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Synthesis of Novel Single Source Precursors to Complex Nanoparticles

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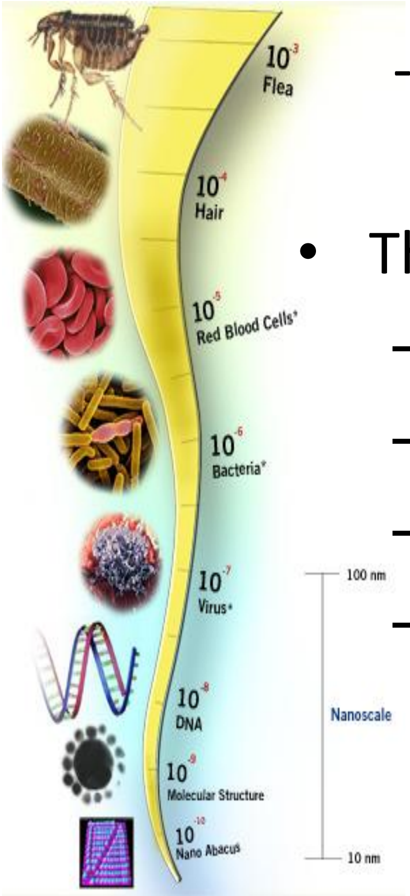
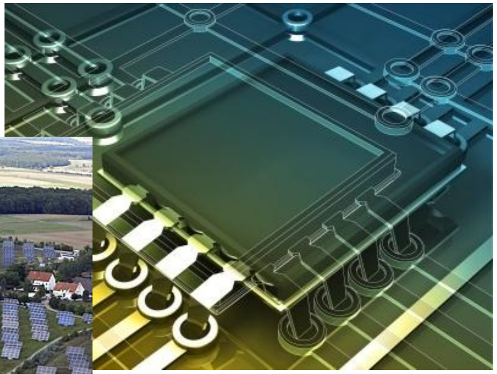
Complex Nanoparticles are Used in a Variety of Different Applications

- Complex nanoparticles are multi-cation metal oxide materials that are 100 nm in size or smaller
  - simple nanoparticles have only one cation

- These particles can serve multiple uses such as:
  - Photovoltaic Components
  - Semi Conductors
  - Electronic Device Components
  - Scintilators





Currently Complex Nanoparticles in the Boyle Lab are Synthesized Through Several Techniques

Solvothermal

Solution Precipitation

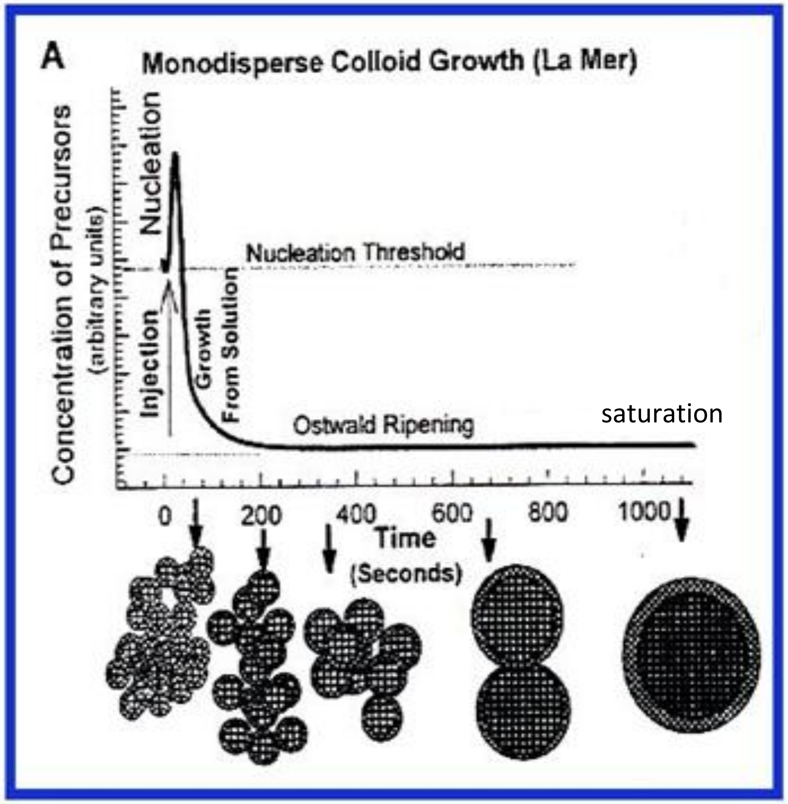
Precursor Decomposition Temperatures can Influence Nanoparticle Formation

•Supersaturation is the state of a solution being more concentrated than normally possible

•Compounds decompose and initiate a nucleation shower

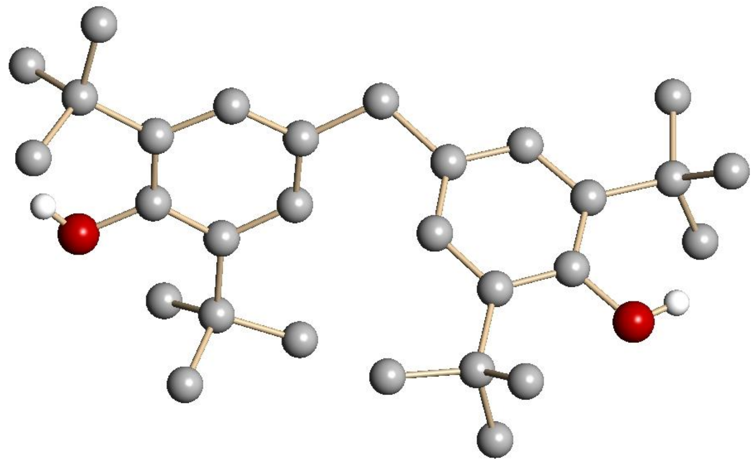
•As soon as particles fall out of solution they begin to agglomerate through Ostwald Ripening

 −Varying decomposition temperatures however, can lead to problems when synthesizing complex nanoparticles.



