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Using Coordination Chemistry To Develop New Routes To Materials And Nanocomposites

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University of Manchester,

Head School of Chemistry.

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Plan for the Lecture

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

- **Two examples**

- **Use a compound as a precursor and decompose it!**

- **Use labile chemistry to control delivery rates**

Plan for the Lecture

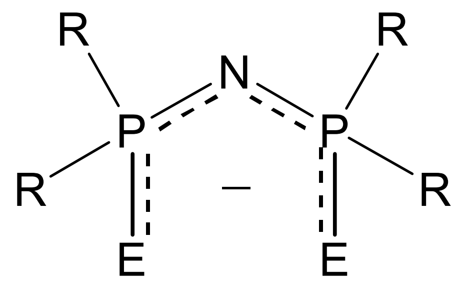
Part 1 Build and Destroy!

- **Dichalcogenoimidodiphosphinates**
- Diseleno-phosphinates
- New routes to selenohosphinates
- Why bother the CIGS systems

Part 2 Mass transfer

- PbS at interfaces

Dichalcogenoimidodiphosphinate Ligands



1 E = O
2 E = S
3 E = Se
4 E = Te

a R = Ph
b R = ^{i}Pr

$$Na[(P^{i}Pr_2)_2N] \quad + \quad Te \xrightarrow[\text{Toluene}]{\text{TMEDA}} (tmeda)Na[N(TeP^{i}Pr_2)_2]$$

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.

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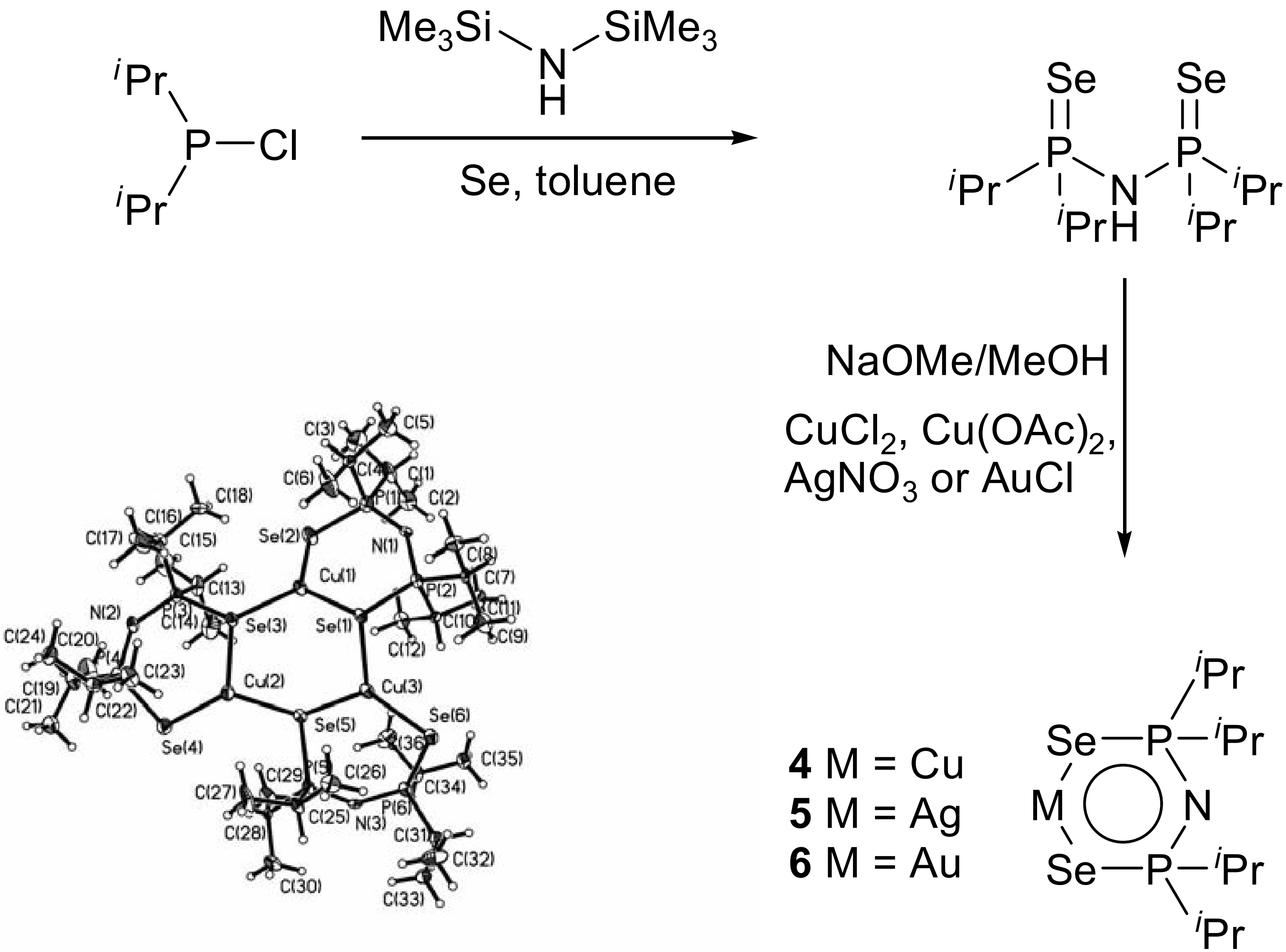


Dalton Transactions 2003, 1500-1504; J. Mater. Chem., 2004, 14, 233.

$$Na[(P^iPr_2)_2N] + 2Te \xrightarrow[\text{TMEDA}]{\text{Hot Toluene}} (tmeda)\ Na[N(TeP^iPr_2)_2]$$

$$MX_2 + 2\ (tmeda)Na[N(TeP^iPr_2)_2] \xrightarrow[\text{-2 NaX, -tmeda}]{\text{Diethyl ether}} M[(TeP^iPr_2)_2N]_2$$

M = Cd (**1**), X = I; M = Hg (**2**), X = Cl, tmeda = tetramethylethanediamine

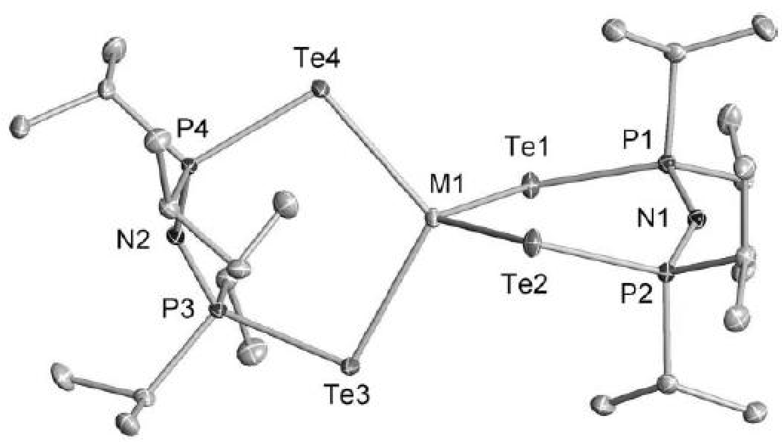
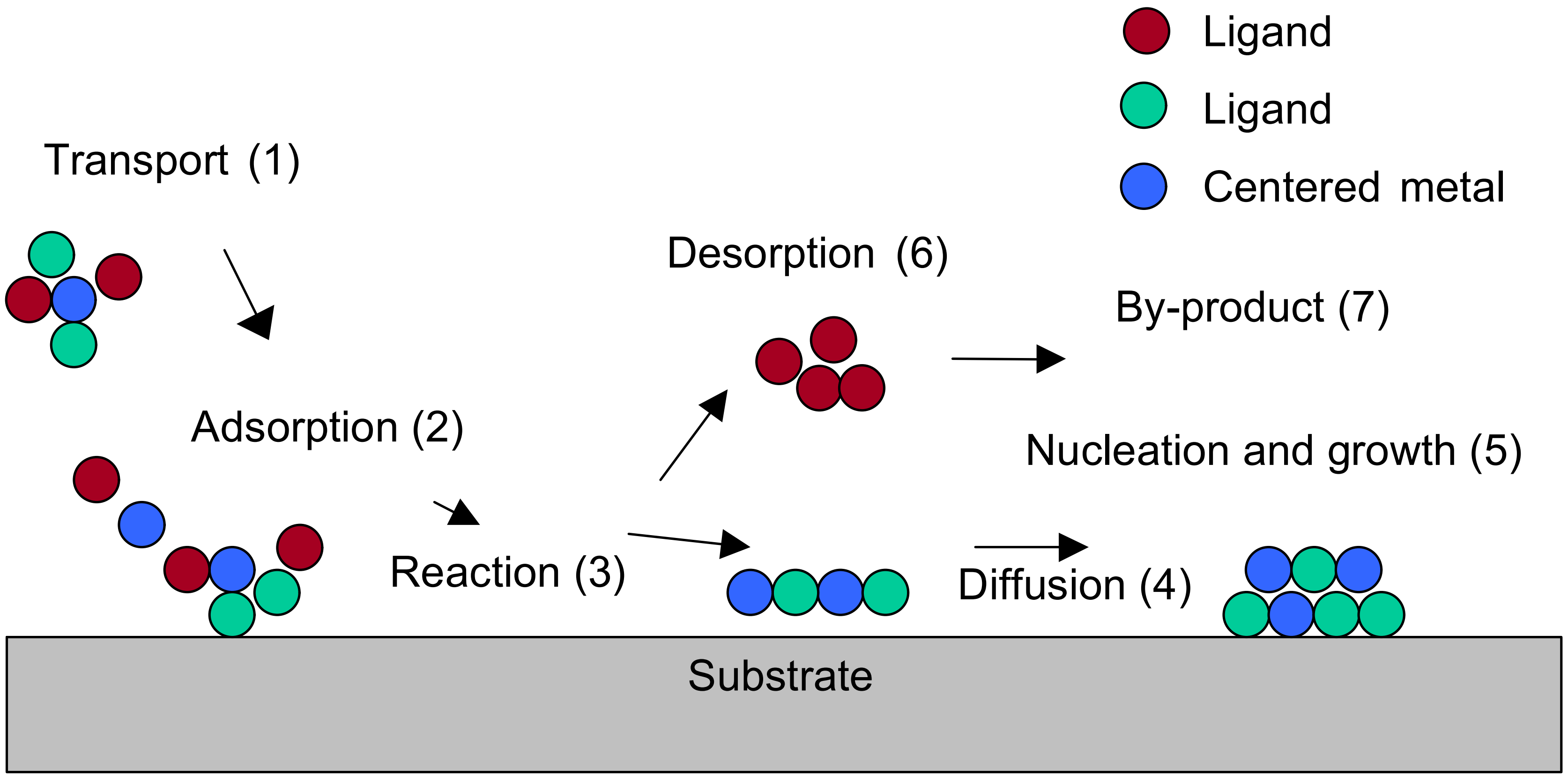


Fig. 1 Thermal ellipsoid plot (30% probability) of the structure of **2a** (M = Zn), **2b** (M = Cd) and **2c** (M = Hg). Hydrogen atoms have been omitted for clarity.

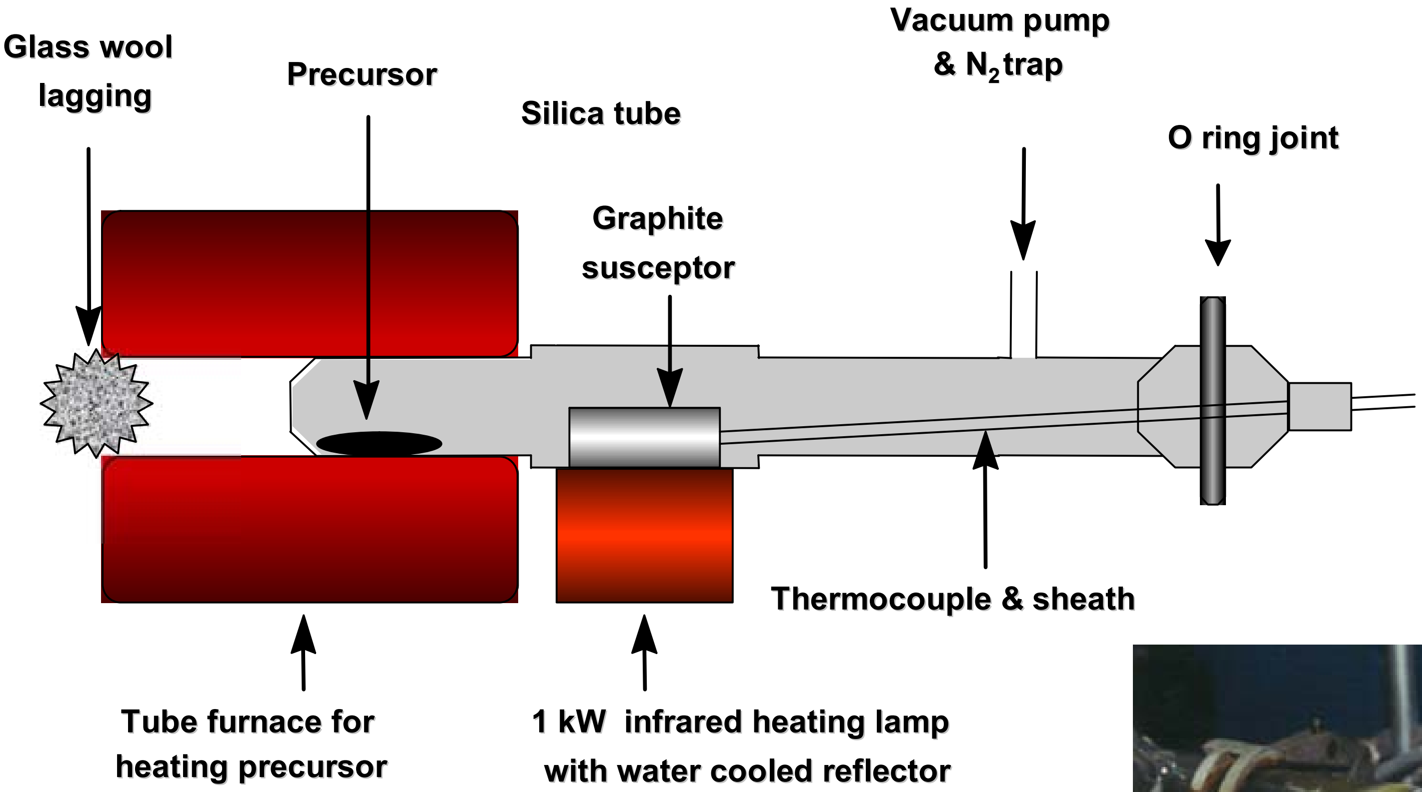
Synthesis and structures of M[N(TePPr$^i_2$)$_2$-*Te*,*Te′*]$_n$ (*n* = 2, M = Zn, Cd, Hg; *n* = 3, M = Sb, Bi): the first ditelluroimidodiphosphinato p- and d-block metal complexes

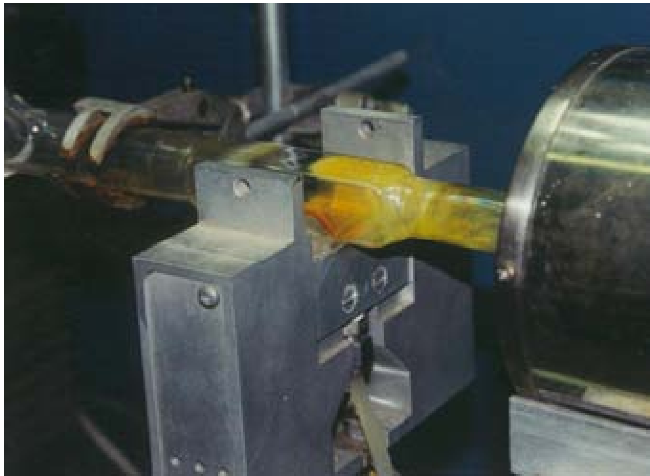
Tristram Chivers,* Dana J. Eisler and Jamie S. Ritch
Department of Chemistry, University of Calgary, Calgary, AB, Canada T2N 1N4. E-mail: chivers@ucalgary.ca; Fax: (+1)403-289-9488; Tel: (+1)403-220-5741

The 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*. H_2S, H_2Se, NH_3, PH_3, AsH_3, SiH_4 etc.
- Environment and safety conditions: particularly important for industrial processes.

