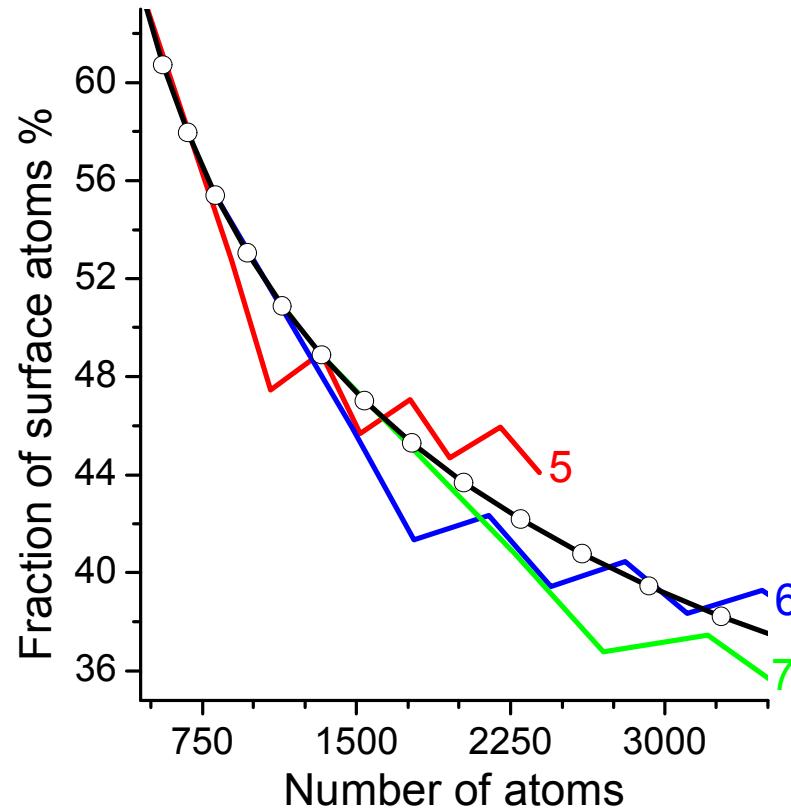
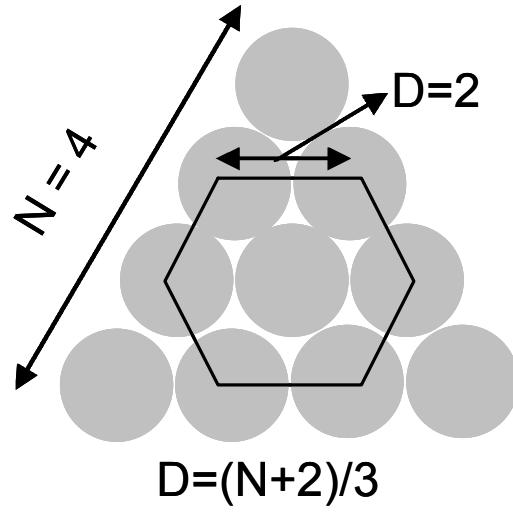
Surface atoms = 26