Single Source Precursors will be Investigated Through the use of the 4DBP Ligand

- We hope to synthesize a family of di-substituted precursors to understand the coordination behavior of the ligand



4,4′-Methylenebis(2,6-di-*tert*-butylphenol)
($H_2$4-DBP)

- Once the bi-substituted reactions are completed mixed metal alkoxide reactions will take place in an attempt to synthesize novel single source precursors to complex nanoparticles

Initial Reactions Were Performed to Determine the Coordination Behavior of 4DBP

$$2M(OR)_x + H_2 4DBP \xrightarrow{Solv} M_2(OR)_y(4DBP)$$

- The various metal alkoxides were reacted in solution on a 2:1 molar ratio in an argon filled glovebox
- Once the metal alkoxides and ligand were combined the reaction was stirred for 12 hours
- The reactions were then characterized

Instruments Used to Characterize Reactions

- FTIR (Fourier Transform Infrared Spectroscopy)
- EA (Elemental Analysis)
- NMR (Nuclear Magnetic Resonance)
- TGA/DTA (Thermo Gravometric Analysis/Differential Thermal Analysis)
- Single Crystal XRD (X-Ray Diffraction)
- PXRD (Powder X-Ray Diffraction)

TGA/DTA

NMR

Single Crystal XRD

FTIR

Elemental Analysis

Synthesis of Various Single Source Precursors Using 4DBP

$$2M(OR)_x + H_2 4DBP \xrightarrow{Solv} M_2(OR)_y(4DBP)$$

Assorted Reactants:

Initial Reactions:

$Ti(OPr^i)_4$	$Zr(OPr^i)_4$	$Hf(OEt)_4$	$Ta(OEt)_5$	$Nb(OEt)_5$
$Ti(OBu^t)_4$	$Zr(OBu^t)_4$	$Hf(OBu^t)_4$	Ta(ONet)	Nb(ONet)
$Ti(ONep)_4$	$Zr(ONep)_4$	$Hf(ONep)_4$		

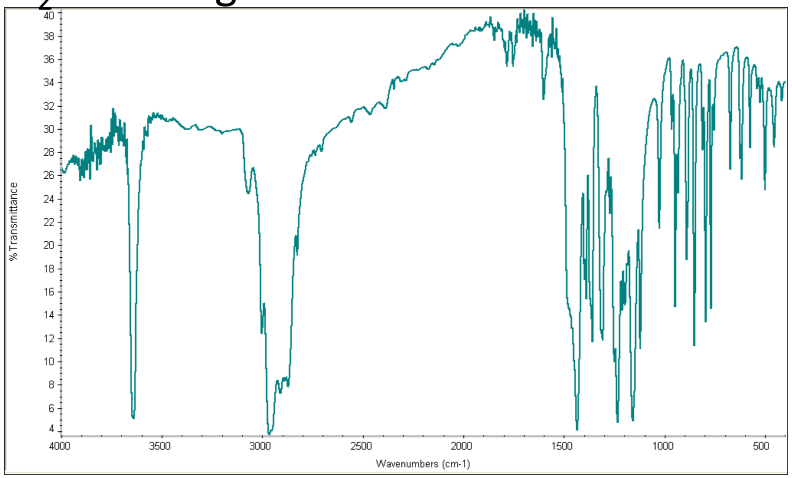
Secondary Reactions:

MgBrMes	$Y(ONep)_3$	$Al(Me)_3$
$Zn(Et)_2$	$Eu(ONep)_3$	$Al(Et)_3$
	$Gd(ONep)_3$	$Al(Bu^i)_3$
	$Er(ONep)_3$	

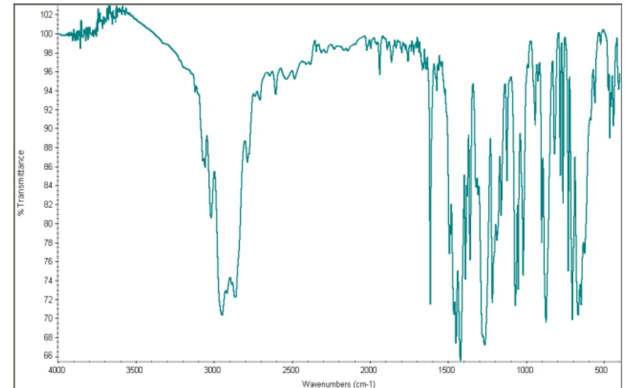
Fourier Transfer Infrared Spectroscopy (FTIR) Results Show a Reaction has Occured

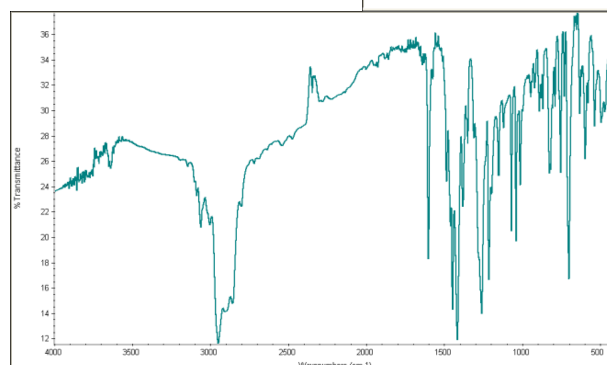
$$2M(OR)_x + H_2 4DBP \xrightarrow{\text{Solv.}} M_2(OR)_y\ (4DBP)$$