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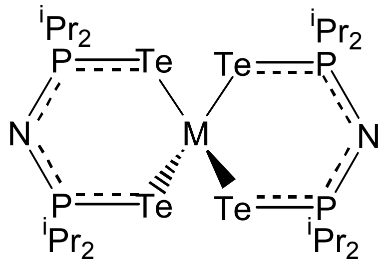
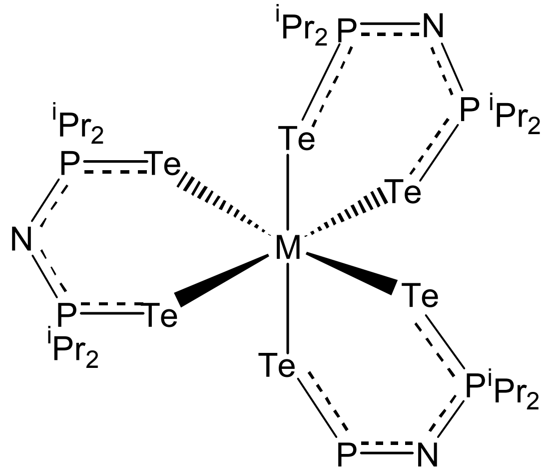
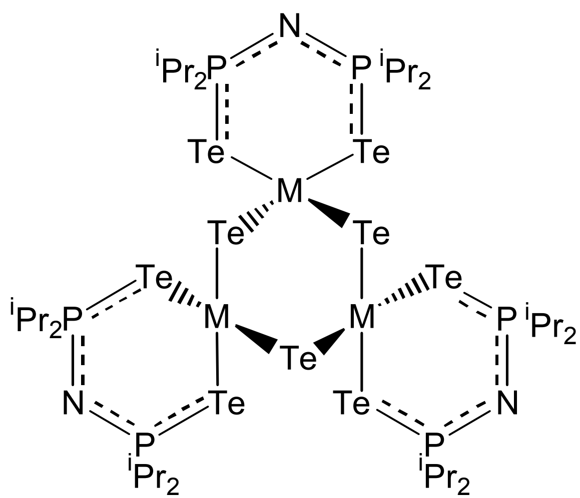


M = Cd



M = Sb

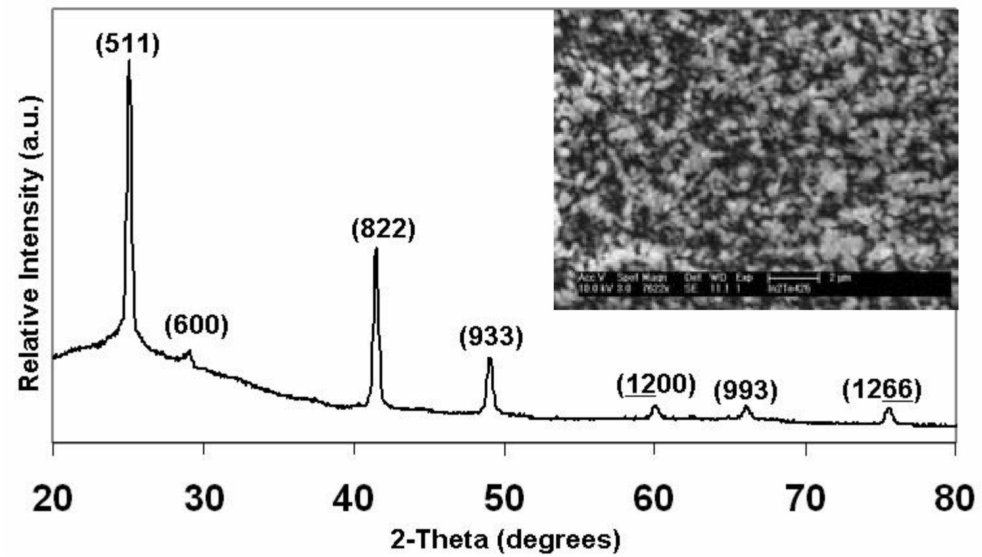


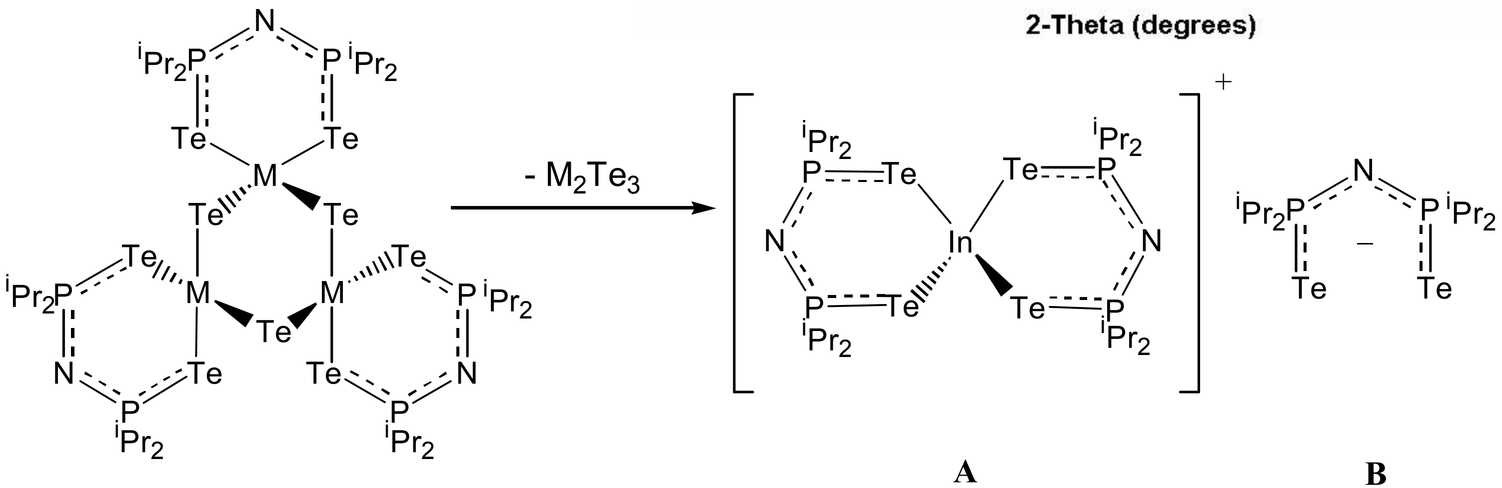
1 M = In
2 M = Ga

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

AACVD from $\{In(\mu\text{-}Te)[N(^{i}Pr_2PTe)_2]\}_3$

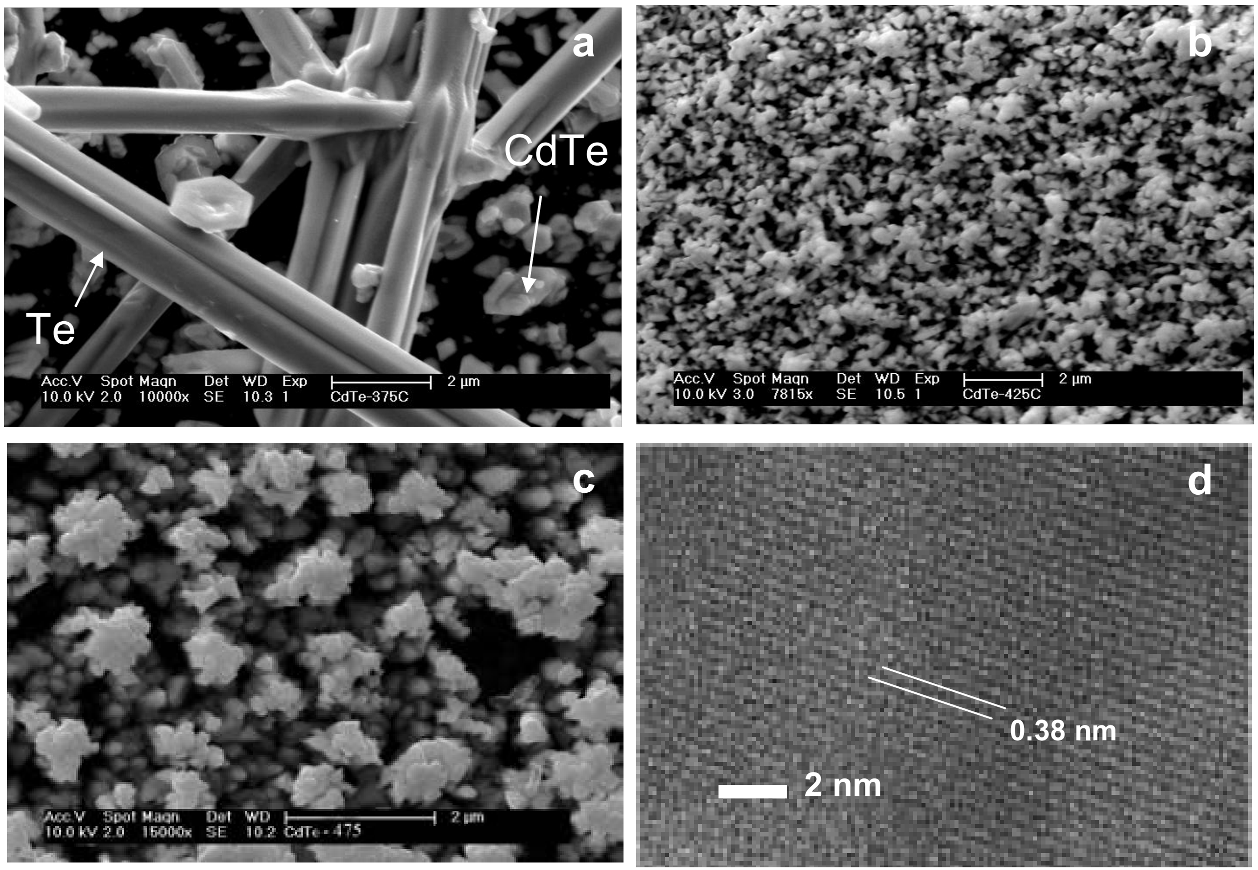
• pXRD of cubic In_2Te_3 thin films at 425 °C with a dynamic argon flow rate of 240 sccm.





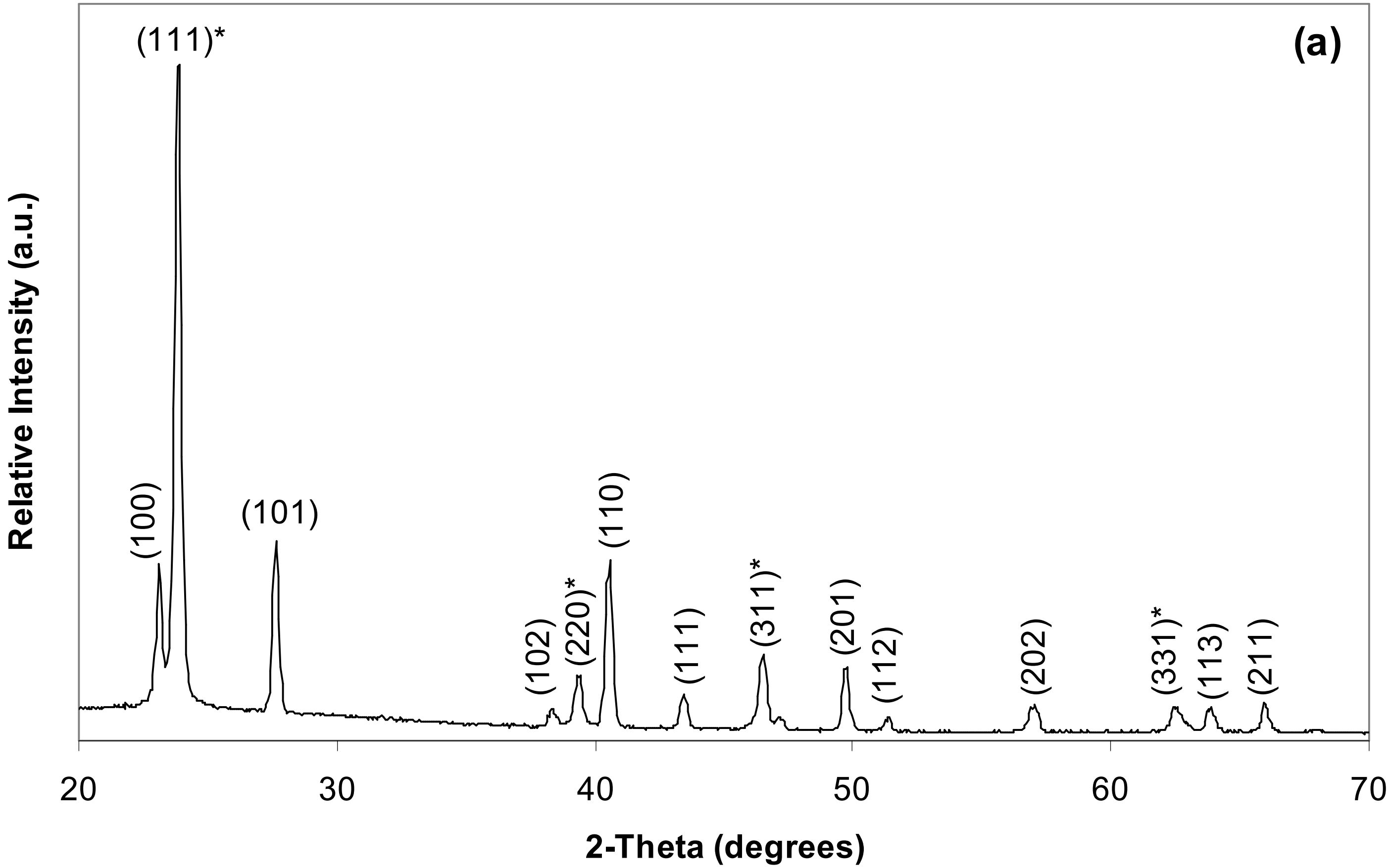
1 M = In

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

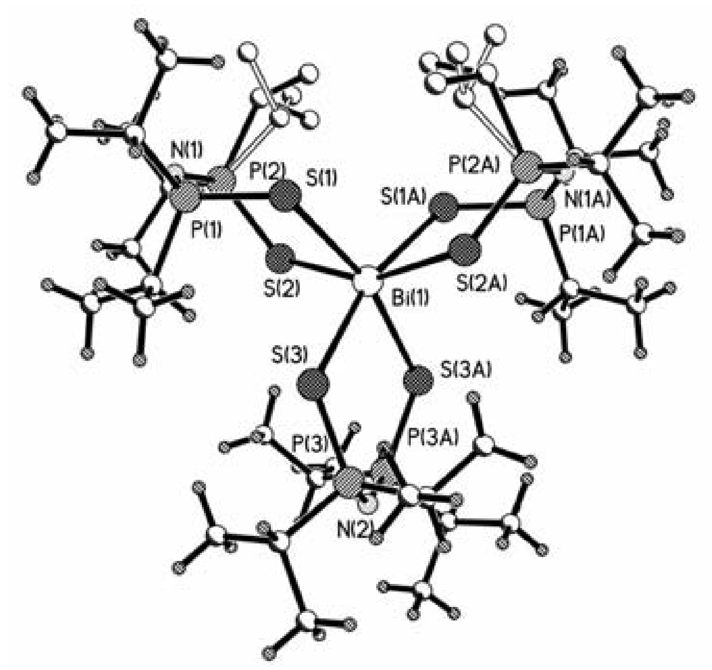


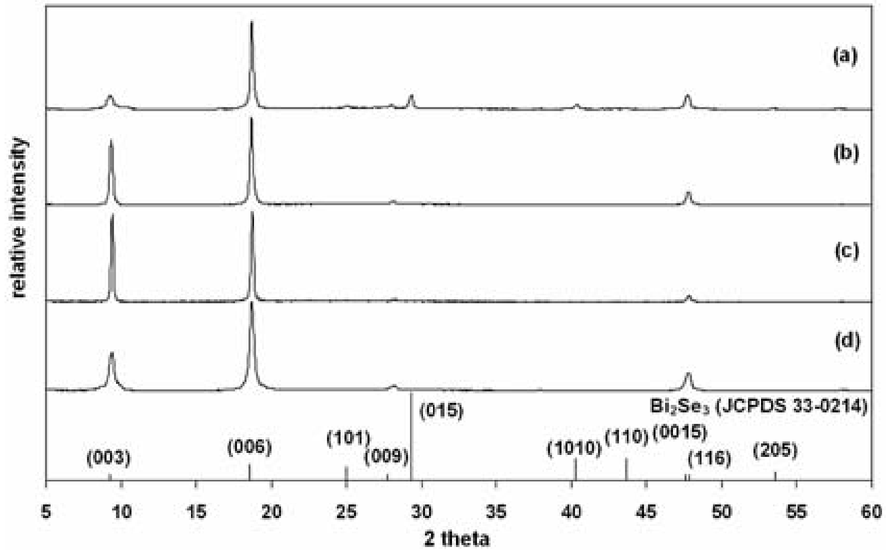
SEM of (a) CdTe and Te deposited at 375^{o}C;

CdTe deposited at (b) 425^{o}C, (c) 475^{o}C; (d) HRTEM of film deposited at 475^{o}C.