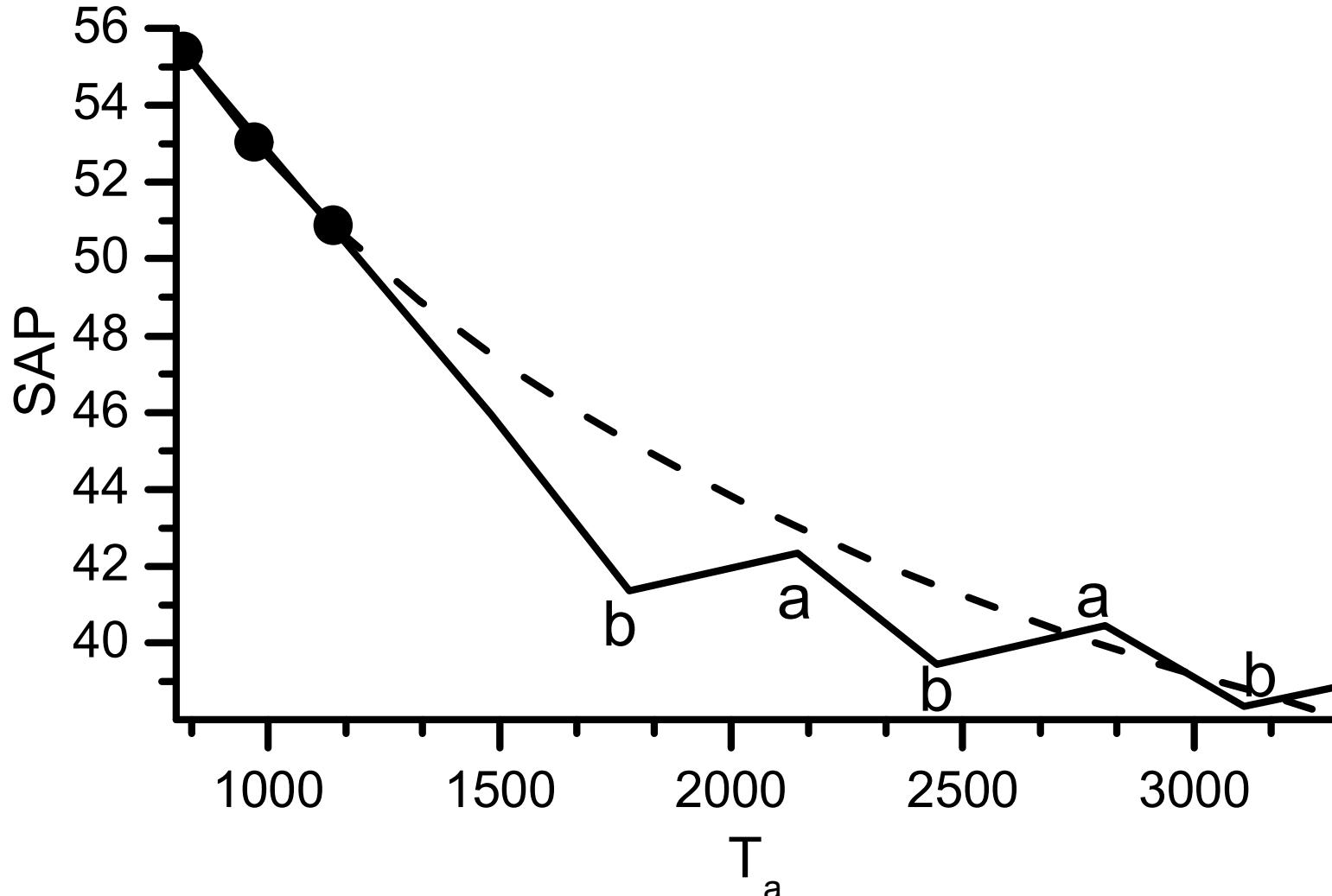
| Shape   | Total atoms                                   | Surface atoms      |
|---|---|--------------------|
| <b>Cube</b><br>Bcc packing                            | $(N+1)^3 + N^3$                               | $6N^2 + 2$         |
| <b>Cube</b><br>Fcc packing                            | $4N^3 + 6N^2 + 3N + 1$                        | $12N^2 + 2$        |
| <b>Octahedron</b><br>Fcc packing                      | $\frac{2N^3}{3} + \frac{N}{3}$                | $4N^2 - 8N + 6$    |
| <b>Tetrahedron</b><br>Fcc packing                     | $\frac{N^3}{6} + \frac{N^2}{2} + \frac{N}{3}$ | $2N^2 - 4N + 4$    |
| <b>Cuboctahedron</b><br>triangular faces, fcc packing | $\frac{10N^3}{3} - 5N^2 + \frac{11N}{3} - 1$  | $10N^2 - 20N + 12$ |