H_2-4DBP Ligand



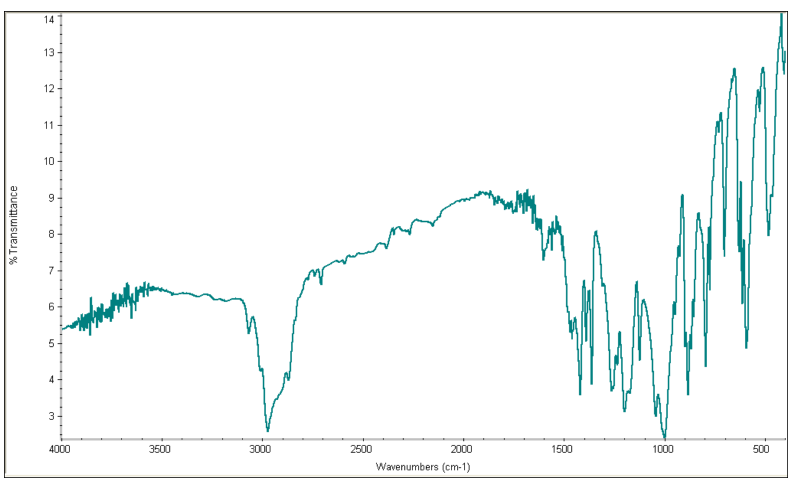
$Al_4Bu^i{}_4py_2$4-DBP



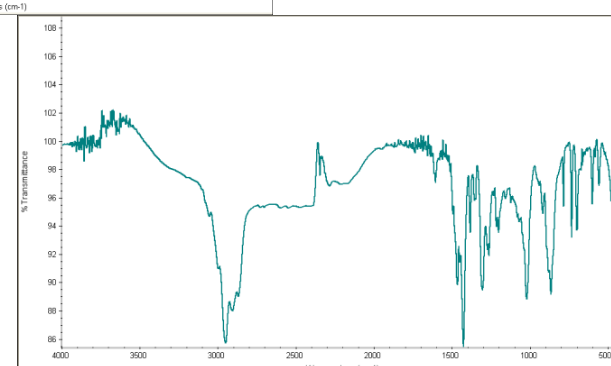


$Zn_2(Et)_2(4DBP)(py)_4$

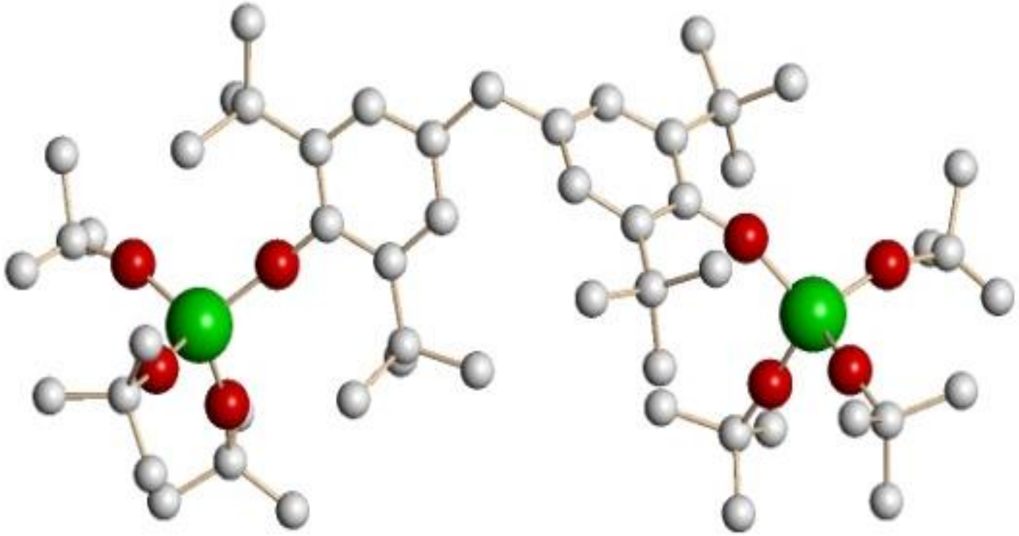
$Ti_2(OBu^t)_6$4DBP



$Mg_2Br_2$4-DBP$(THF)_3$



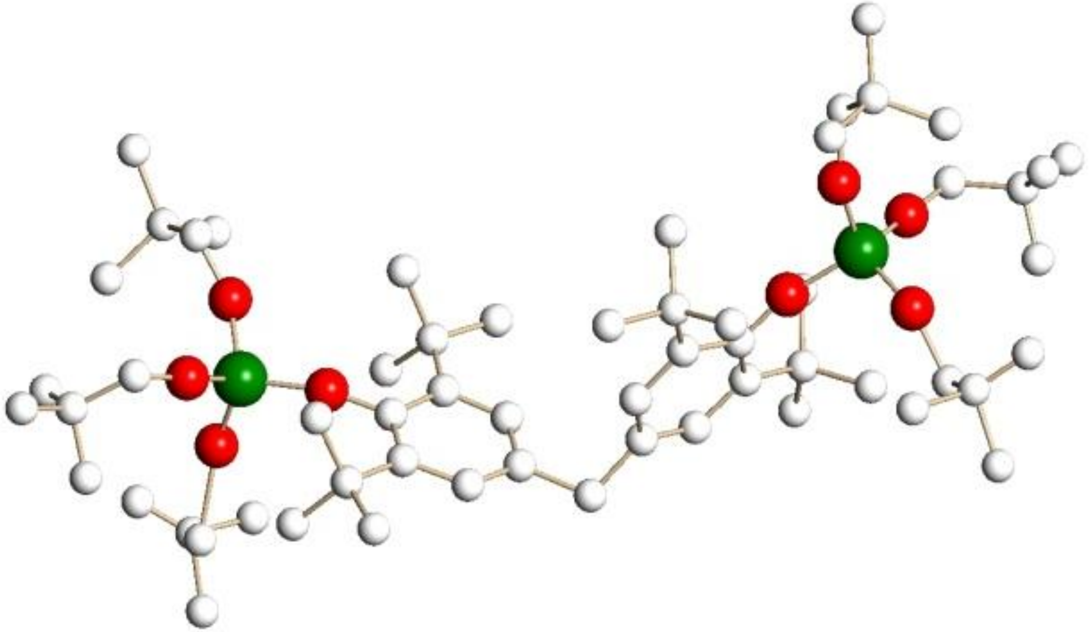
$M_2(OBu^t)_6(4DBP)$ Crystals Adopt a Tetrahedral Geometry