Cubic CdTe marked with asterisk and Hexagonal Te film





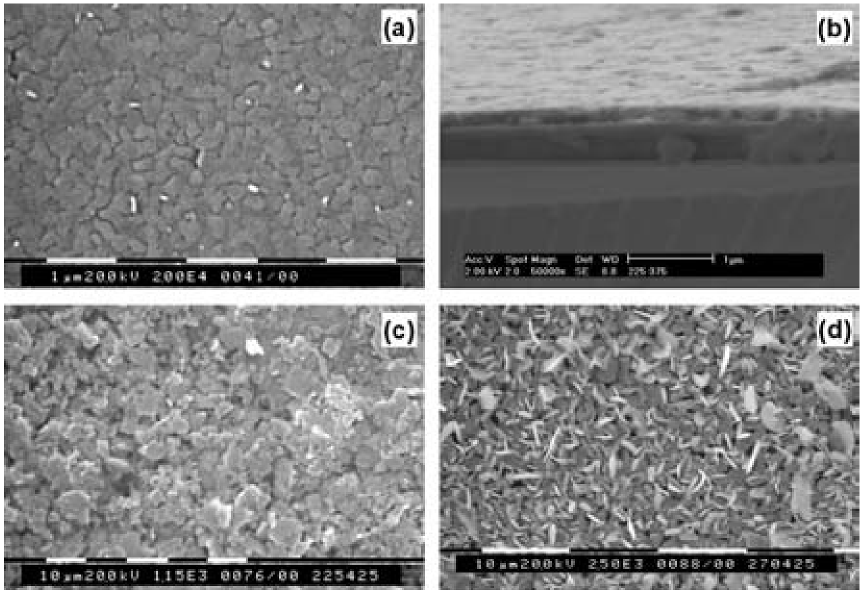
films grown by LP-MOCVD of $Bi[(SeP^{i}Pr_2)_2N]_3$ at

(a) T_{prec} = 275 °C, T_{subs} = 425 °C,

(b) T_{prec} = 225 °C, T_{subs} = 425 °C,

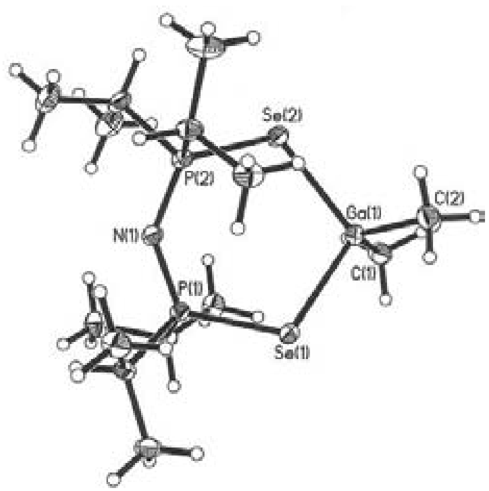
(c) T_{prec} = 225 °C, T_{subs} = 400 °C,

(d) T_{prec} = 225 °C, T_{subs} = 375 °C.

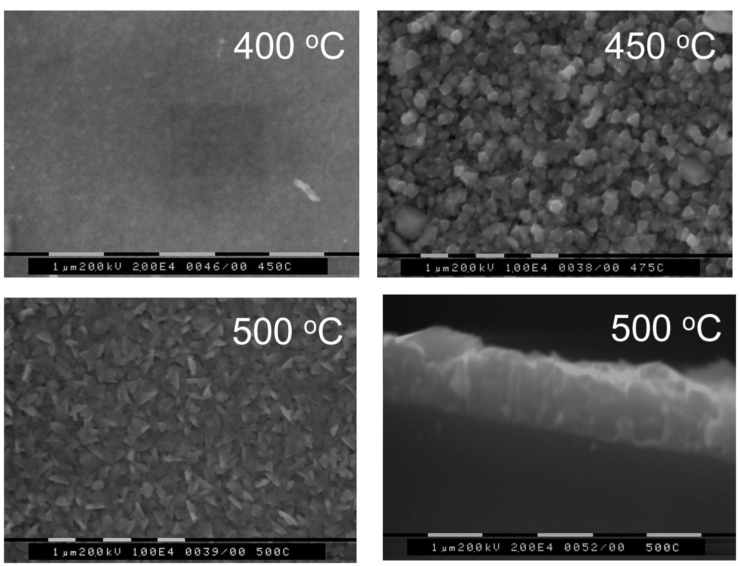


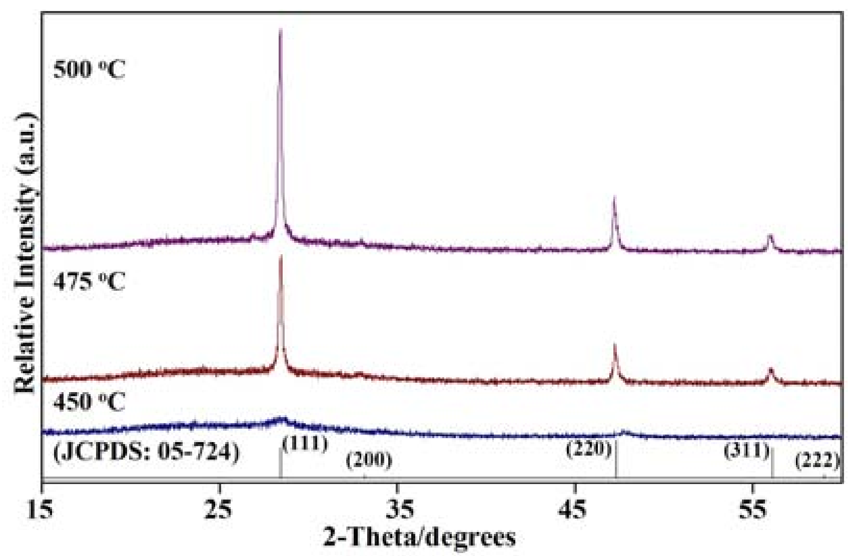
Dalton Transactions 2003, 1500-1504

$[NH(SeP^iPr_2)_2] + Et_3Ga \xrightarrow{\text{Toluene}} [Et_2Ga(SeP^iPr_2)_2N]$



$\xrightarrow[\text{Pre}_{\text{Temp}} = 185\ ^oC]{\text{LP-MOCVD}}$ **Cubic Ga_2Se_3**

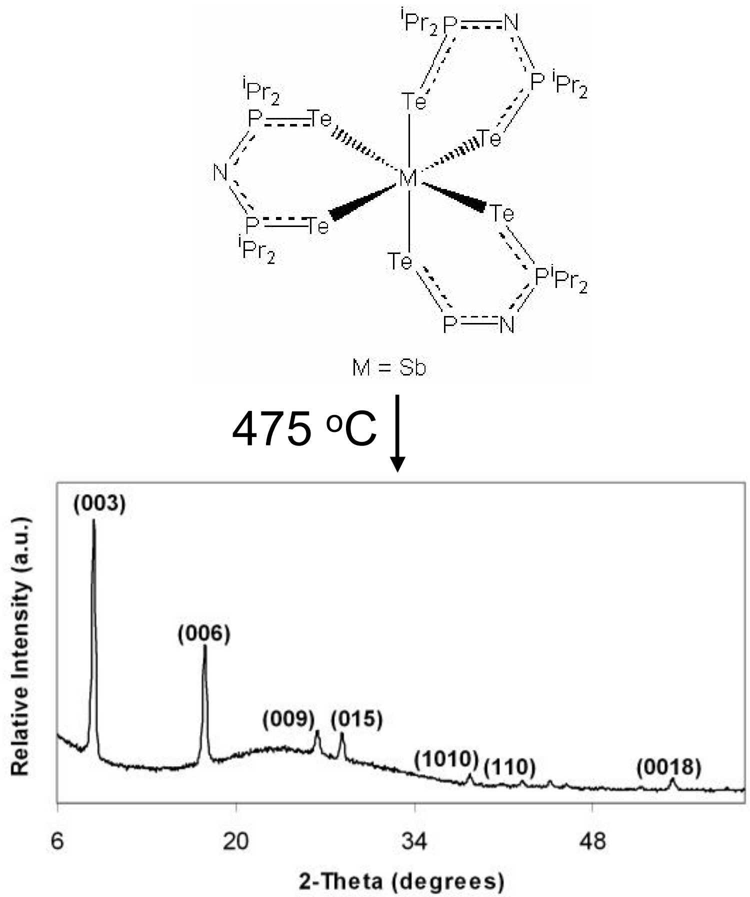


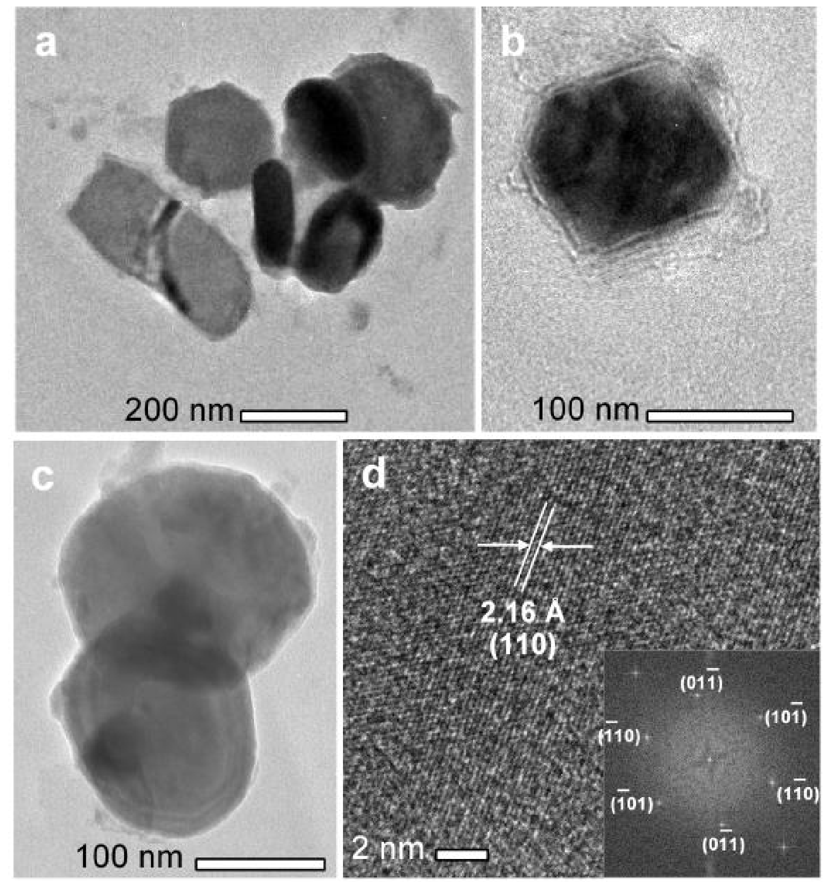


J.-Ho Park, M. Afzaal, M. Helliwell, M. A. Malik, P O'Brien, and J. Raftery, Chem. Mater. 15, 2003, 4205.

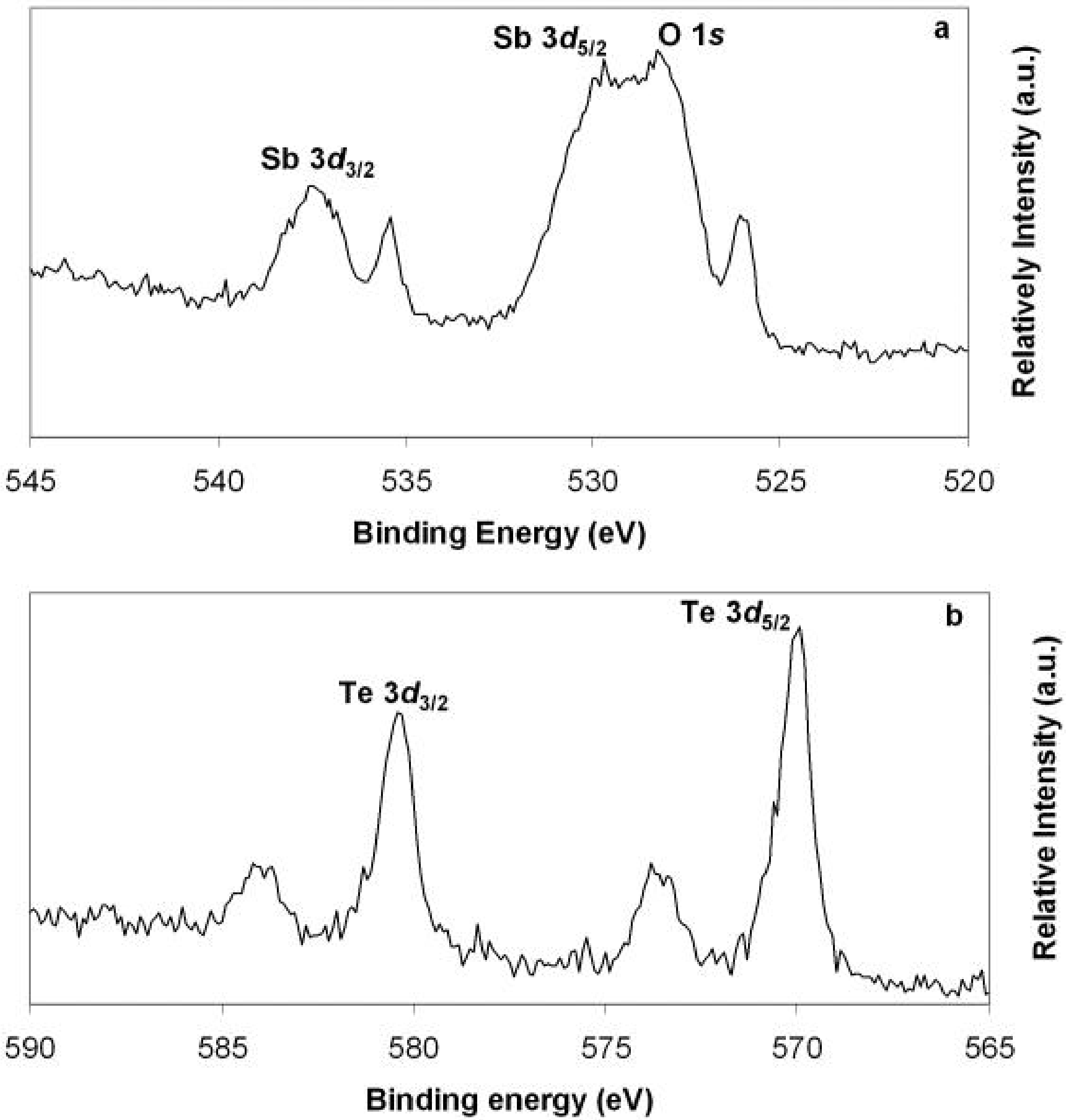
AACVD studies of $Sb[(TeP^{i}Pr_2)_2N]_3$

• pXRD of rhombohedral Sb_2Te_3 thin films at 475 ^{o}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.



Survey XPS scan for

(a) Te and

(b) Sb

films grown at 475 °C.

Plan for the Lecture

Part 1 Build and Destroy!