**Relationship between the number of shells N and the total number of atoms and surface atoms for different shapes**

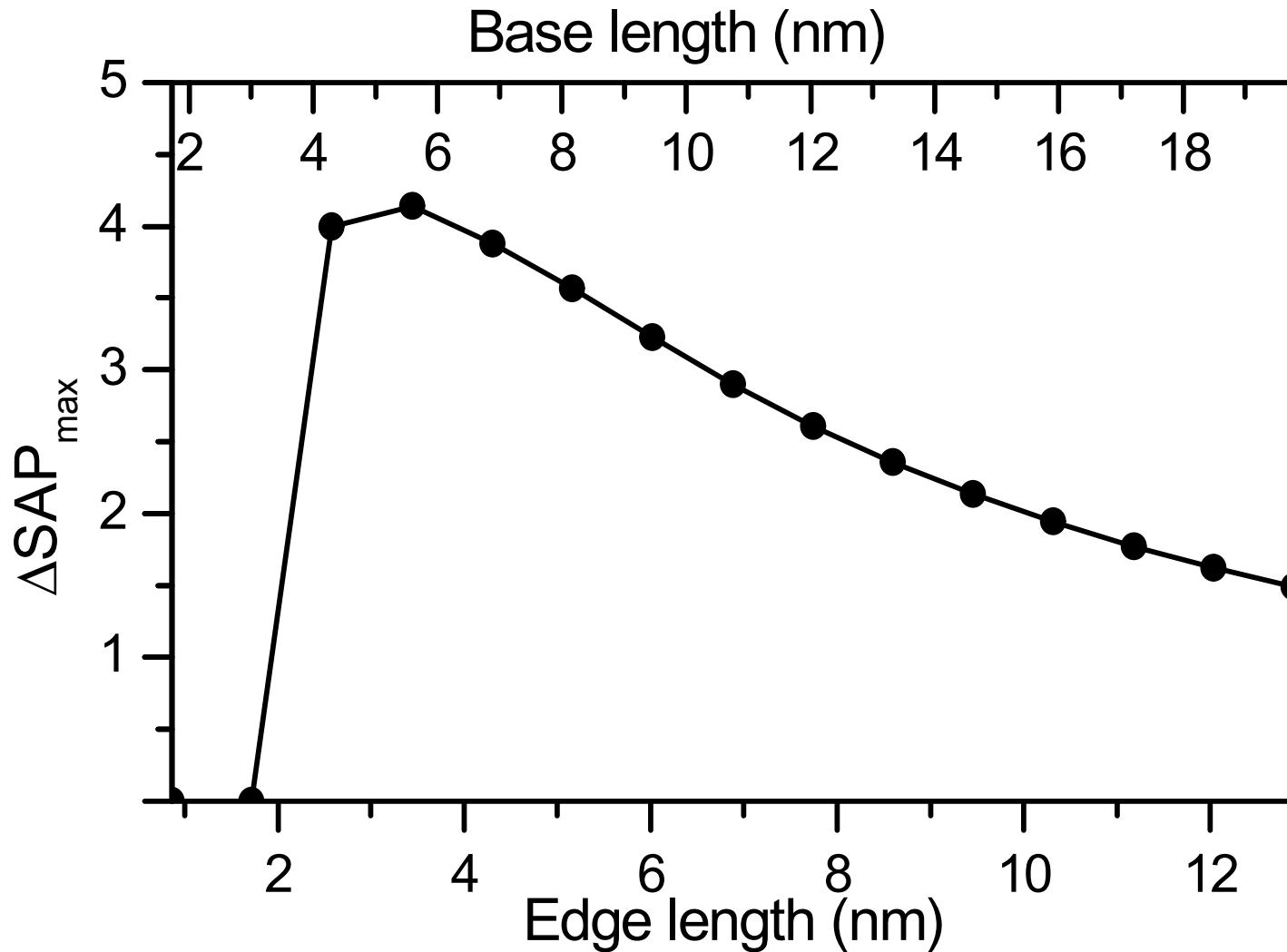
P. John Thomas and P. O'Brien  
J. Amer. Chem. Soc., 128, 2006 5615-5615







Plot showing the changes in the surface atom percentage (SAP) accompanying the growth of four hexagonal branches. The dotted line represents the SAP profile that the seed would have adopted if branching had not taken place.



:Plot showing changes in the maximum difference in the surface atom percentage ( $\Delta\text{SAP}_{\text{max}}$ ) between the tetrahedron and the corresponding structures with four hexagonal branches grown from a CdSe seed.

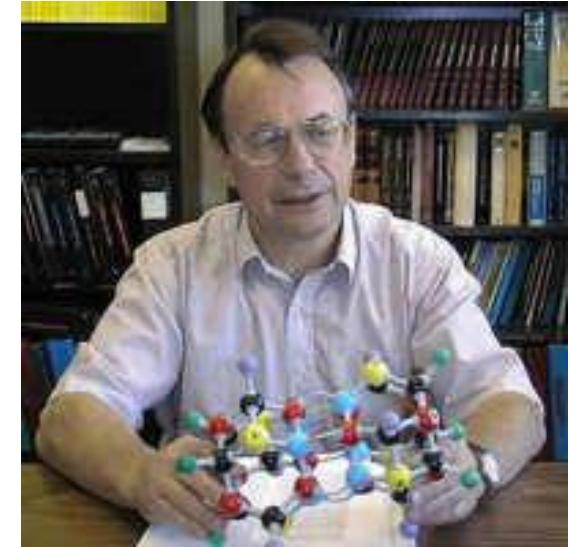
# Plan for the Lecture

*'Using Chemistry to Control Material Deposition: why choose to use a chemical method ?'*