$M_2(OBu^t)_6(4DBP)$

- Green = Metal
- Gray/White = Hydrocarbons
- Red = Oxygen

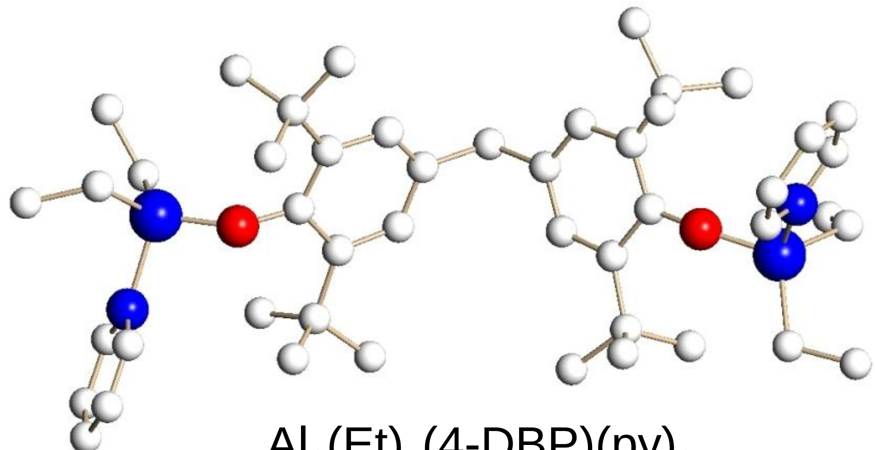
Ti_2(4DBP)(ONep)$_6$ Crystals Adopt a Tetrahedral Geometry



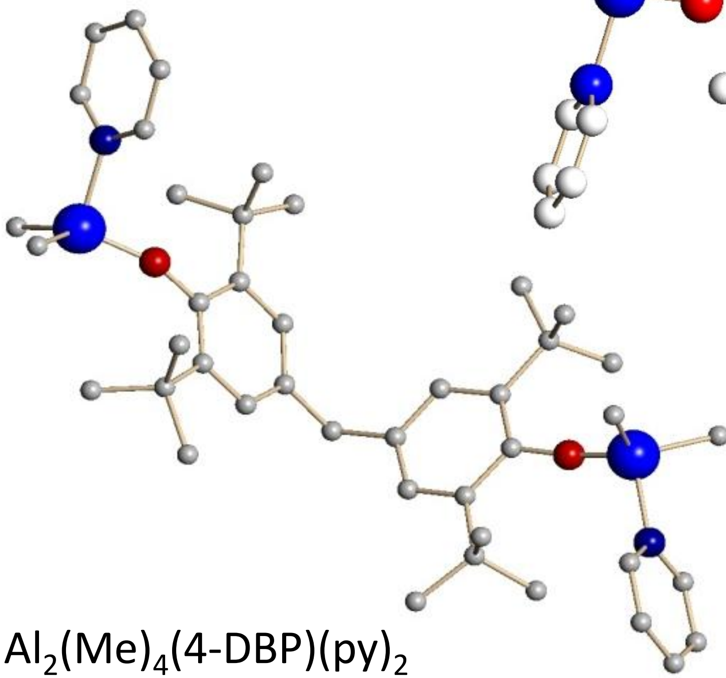
Ti_2(4DBP)(ONep)$_6$

- Green = Titanium
- Gray/White = Hydrocarbons
- Red = Oxygen

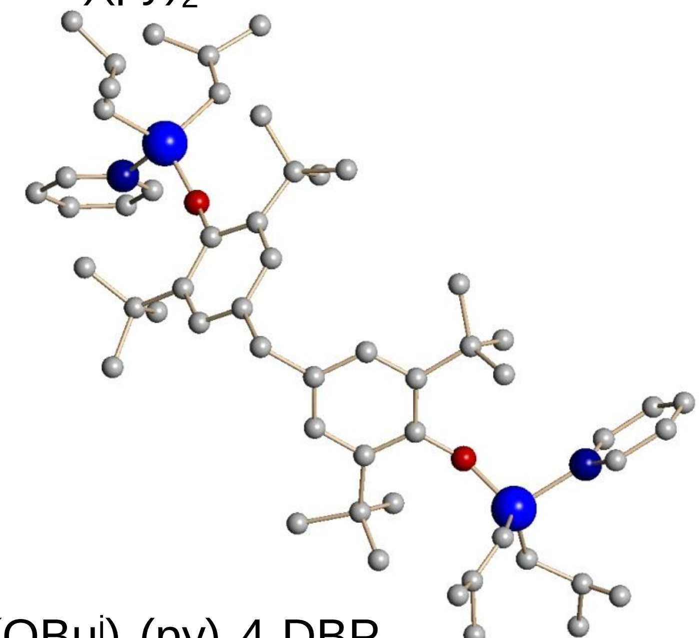
Aluminum Derivative 4DBP Compounds Adopt a Tetrahedral Geometry and Attach Pyridine Rings