- Dichalcogenoimidodiphosphinates
- **Diseleno-phosphinates**
- New routes to selenohosphinates
- Why bother the CIGS systems

Part 2 Mass transfer

- PbS at interfaces

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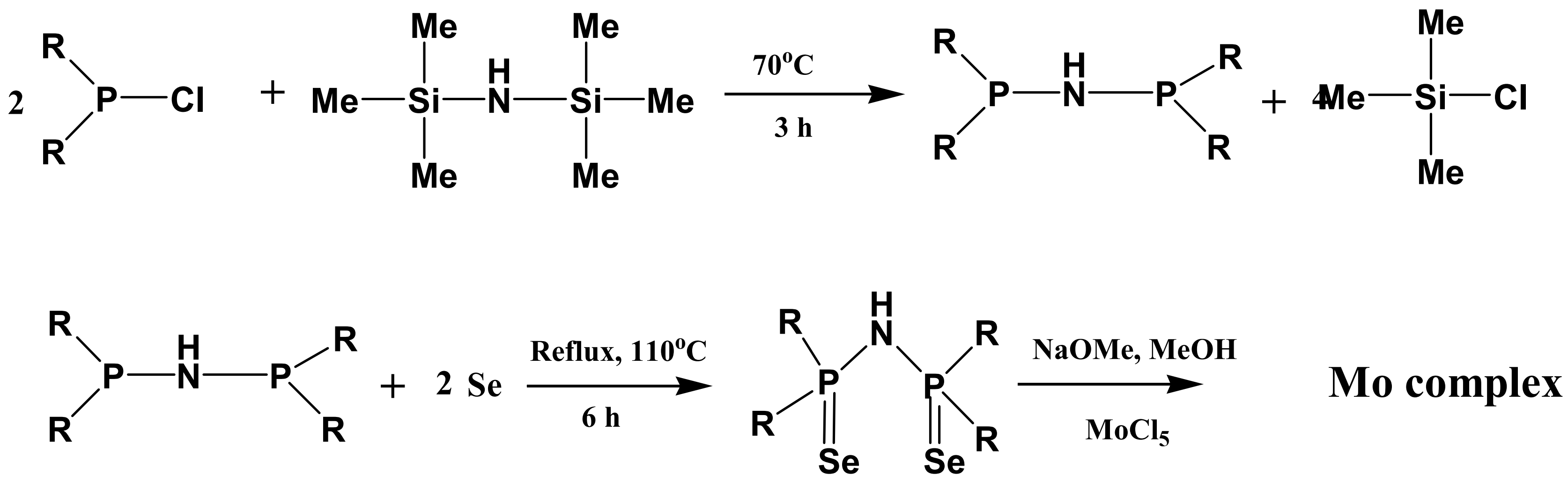
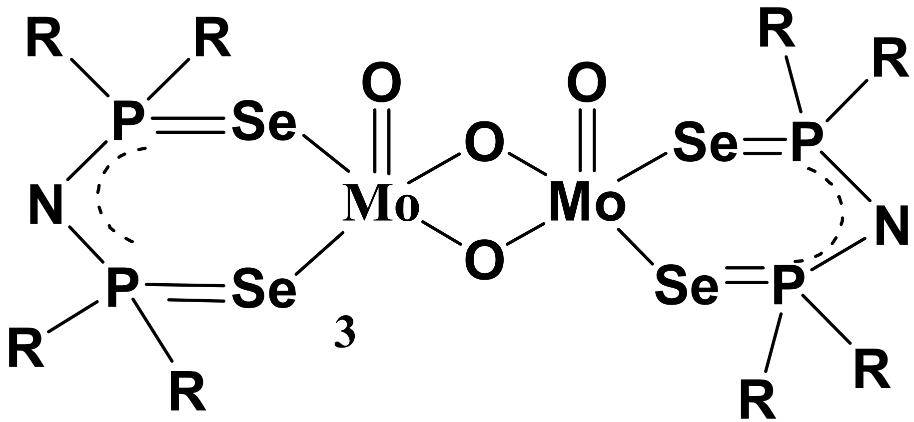
A Serendipitous Synthesis of Diselenophosphinates



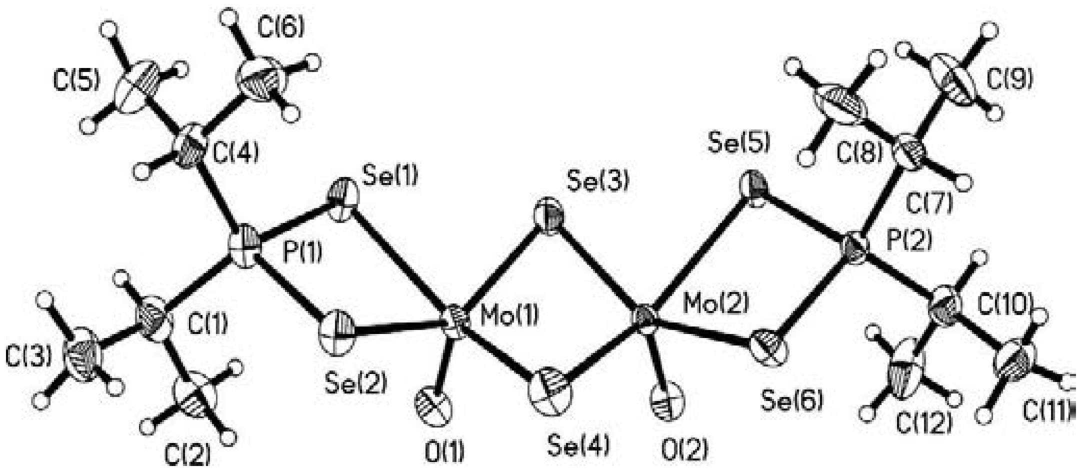
R = ^{i}Pr



$R = {}^{i}Pr$

Expected Product

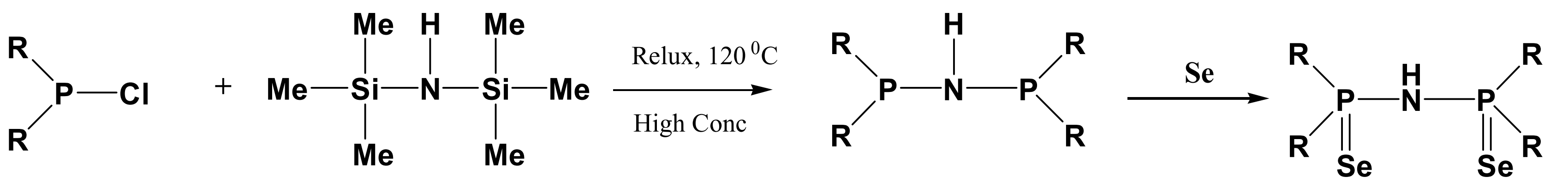
HOWEVER!



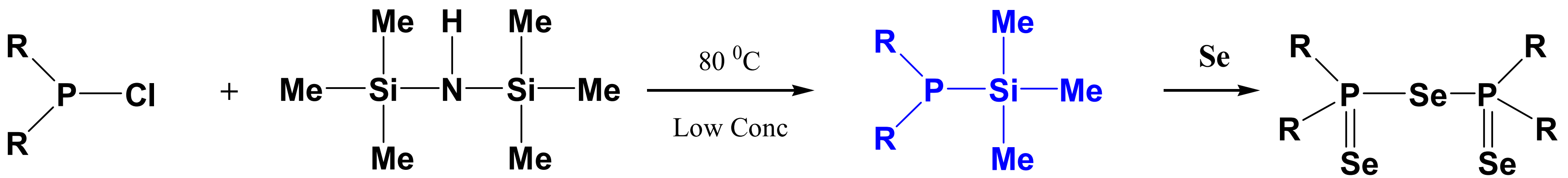
Obtained Product

Possible Mechanism?

Main Product



By-Product

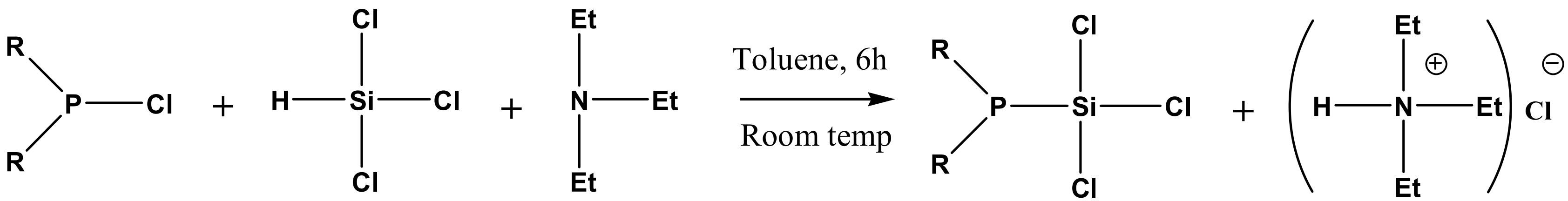


R = ^{i}Pr, Ph

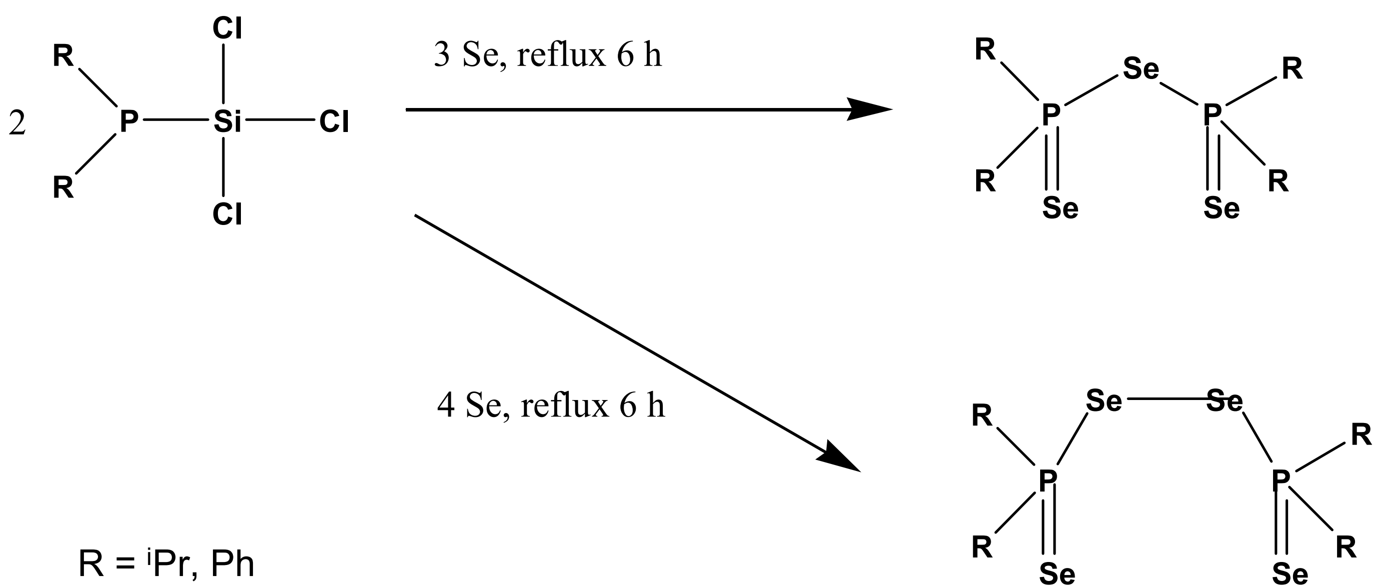
Inserting of Se into P-Si bond of the intermediate $R_2PSi(Me)_3$?

Novel Synthetic Route to Se Phosphinates

Step 1: Making the intermediate



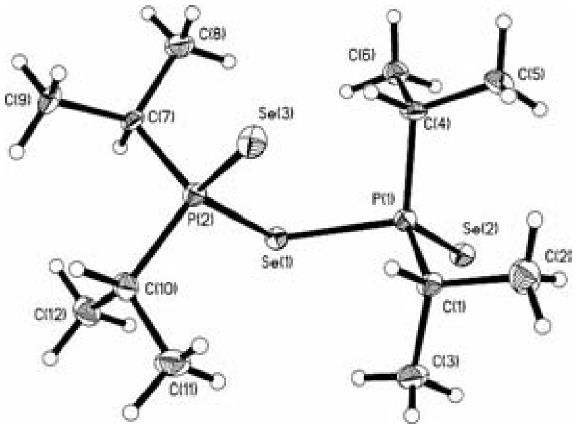
Step 2: Inserting Se



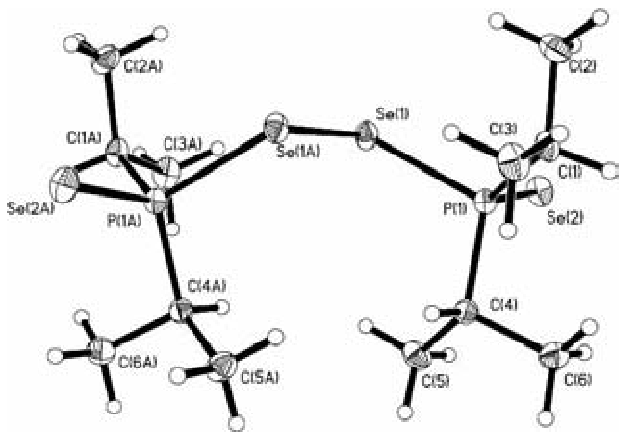
R = ^{i}Pr, Ph

Q. C. Nguyen, M. Mohammad, M. A. Malik, P. O'Brien, Chem. Commun., 2006, 2179.

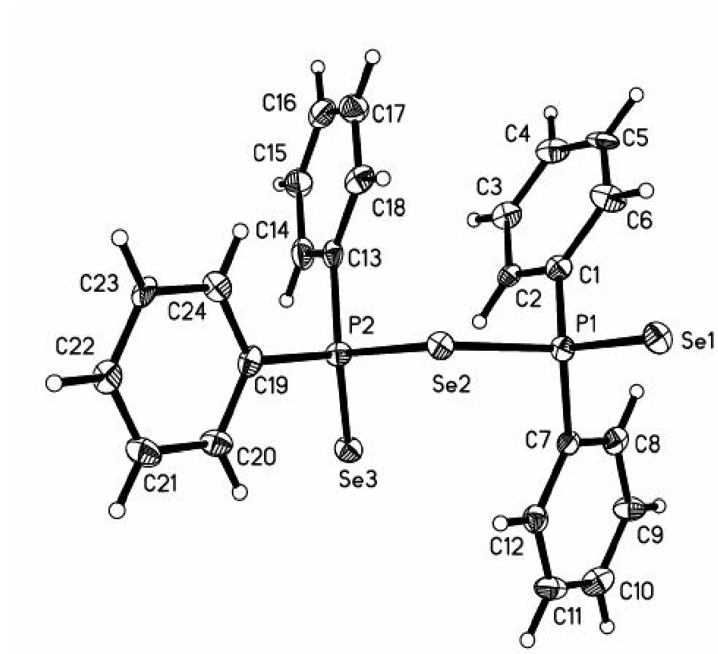
X-ray Crystal Structures



$(^{i}Pr_2PSe)_2Se$

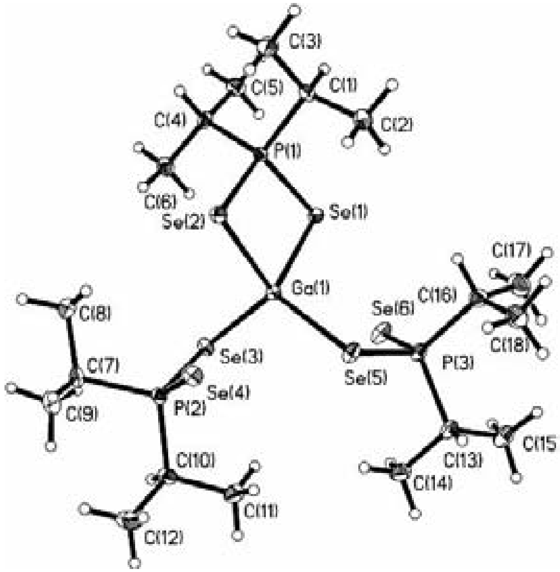


$(^{i}Pr_2PSe)_2Se_2$

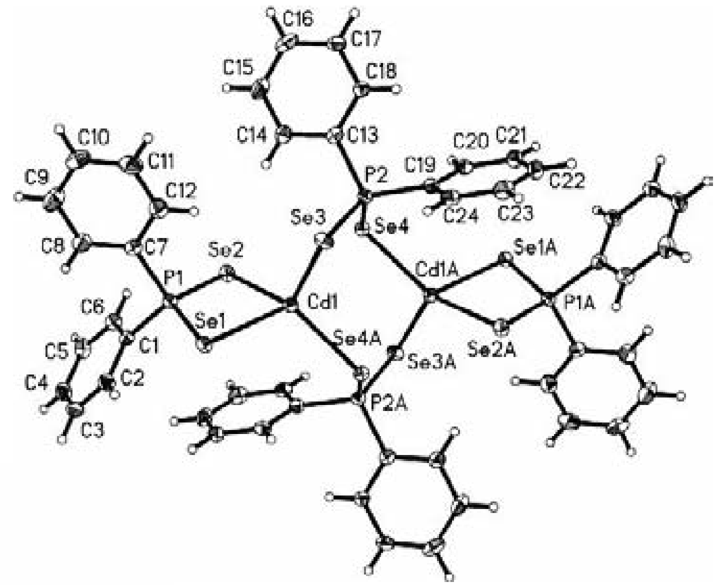


$(Ph_2PSe)_2Se$

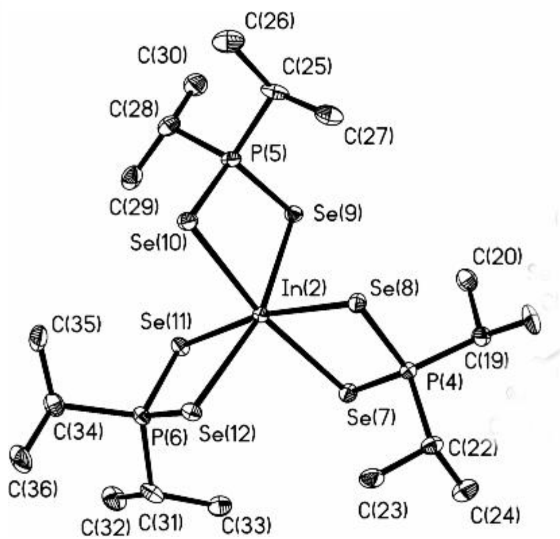
Inorganic complexes



[Ga(^{i}Pr$_2$PSe$_2$)$_3$]