- And Finally**
- Some Thanks**

# Thanks

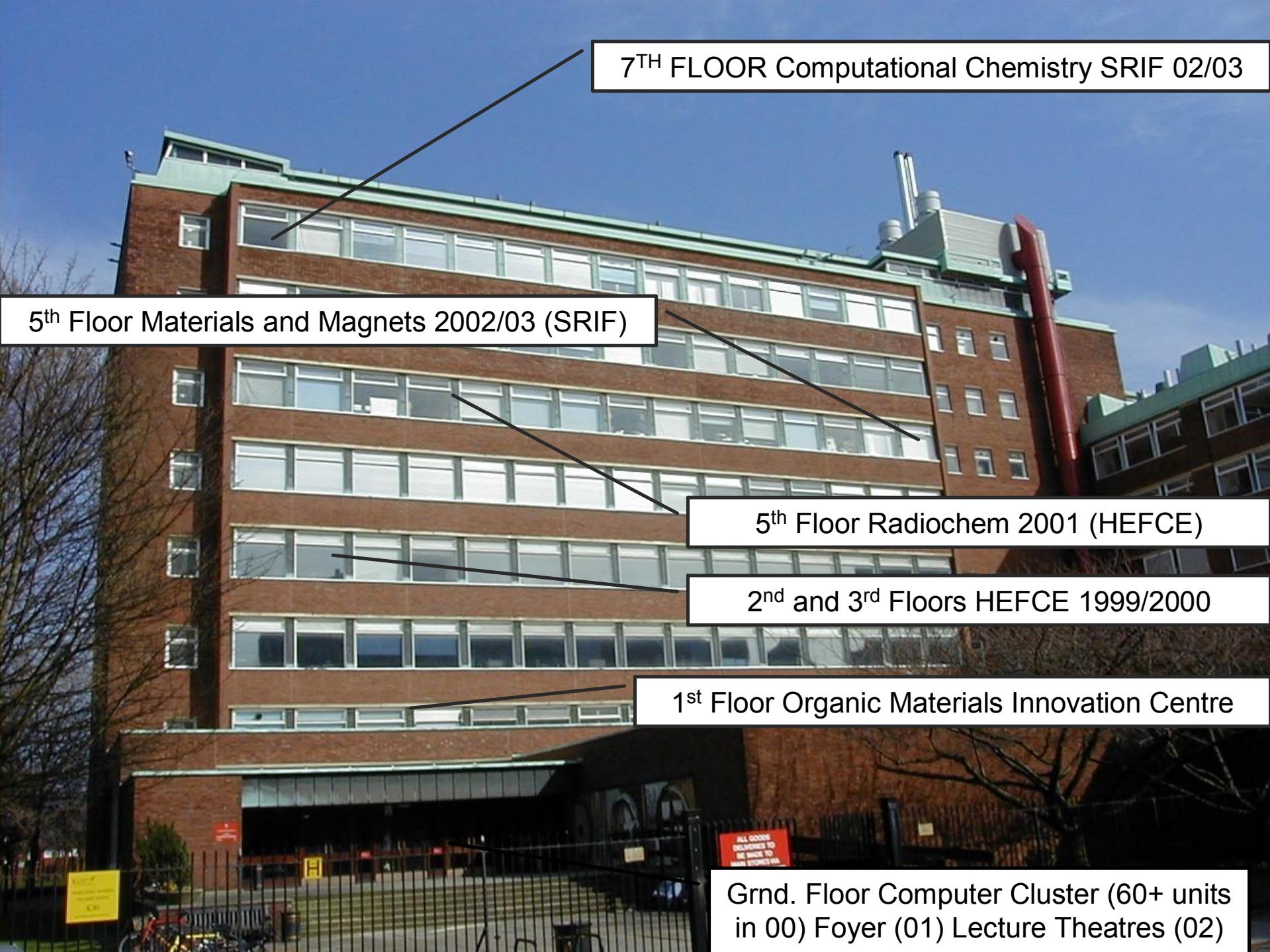
- EPSRC
  - RCUK
  - University of Manchester
- 
- Mohammed Afzaal
  - Chin Ngyuan
  - Azad Malik
  - Colin Byrom
  - Shivram Garj (Boyscast)





# A New University for the 21<sup>st</sup> Century

- Established on 1<sup>st</sup> October 2004
- Royal Charter granted on 22<sup>nd</sup> October 2004
- 34 000 students from over 150 countries (1/3 postgraduate)
- 2000 academic staff & 1200 research staff
- £504M turnover (2004-5)
- £300M capital investment programme
- Manchester 2015 Agenda launched