$Al_2(Et)_4(4\text{-}DBP)(py)_2$



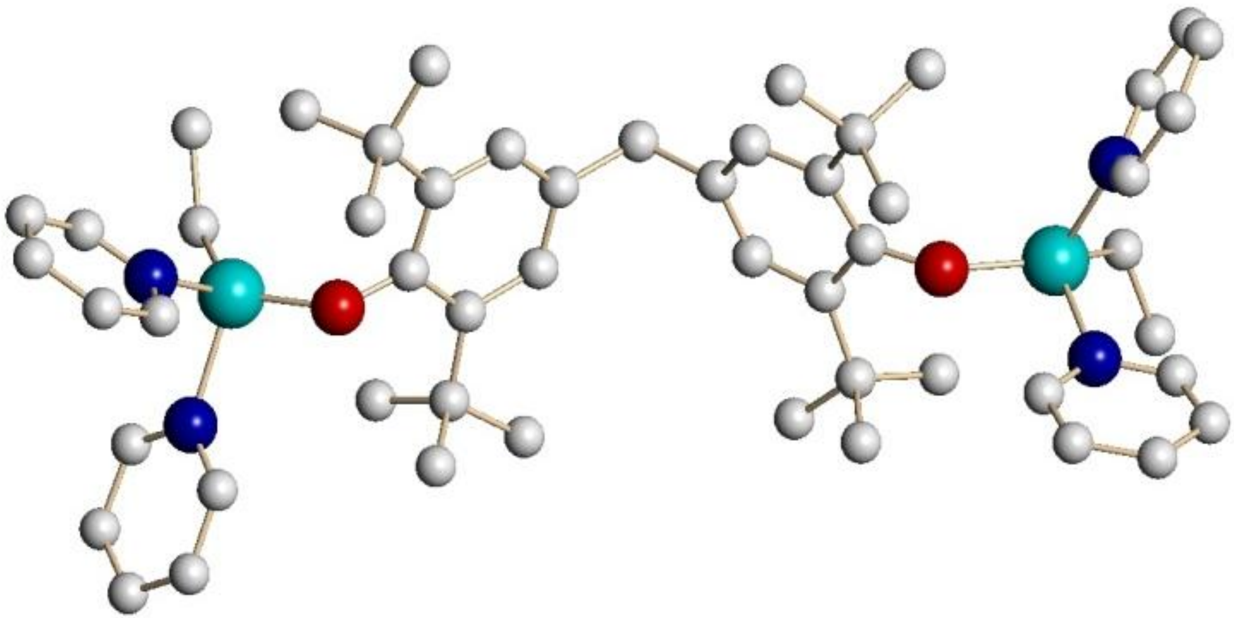
$Al_2(Me)_4(4\text{-}DBP)(py)_2$



$Al_4(OBu^i)_4(py)_2$4-DBP

- Blue = Aluminum
- Dark Blue = Nitrogen
- Gray/White = Hydrocarbons
- Red = Oxygen

$Zn_2(Et)_2(4DBP)(py)_4$ Adopts a Tetrahedral Geometry About the Metal Centers

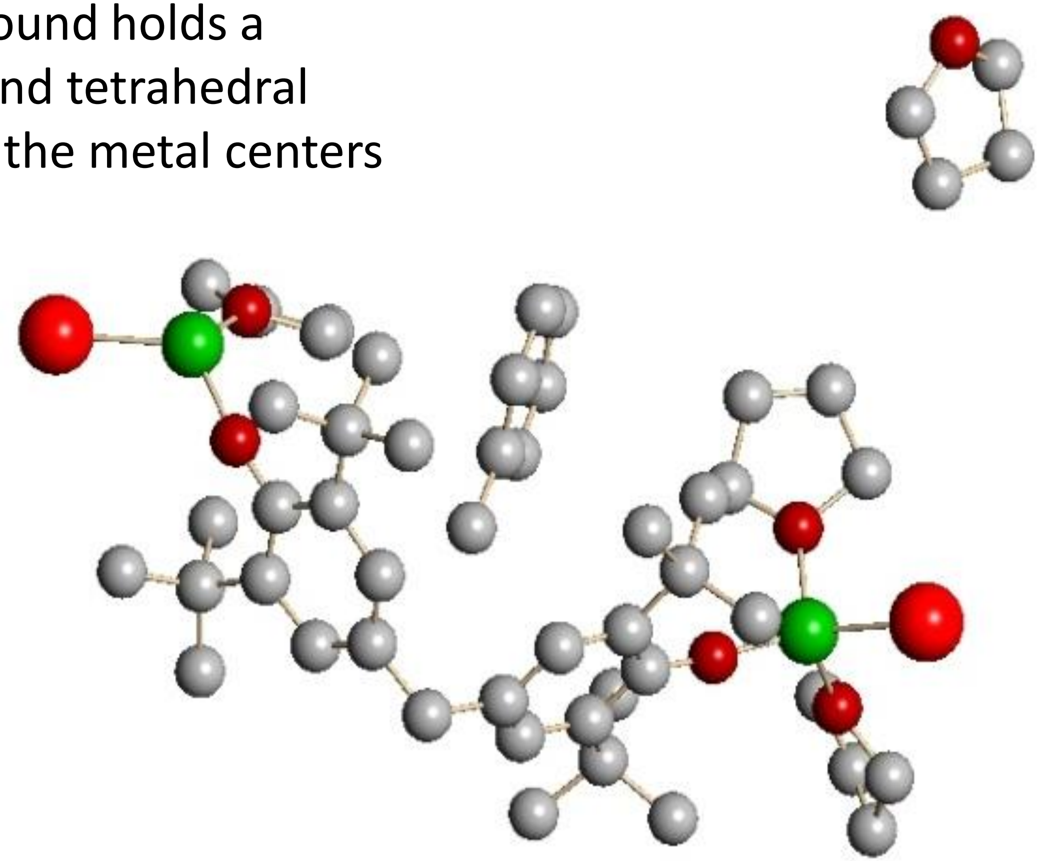


$Zn_2(Et)_2(4DBP)(py)_4$

- Turquoise = Zinc
- Dark Blue = Nitrogen
- Gray/White = Hydrocarbons
- Red = Oxygen

The MgBr 4DBP Derivative Adopts an Asymetric Crystal Structure

- The MgBr compound holds a trigonal planar and tetrahedral geometry about the metal centers

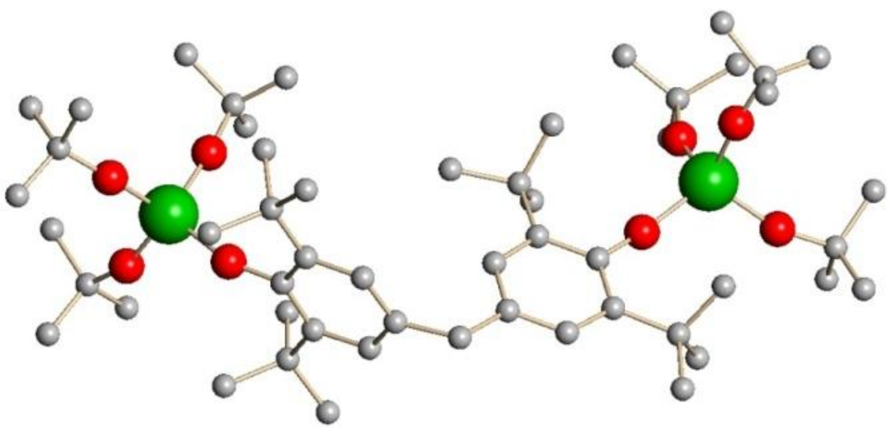


$Mg_2Br_24DBP(THF)_3$●tol THF

- •Green = Magnesium
- •Gray/White = Hydrocarbons
- •Red = Bromine
- •Dark Red = Oxygen