[Cd$_2$(Ph$_2$PSe$_2$)$_4$]



[In(^{i}Pr$_2$PSe$_2$)$_3$]

C. Q. Nguyen, M. Afzaal, M. A. Malik, P. O’Brien, Chem. Commun., 2006, 2182.

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- Dichalcogenoimidodiphosphinates
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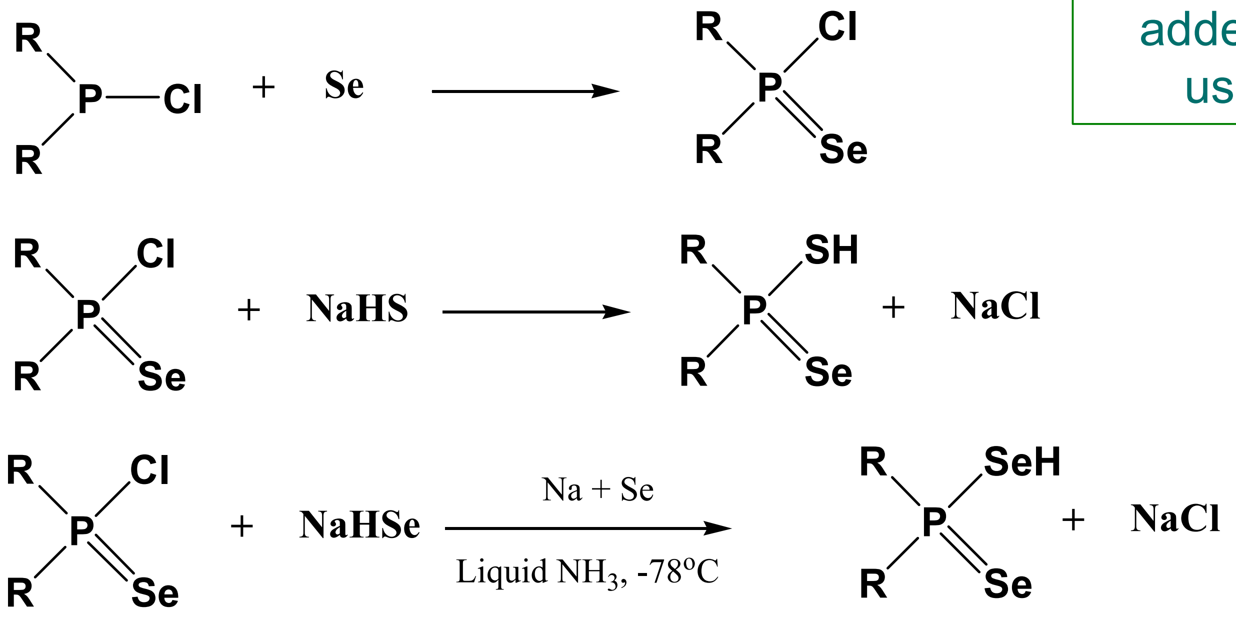
DIALKYLDICHALCOGENOPHOSPHINATES

Previous Work

Not-reproducible with added difficulty of using NaHSe

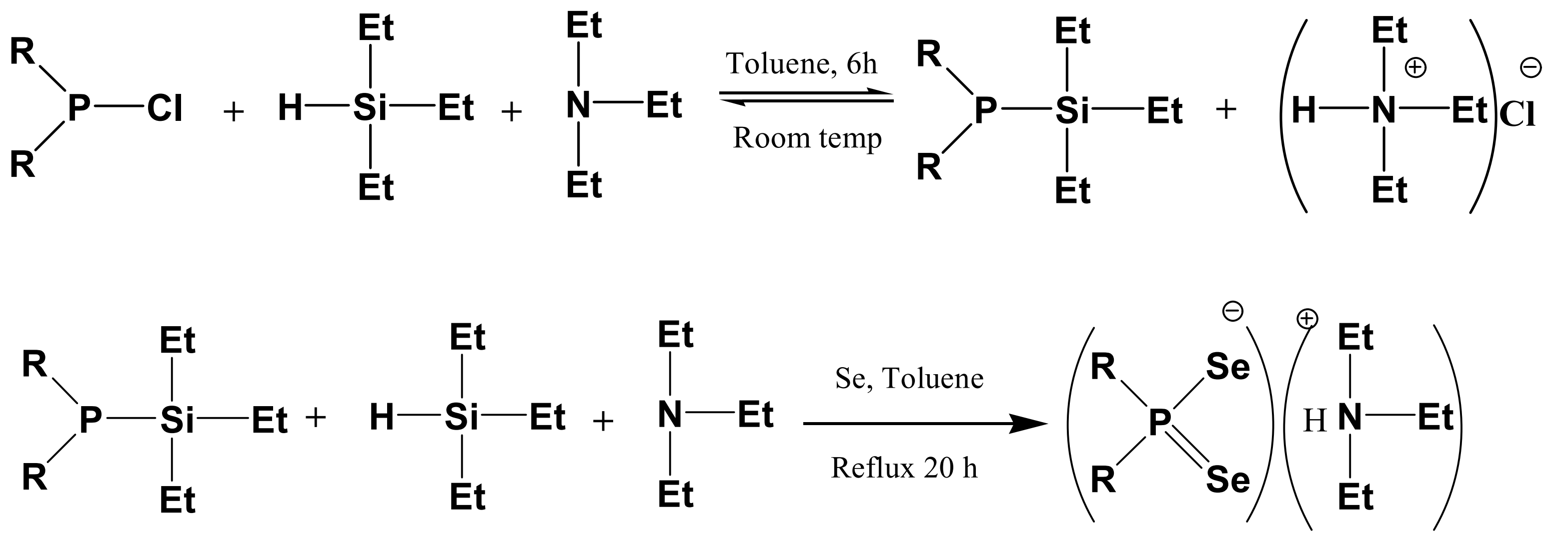


Unstable, never isolated, used *in situ* to make metal complexes, no solid state characterization

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

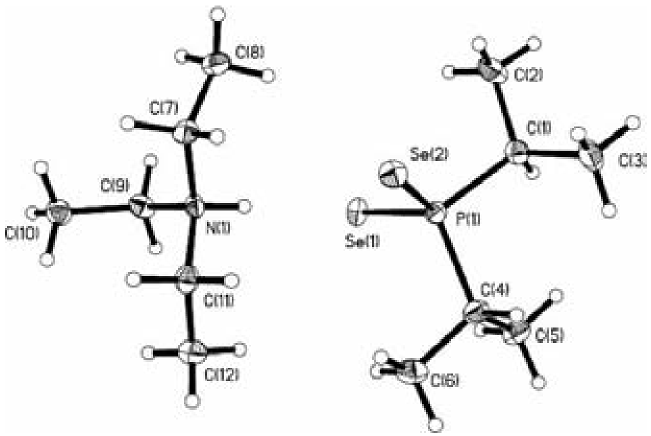
A New Route to R_2PSe_2 Ligands

- Alternatively, use excess Lewis Base NEt_3 to stabilize ionic species e.g. $[(^iPr)_2PSe_2]^-$
- $HSiCl_3/NEt_3$: did not work due to the formation of $[HNEt_3^+][SiCl_3^-]$
- $HSiEt_3/NEt_3$: worked

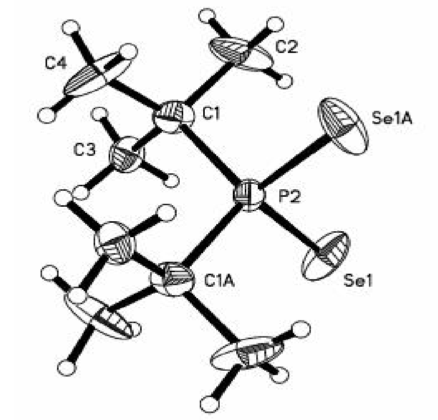


R= ^{i}Pr, Ph, ^{t}Bu

X-ray Crystal Structures

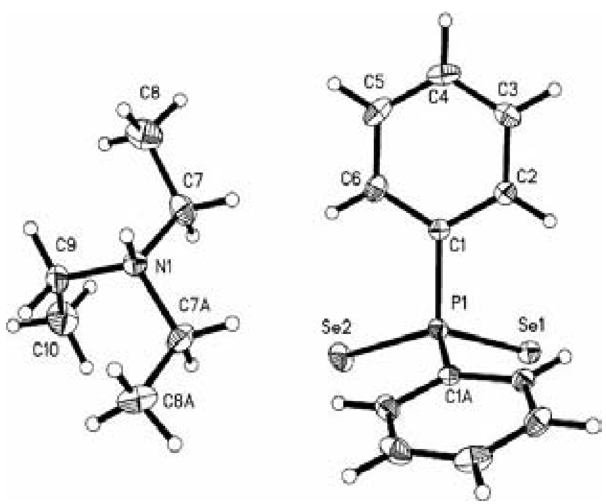


(HNEt$_3$)(^{i}Pr$_2$PSe$_2$)

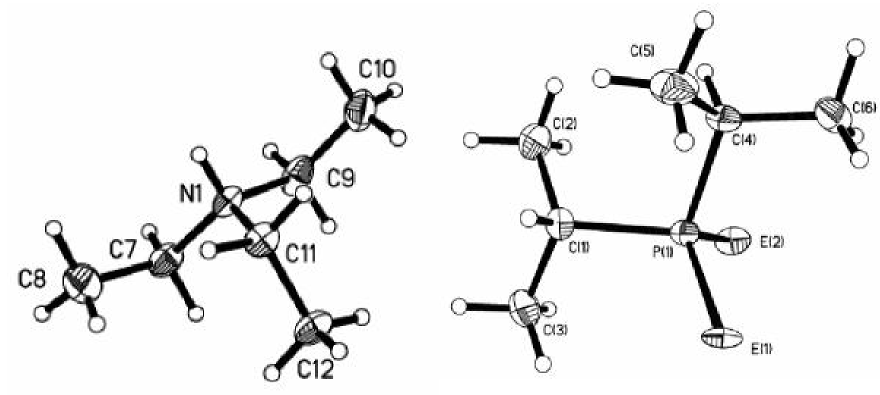


(^{t}Bu$_2$PSe$_2$)

Disorder in the cation hence, not shown

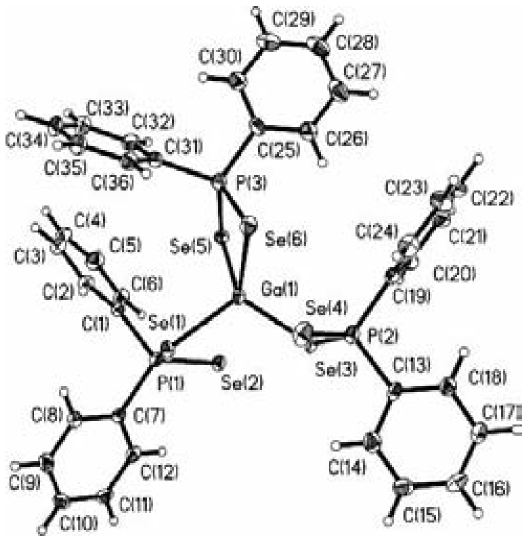


(HNEt$_3$)(Ph$_2$PSe$_2$)

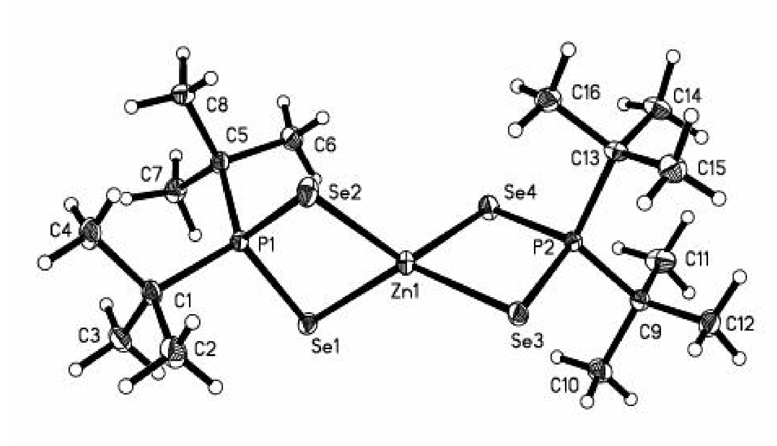


(HNEt$_3$)(^{i}Pr$_2$PSSe)