7<sup>TH</sup> FLOOR Computational Chemistry SRIF 02/03

5<sup>th</sup> Floor Materials and Magnets 2002/03 (SRIF)

5<sup>th</sup> Floor Radiochem 2001 (HEFCE)

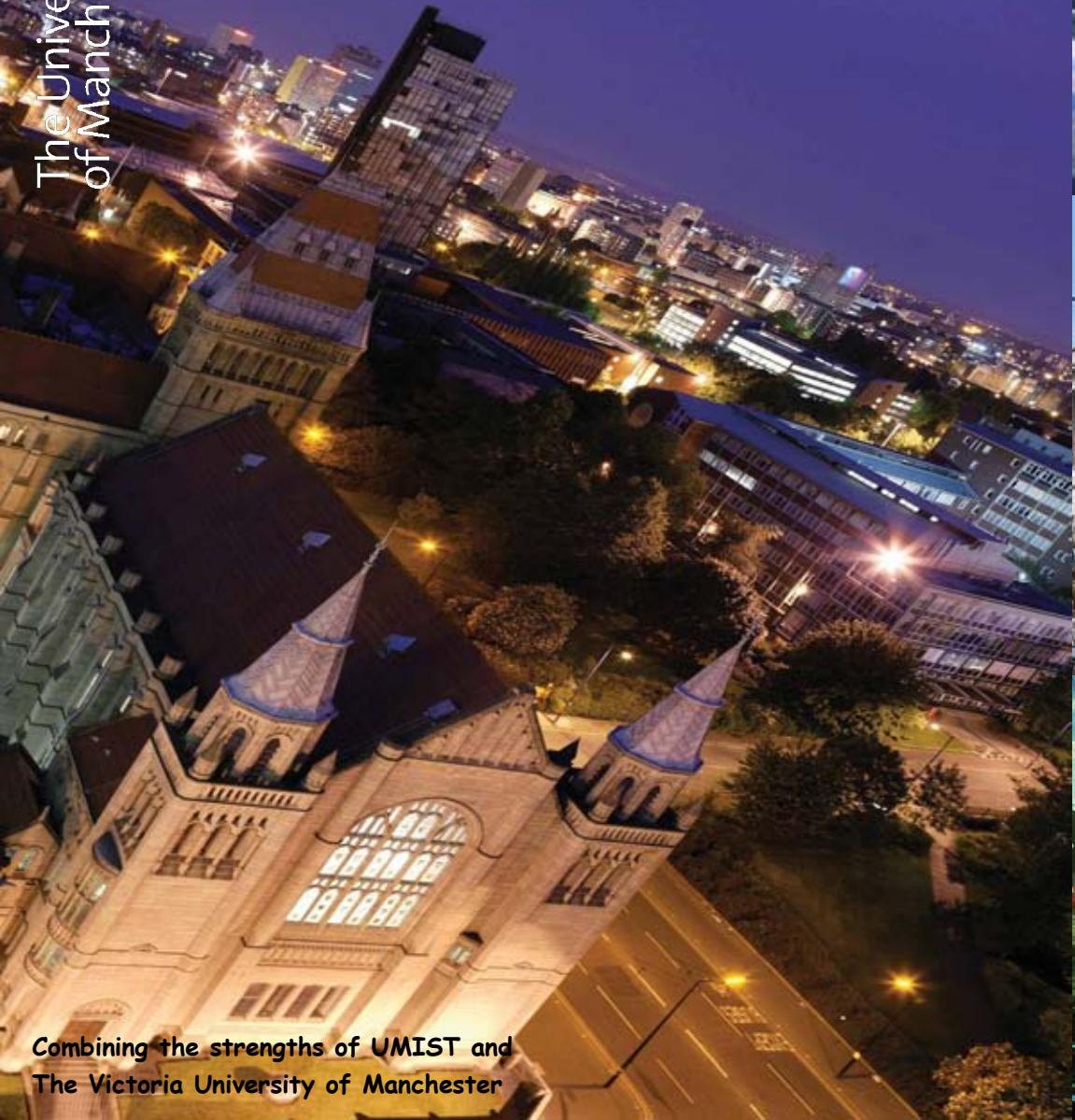
2<sup>nd</sup> and 3<sup>rd</sup> Floors HEFCE 1999/2000

1<sup>st</sup> Floor Organic Materials Innovation Centre

Grnd. Floor Computer Cluster (60+ units  
in 00) Foyer (01) Lecture Theatres (02)



lein



Combining the strengths of UMIST and  
The Victoria University of Manchester