Elemental Analysis and Melting Temperatures of 4DBP Compounds

- Elemental Analysis (EA) of the 4DBP compounds did not agree with our experimental data

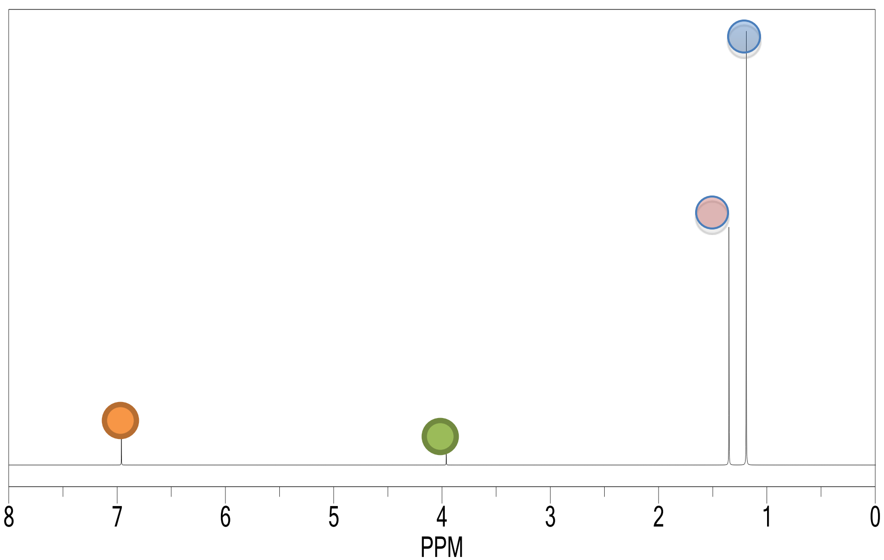


$M_2(OBu^t)_6(4DBP)$

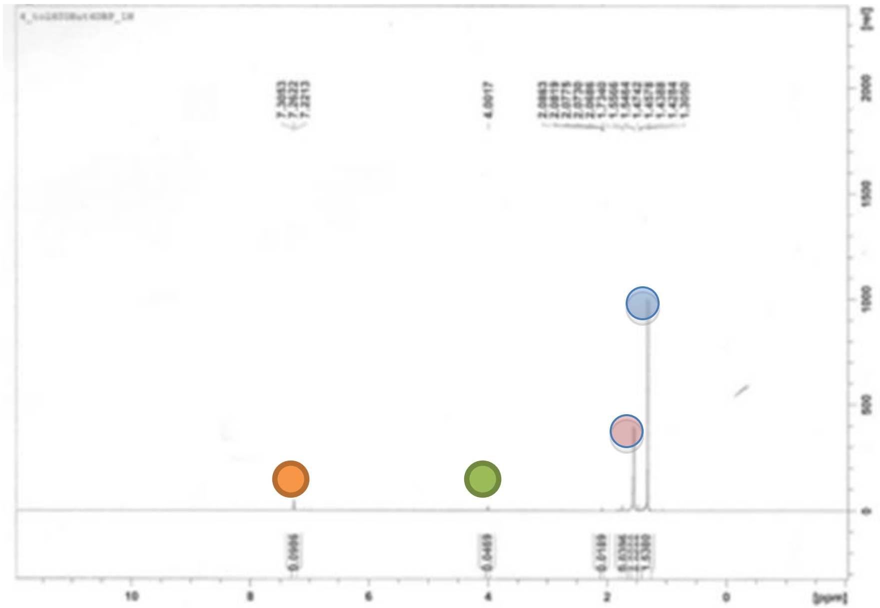
Compound	Melting Point in Degrees Celsius
1. H_2-4DBP	155
2. $TiOBu^t4DBP$	185-210
3. TiONep4DBP	185-190
4. $ZrOBu^t4DBP$	110-115
5. $HfOBu^t4DBP$	120-185
6. AlMe4DBP	220-240
7. AlEt4DBP	220-?
8. $AlOBu^i4DBP$	120-140
9. ZnEt4DBP	Did not melt
10. MgBr4DBP	Did not melt

Nuclear Magnetic Resonance Spectroscopy Data Shows 4DBP Compounds Solution Behavior