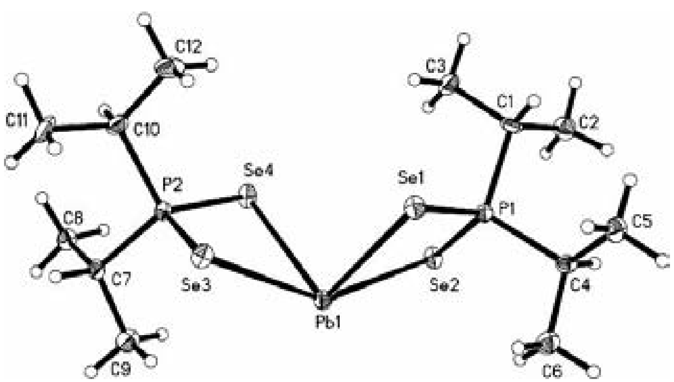
Inorganic complexes



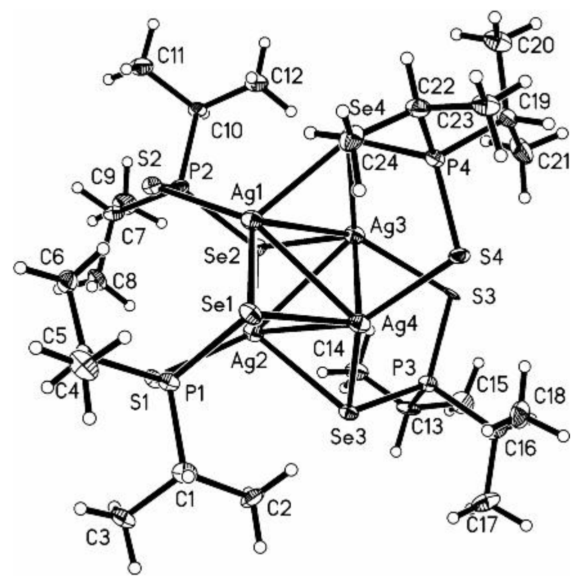
$[Ga(Ph_2PSe_2)_3]$



$[Zn(^tBu_2PSe_2)_2]$



$[Pb(Se_2P^iPr_2)_2]$



$[Ag_4(SSeP^iPr_2)_4]$

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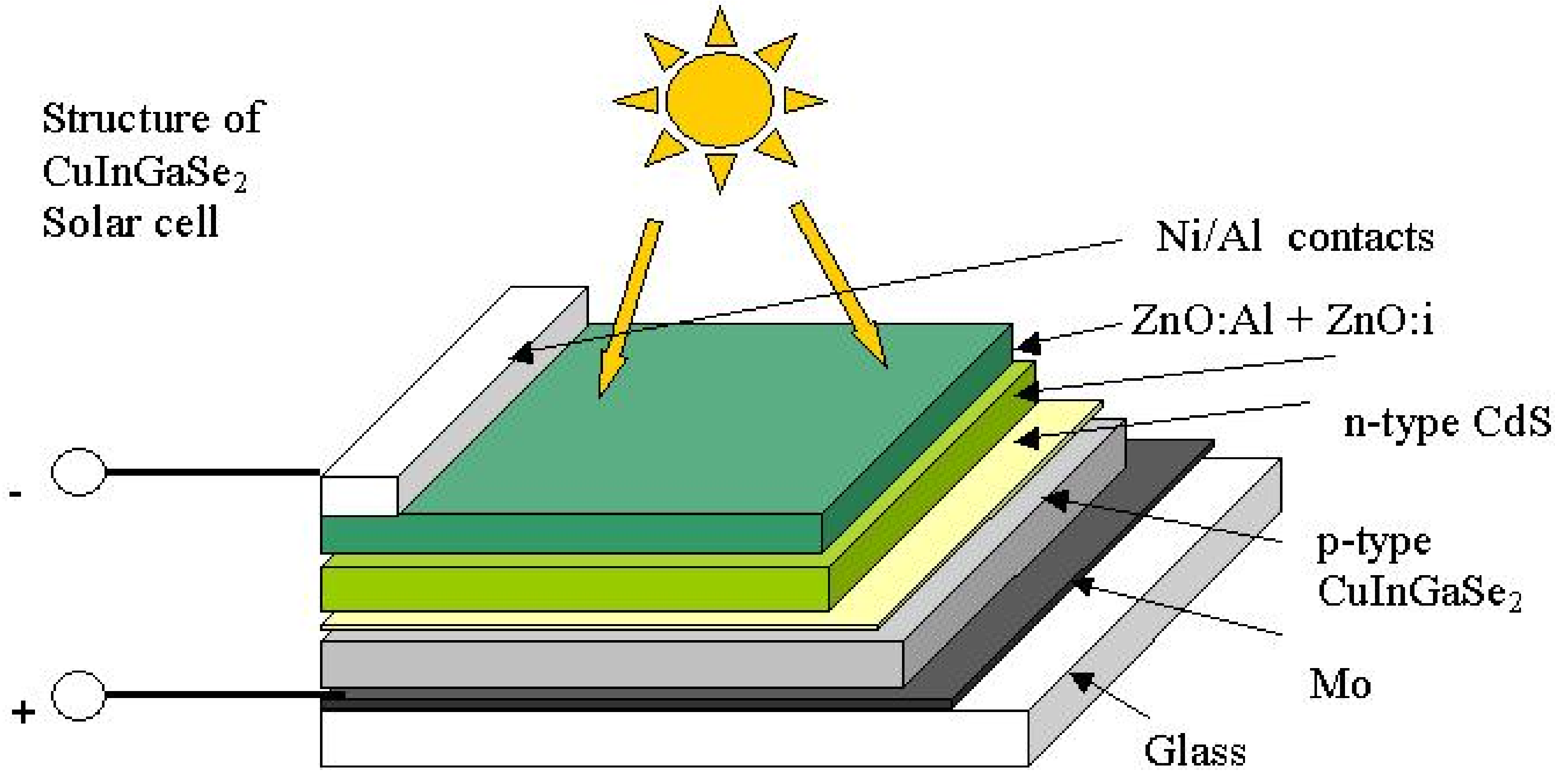


Thin-film solar cells based on CIGS (Cu(In,Ga)Se_2) companies working with CIGS cells include Shell Solar and Würth.

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

http://www.speedace.info/automotive_directory/honda.htm

CIGS Coming Down to Earth

Copper complexes

From CuCl

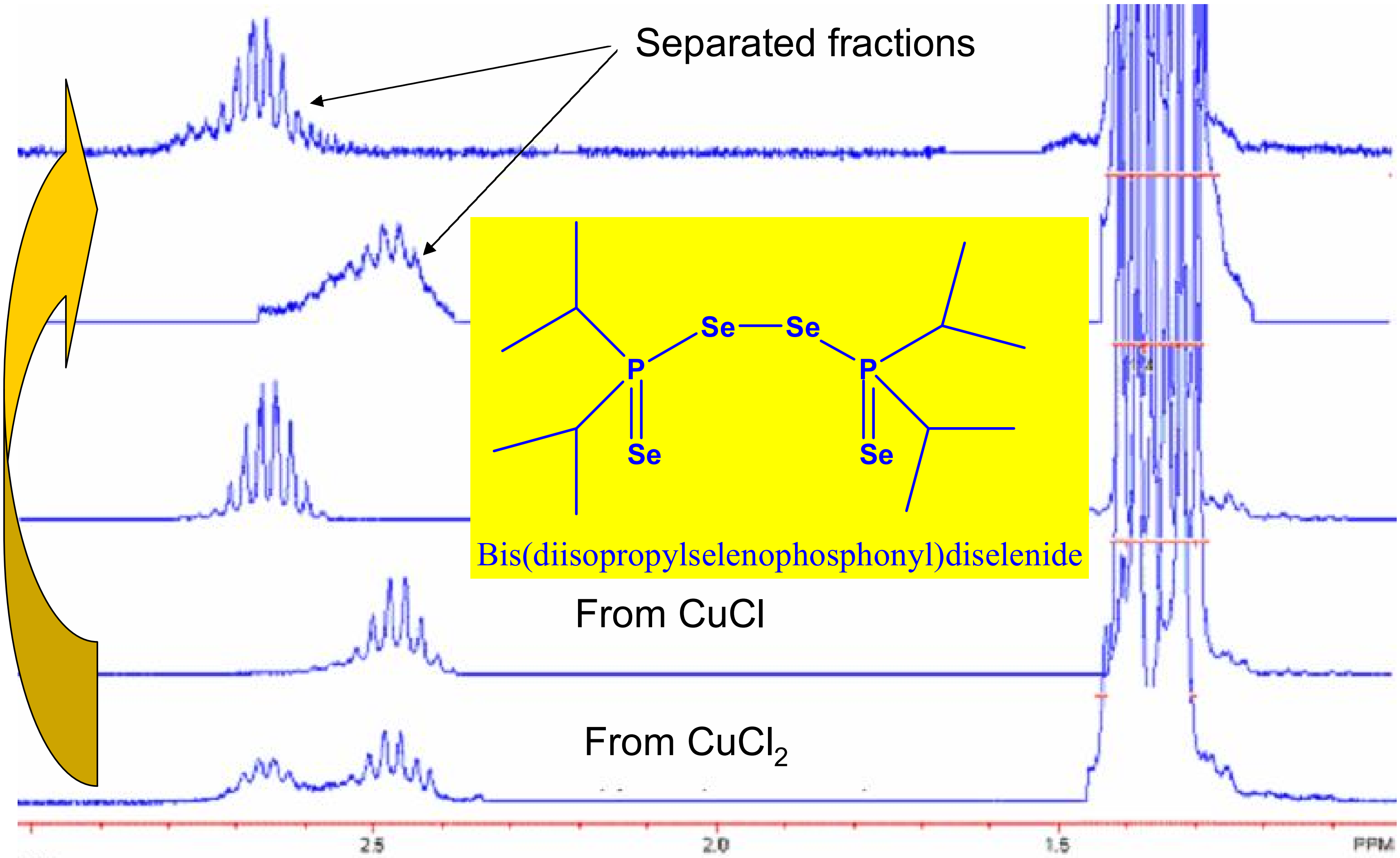
$$4\ (HNEt_3)(^{i}Pr_2PSe_2) + 4\ CuCl \xrightarrow{MeOH} \{(^{i}Pr_2PSe_2)Cu\}_4 + 4\ (HNEt_3)Cl$$

From $CuCl_2$

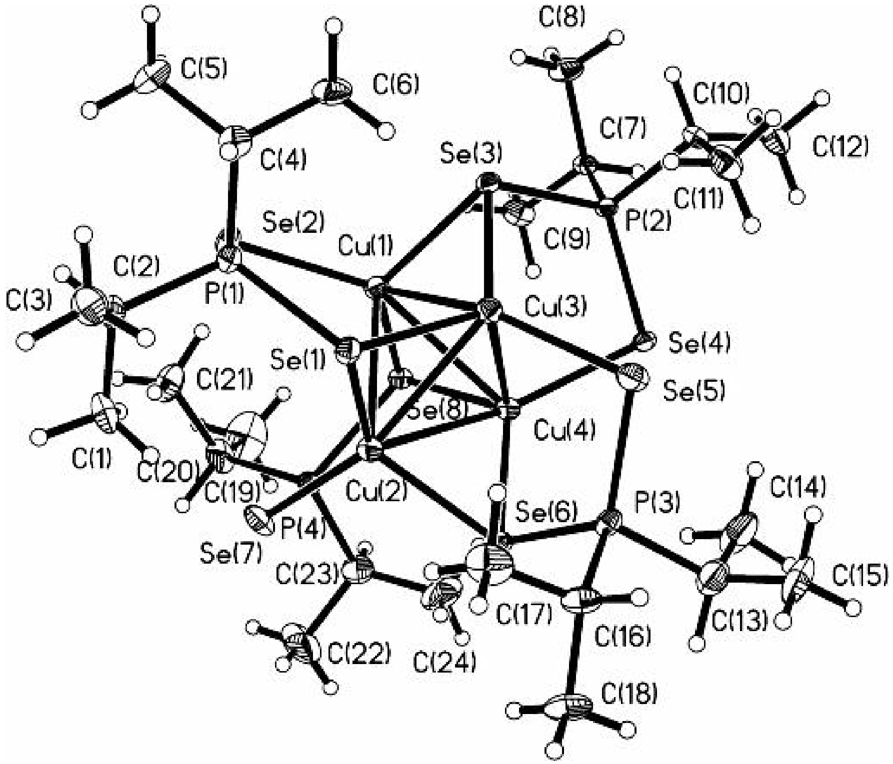
$$8\ (HNEt_3)(^{i}Pr_2PSe_2) + 4\ CuCl_2 \xrightarrow{MeOH} \{(^{i}Pr_2PSe_2)Cu\}_4 + 8\ (HNEt_3)Cl + 2\ (^{i}Pr_2PSe)_2Se_2$$

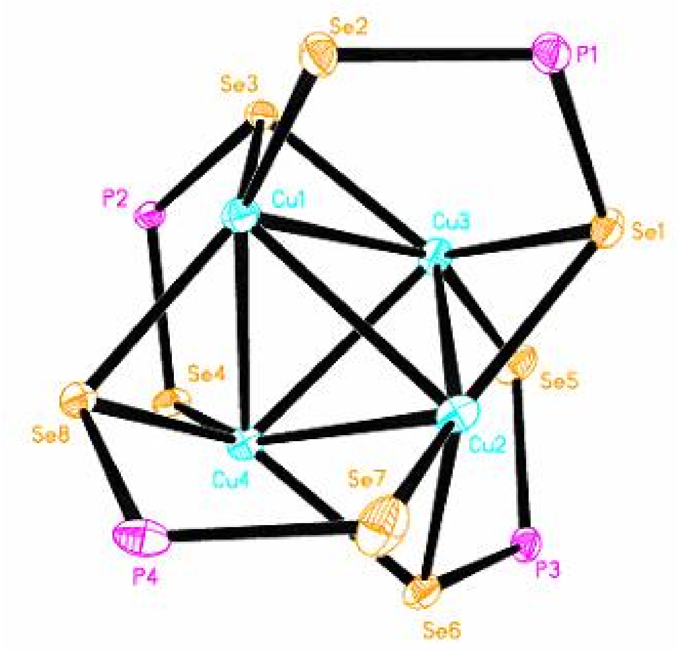
Cu(II) is reduced to Cu(I) by the ligand

NMR of Copper complexes

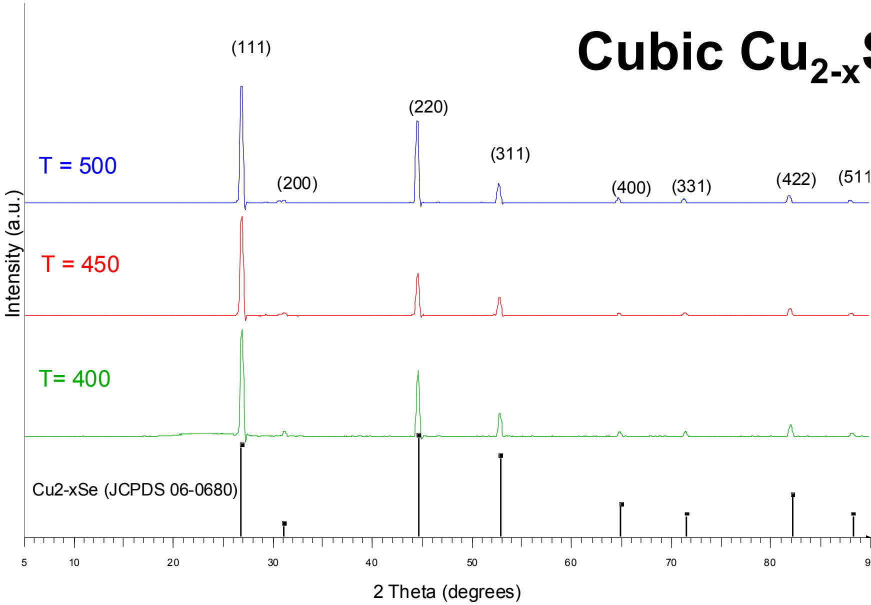


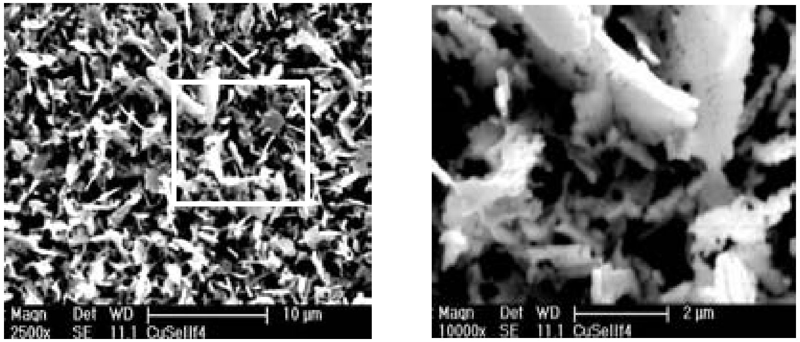
X-ray Structure of Copper complex





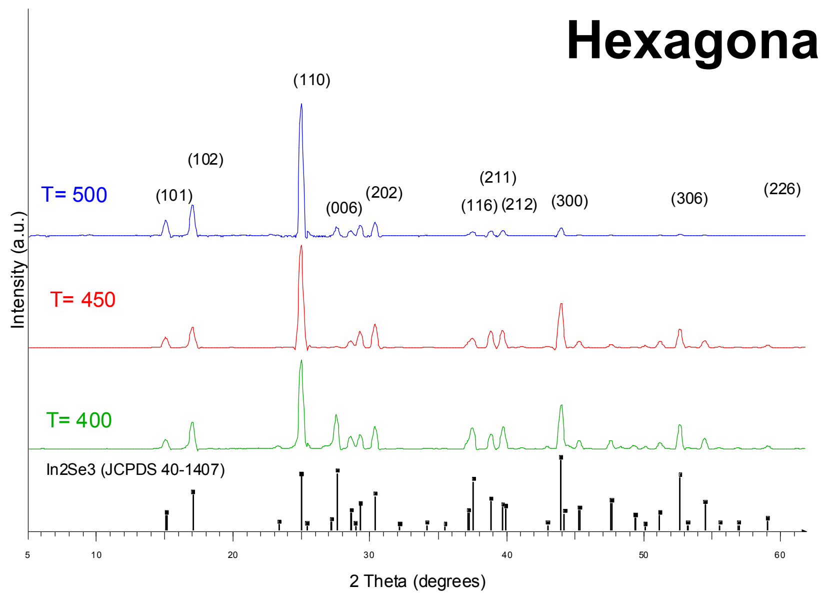
Cubic $Cu_{2-x}Se$

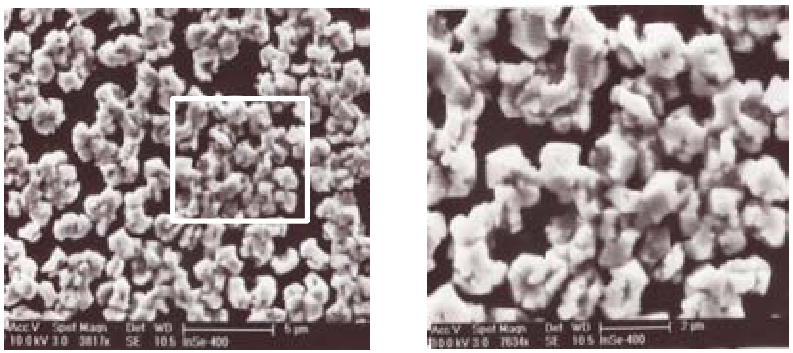




400 °C

Hexagonal In_2Se_3

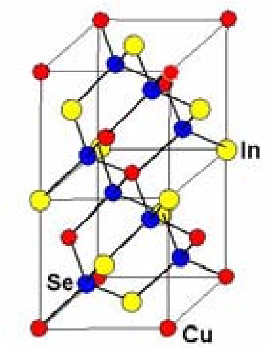


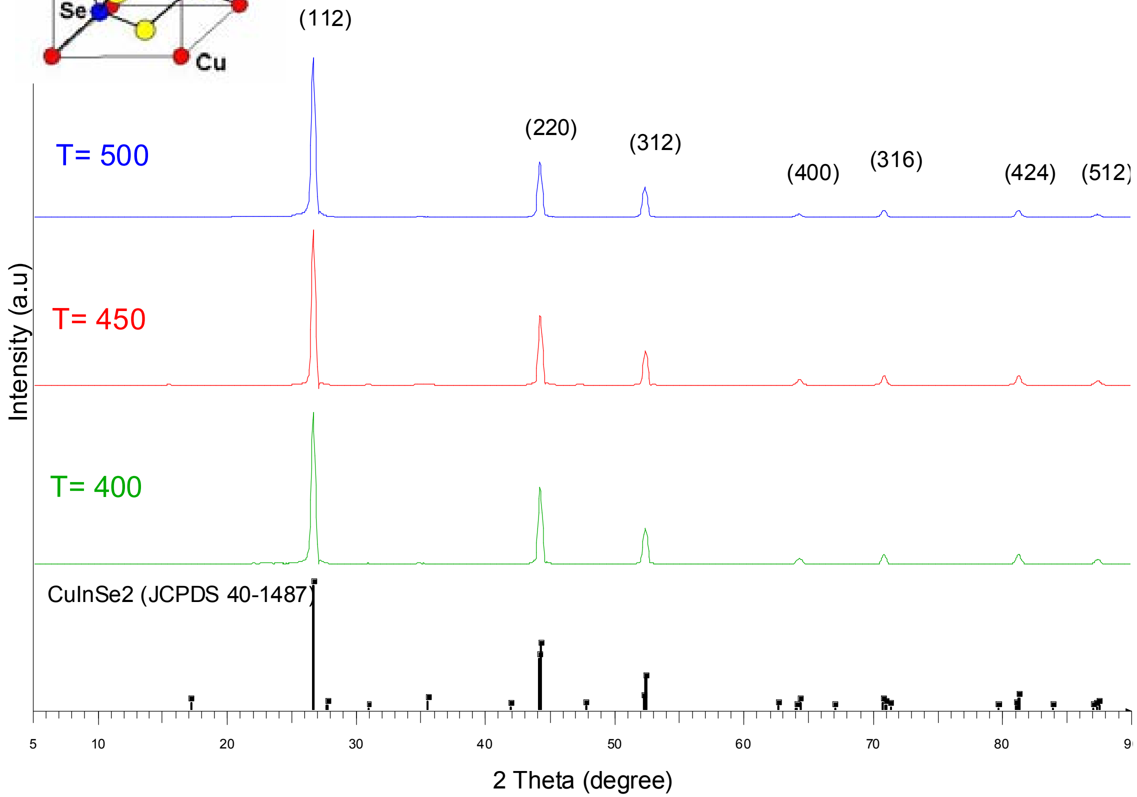


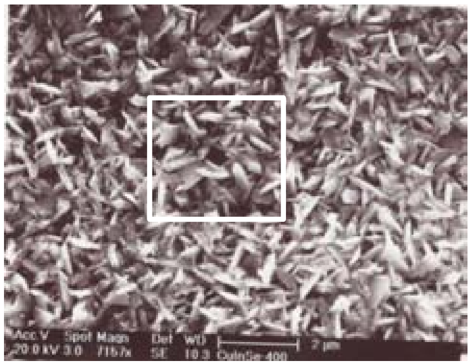
400 °C

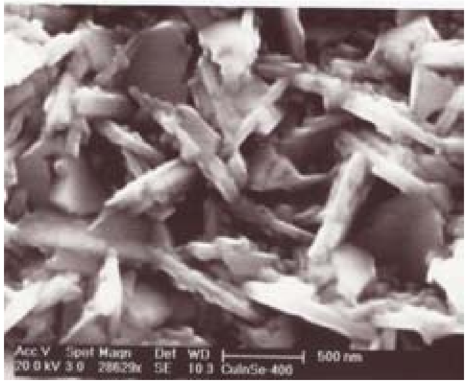
AA-CVD Experiments: Solvent: toluene; Flow rate: 160 sccm; Time: 90 mins; Substrate: Glass

Tetragonal $CuInSe_2$









400 °C

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

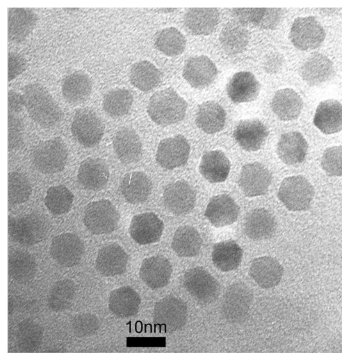
And also Nanoparticles

NANOCO TECHNOLOGIES

illuminating the future

Nanoco's Technology

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

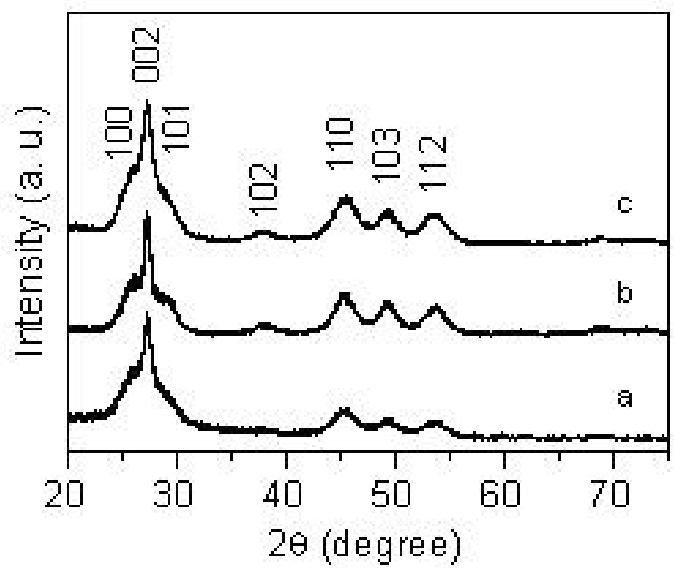


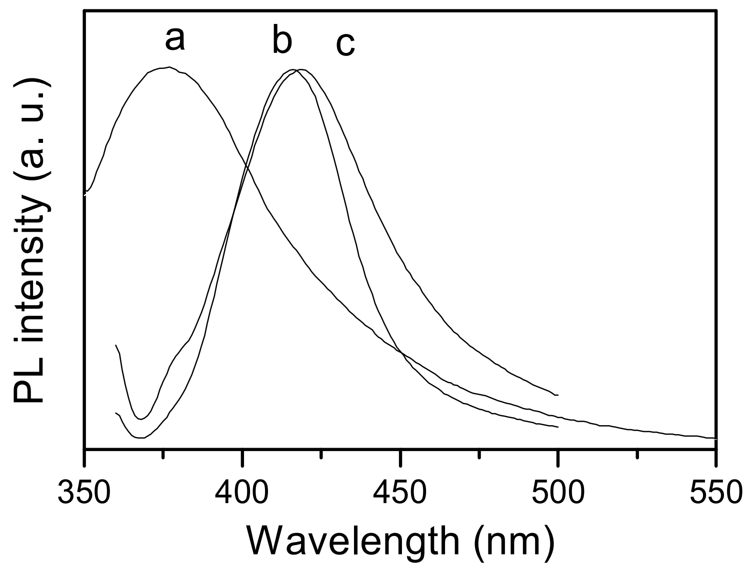
Electron microscope image showing QD
In very ordered patern

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

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

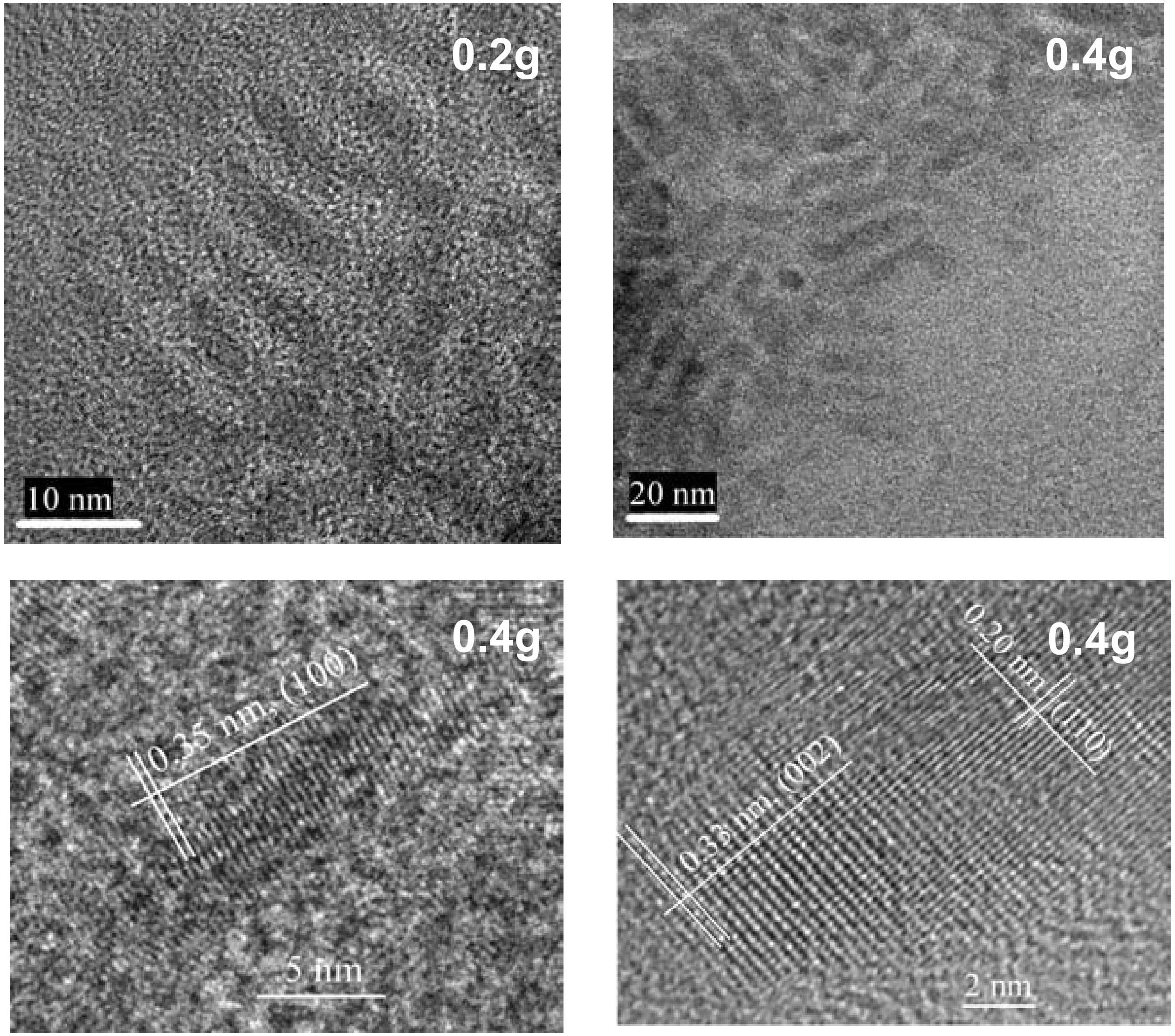




Hexadecylamine (HDA) capped hexagonal ZnSe nanoparticles grown at 300 °C for 30 min from (a) 0.2 g, (b) 0.4 g and (c) 0.6 g of precursor.

Emission Spectra

a = 375 nm (3.30 eV)
b = 414 nm (2.99 eV)
c = 418 nm (2.96 eV)
Vs.
Bulk ZnSe = 459 nm (2.79 eV)



TEM image of ZnSe nanomaterial

MANCHESTER 1824

The University of Manchester

Plan for the Lecture

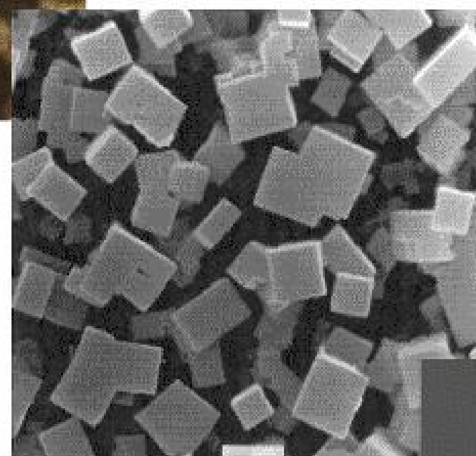
Part 1 Build and Destroy!