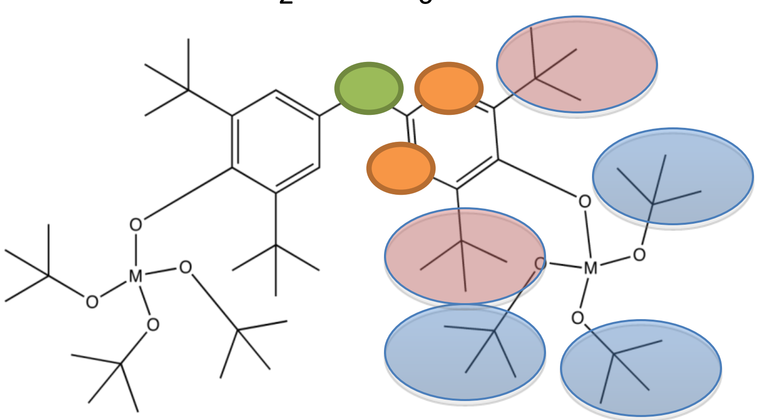
Theoretical



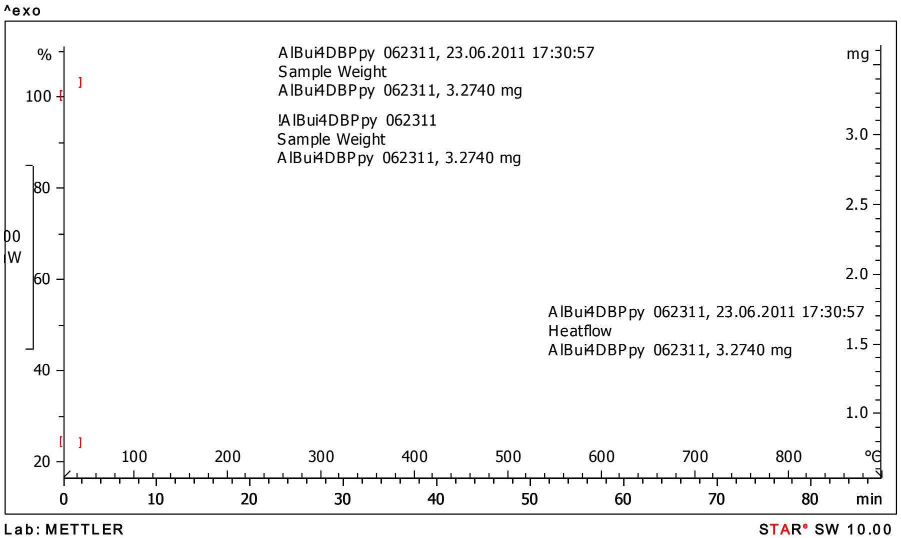
Experimental

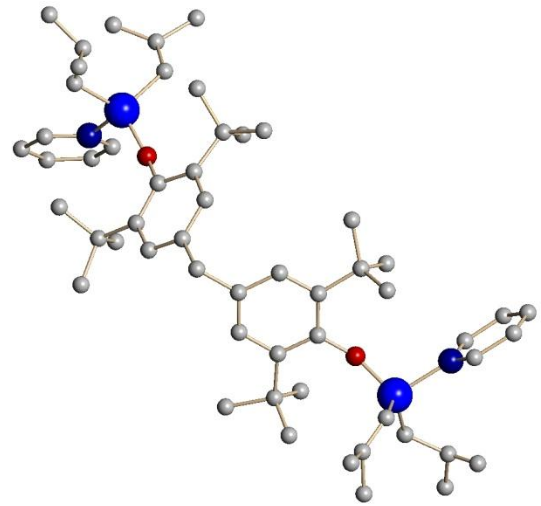


$M_2(OBu^t)_6(4DBP)$

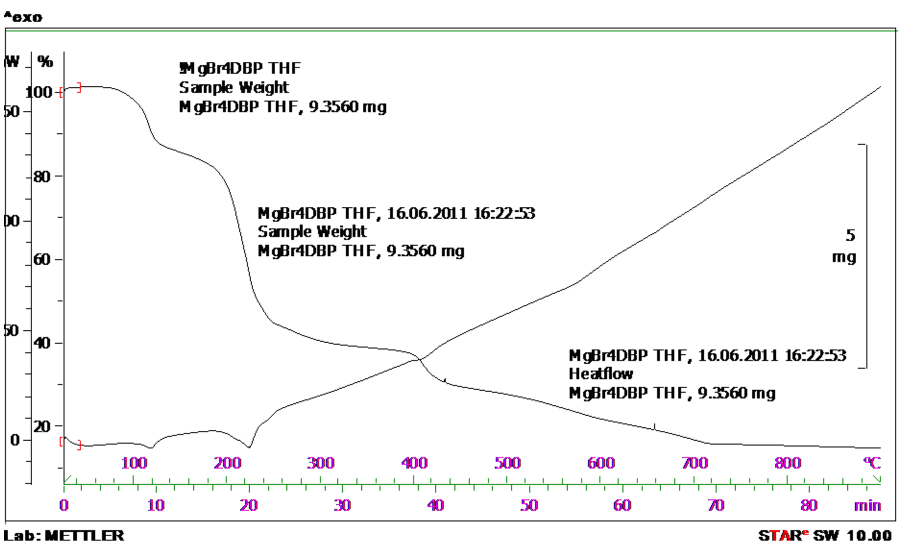


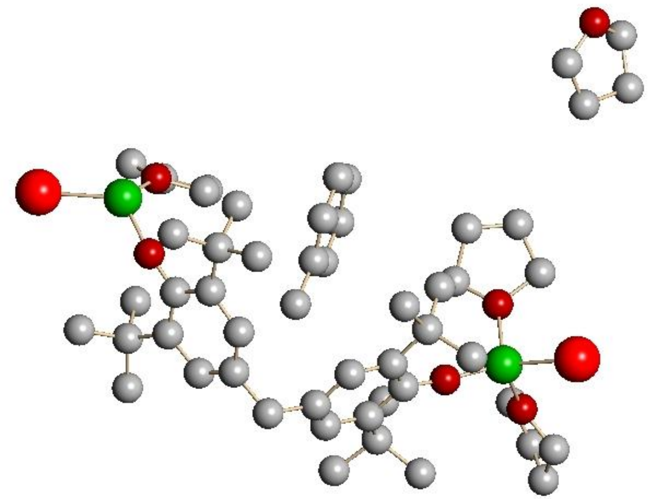
TGA Data of Representative 4DBP Reactions is Consistent with EA Data