- Dichalcogenoimidodiphosphinates
- Diseleno-phosphinates
- New routes to selenohosphinates
- Why bother the CIGS systems

Part 2 Mass transfer

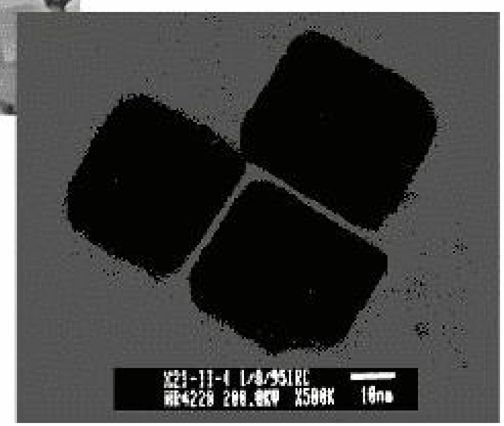
- PbS at interfaces

PbS mineral, *Galena*
Dimensions in millimeters

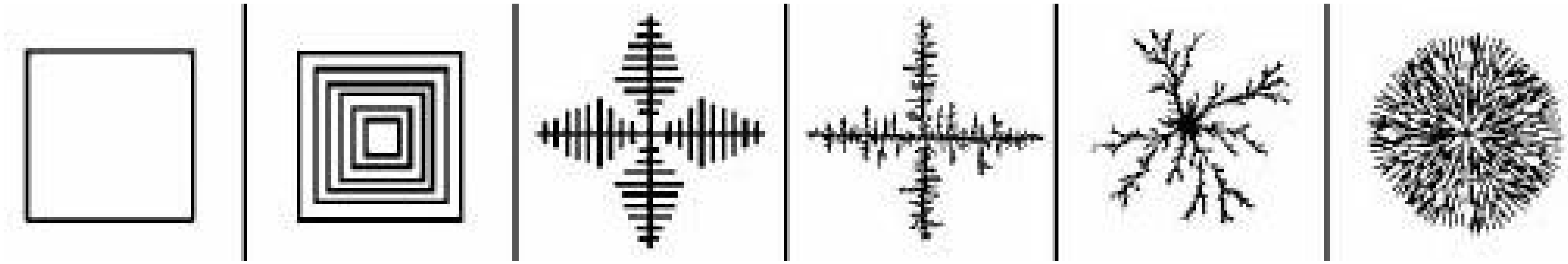


PbS deposited by MOCVD [90]
Scale bar = 1μm

Nanocrystalline PbS [49]
Scale bar = 10 nm

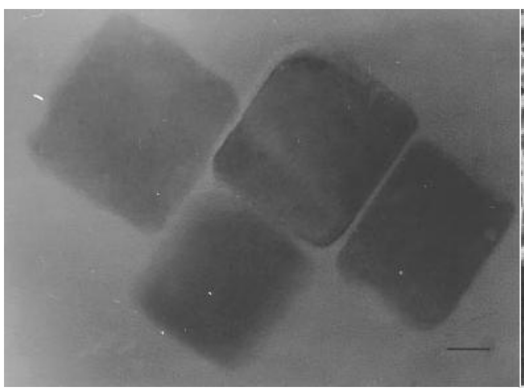


LEAD SULPHIDE NANOPARTICLES



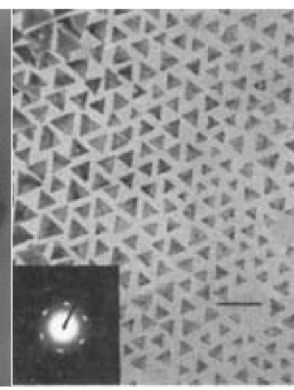
Polyhedral | **Skeletal** | **Single-crystalline ordered dendrite** | **Partially disordered dendrite** | **Disordered polycrystalline dendrite** | **Dense branching morphology**

A Few examples



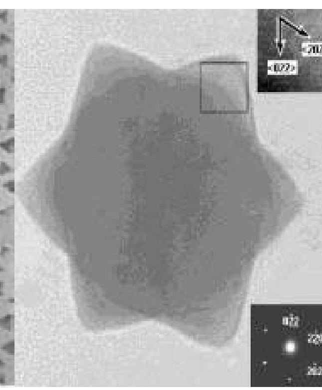
O'Brien et al.

J.Mater.Chem, 1997



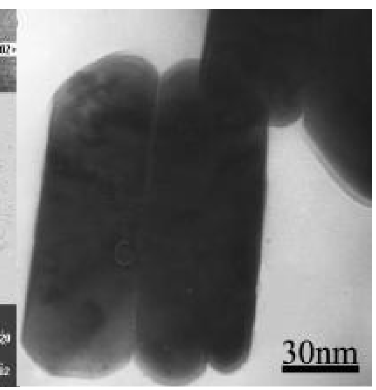
Yang and Fendler

J. Phys.Chem, 1995



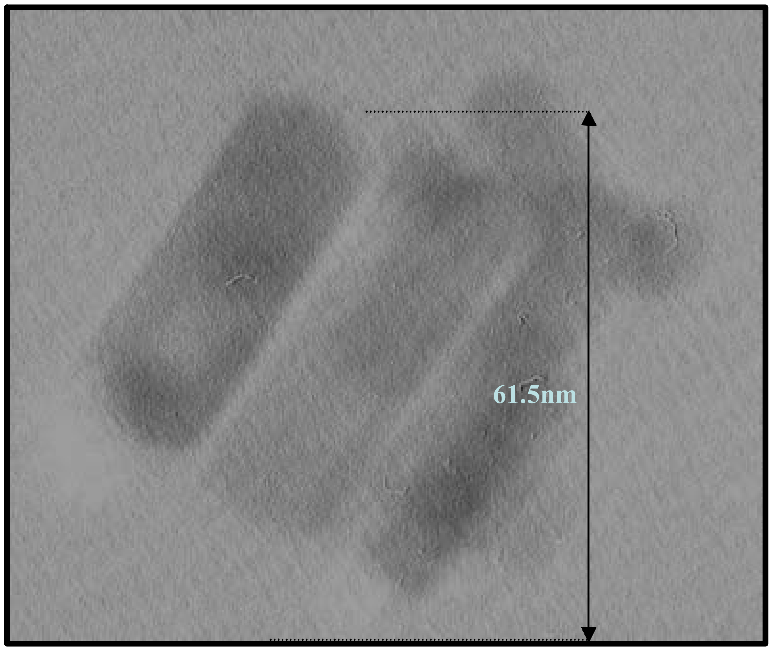
Sheon et al.

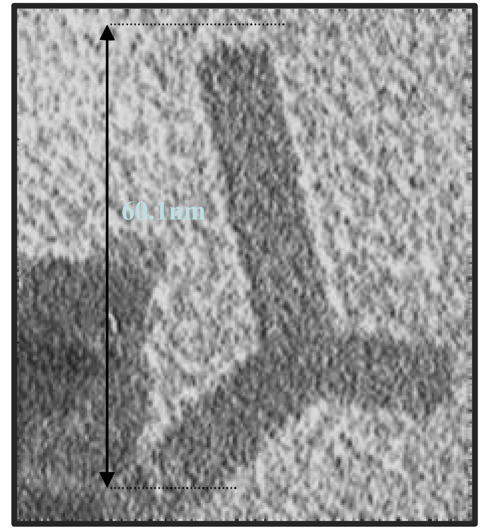
J. Am.Chem. Soc, 2002

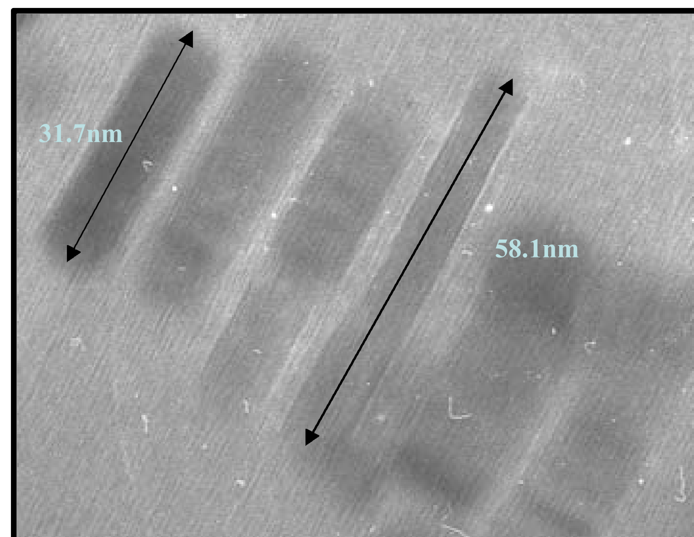


Wang et al.

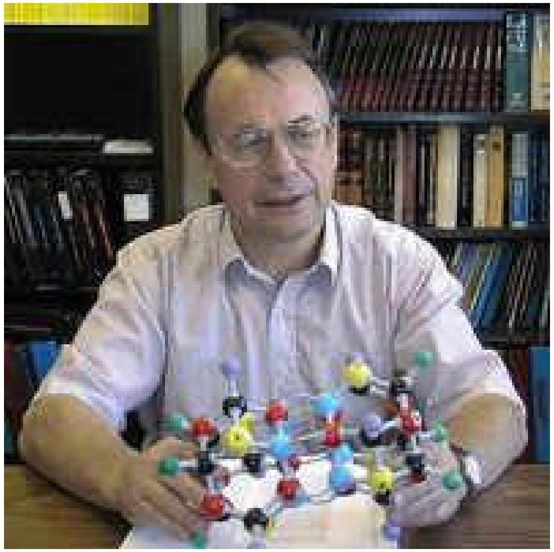
J.Phys.Chem.B, 2006


61.5nm


60.1nm


31.7nm
58.1nm

Thanks

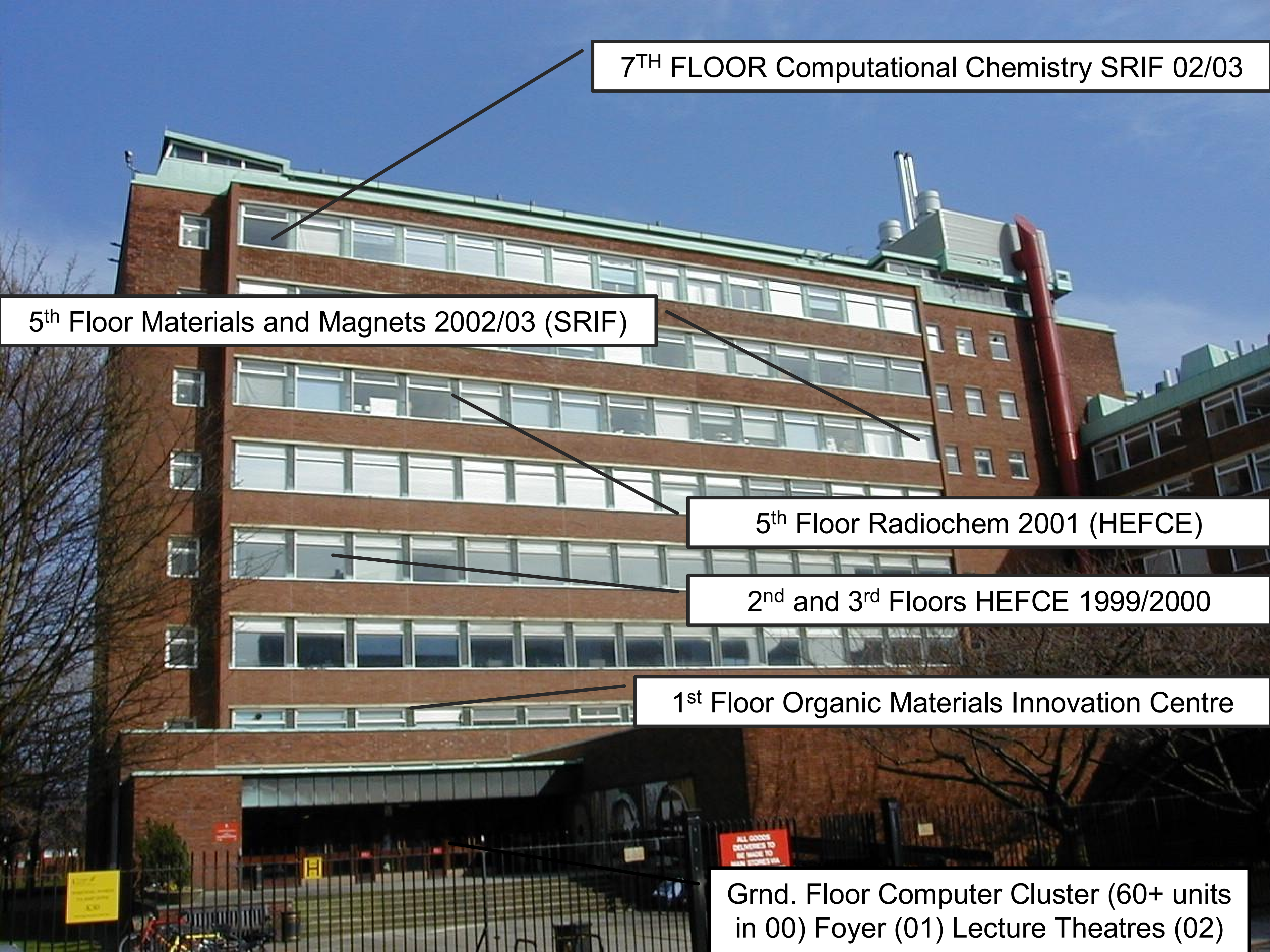


- EPSRC
- RCUK
- University of Manchester

- Mohammed Afzaal
- Chin Ngyuan
- Azad Malik
- Shivram Garj (Boyscast)
- J.P.Thomas
- 'Bobo' Wang

A New University for the 21^{st} Century

- Established on 1^{st} October 2004
- Royal Charter granted on 22^{nd} 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


7TH FLOOR Computational Chemistry SRIF 02/03
5th Floor Materials and Magnets 2002/03 (SRIF)
5th Floor Radiochem 2001 (HEFCE)
2nd and 3rd Floors HEFCE 1999/2000
1st Floor Organic Materials Innovation Centre
Grnd. Floor Computer Cluster (60+ units in 00) Foyer (01) Lecture Theatres (02)

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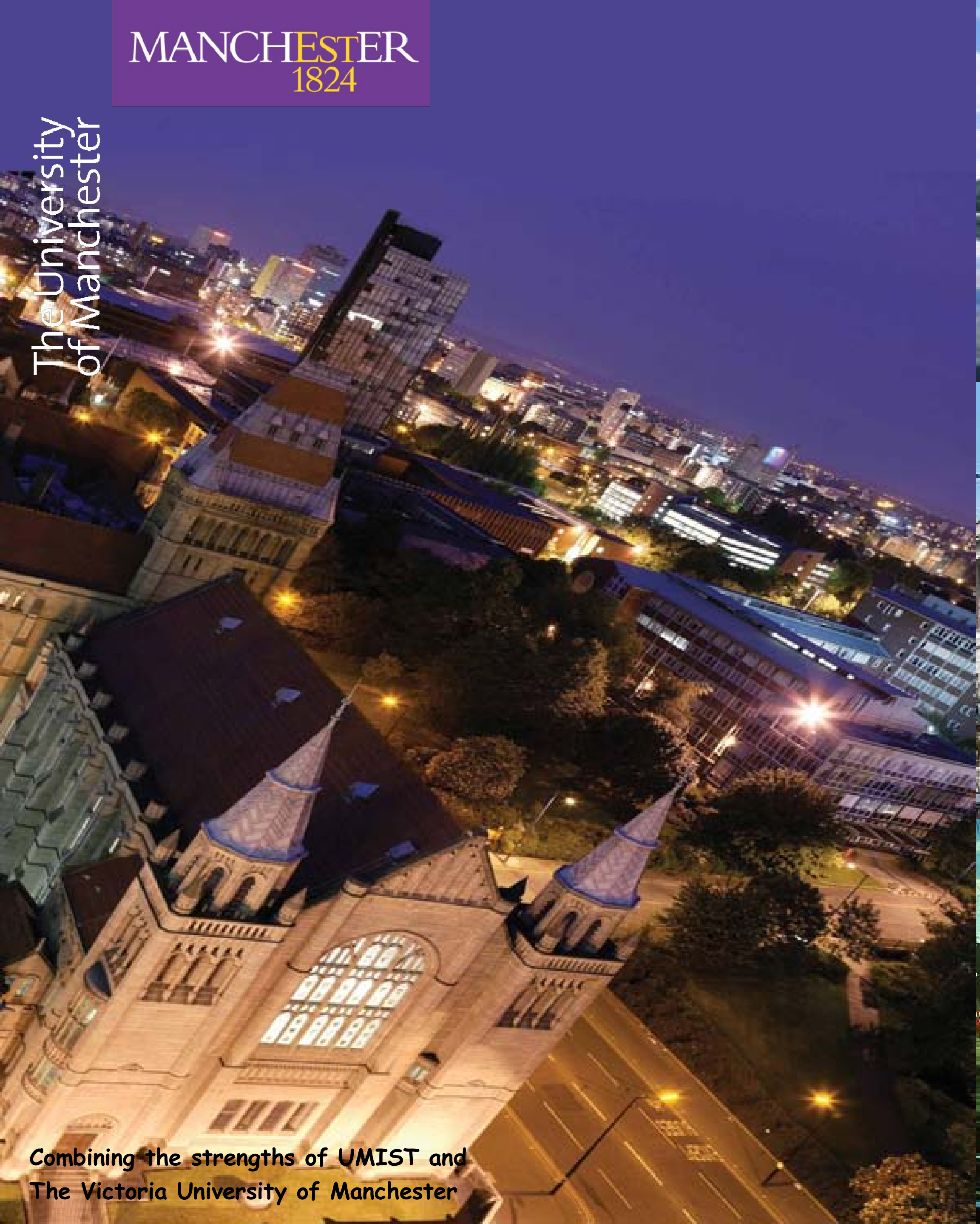

Combining the strengths of UMIST and
The Victoria University of Manchester