11mr031: $Al_4OBu^i_4py_2$4-DBP

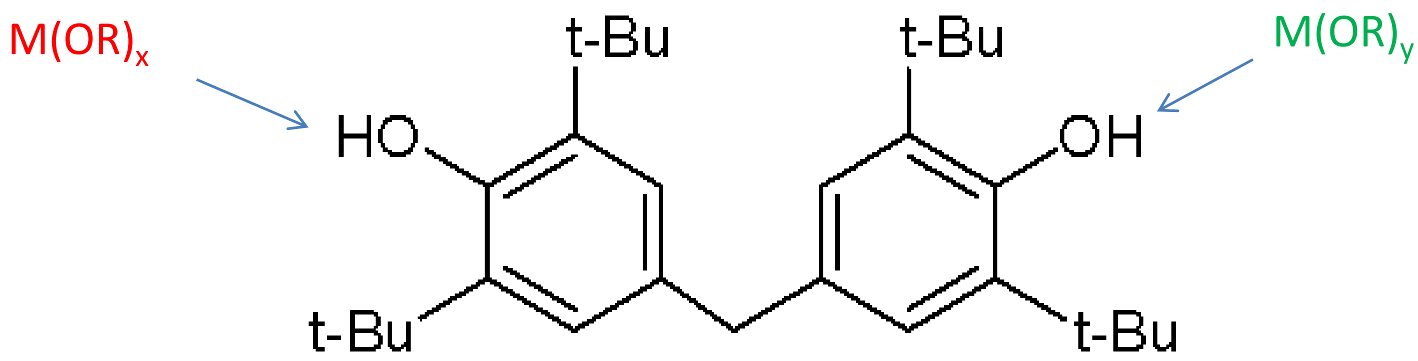




$Mg_2Br_2$4-DBP(THF)$_3$●tol THF

After Initial Reactions, a Disubstitution of Metal Alkoxides Began

$$M(OR)_x + H_2\text{-4DBP} \longrightarrow (OR)_aM(H\text{-4DBP}) \xrightarrow{+\,M(OR)_y} (OR)_aM(4DBP)M(OR)_b$$

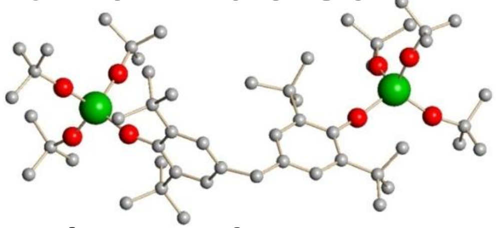


- 1:1:1 molar ratio reactions have begun
- Process
  - A metal was reacted with the 4DBP ligand on a 1:1 ratio and set to stir for 2 hours
  - A second metal was then added to the reaction and set to stir for 12 hours
  - Start characterization proccess

Summary and Conclusions

- H_2-4DBP reactions with single metals were successful

- The 4DBP ligand appears not to react with di-nuclear species

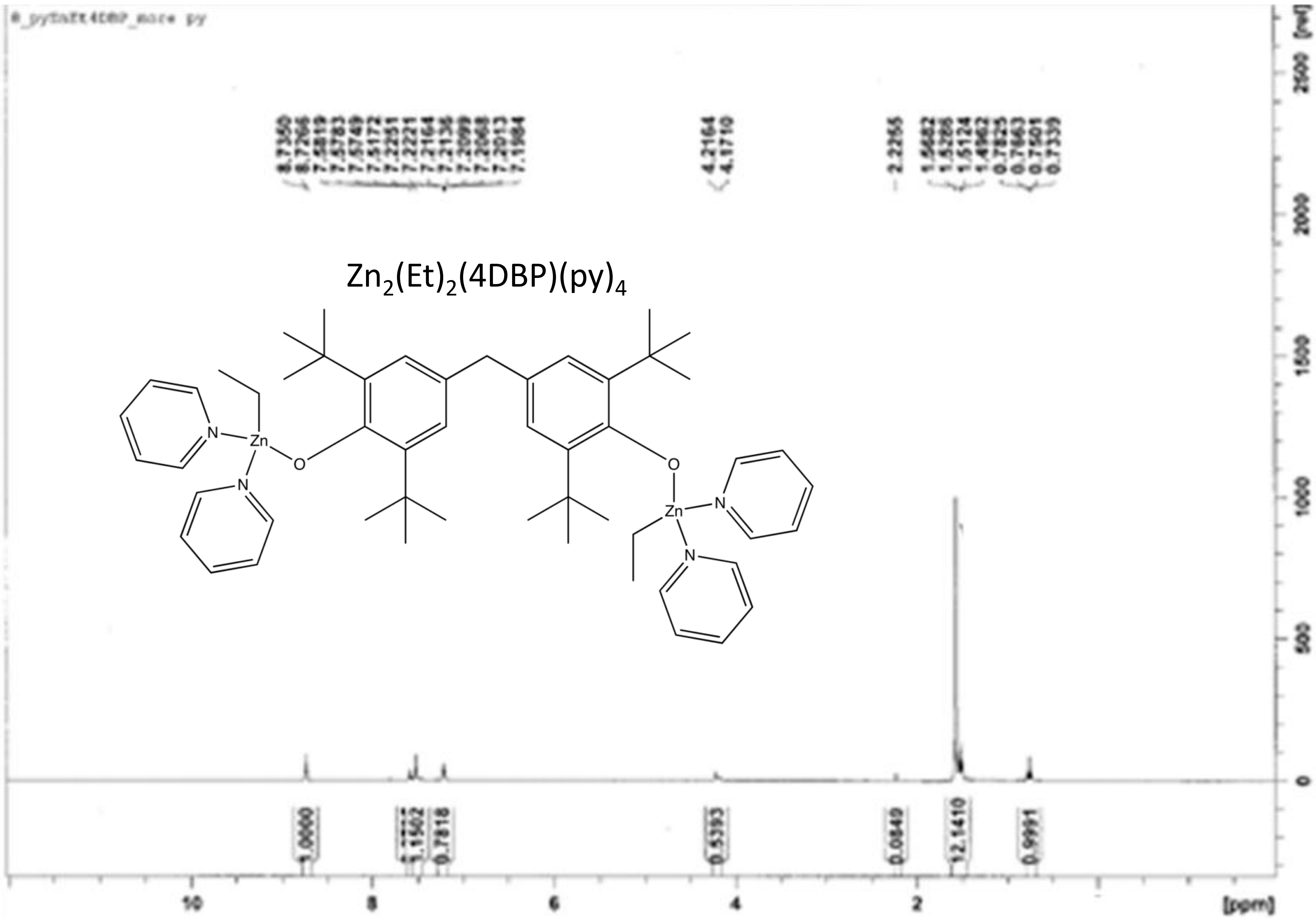


- With a better understanding of the 4DBP ligand, mixed metal reactions have begun

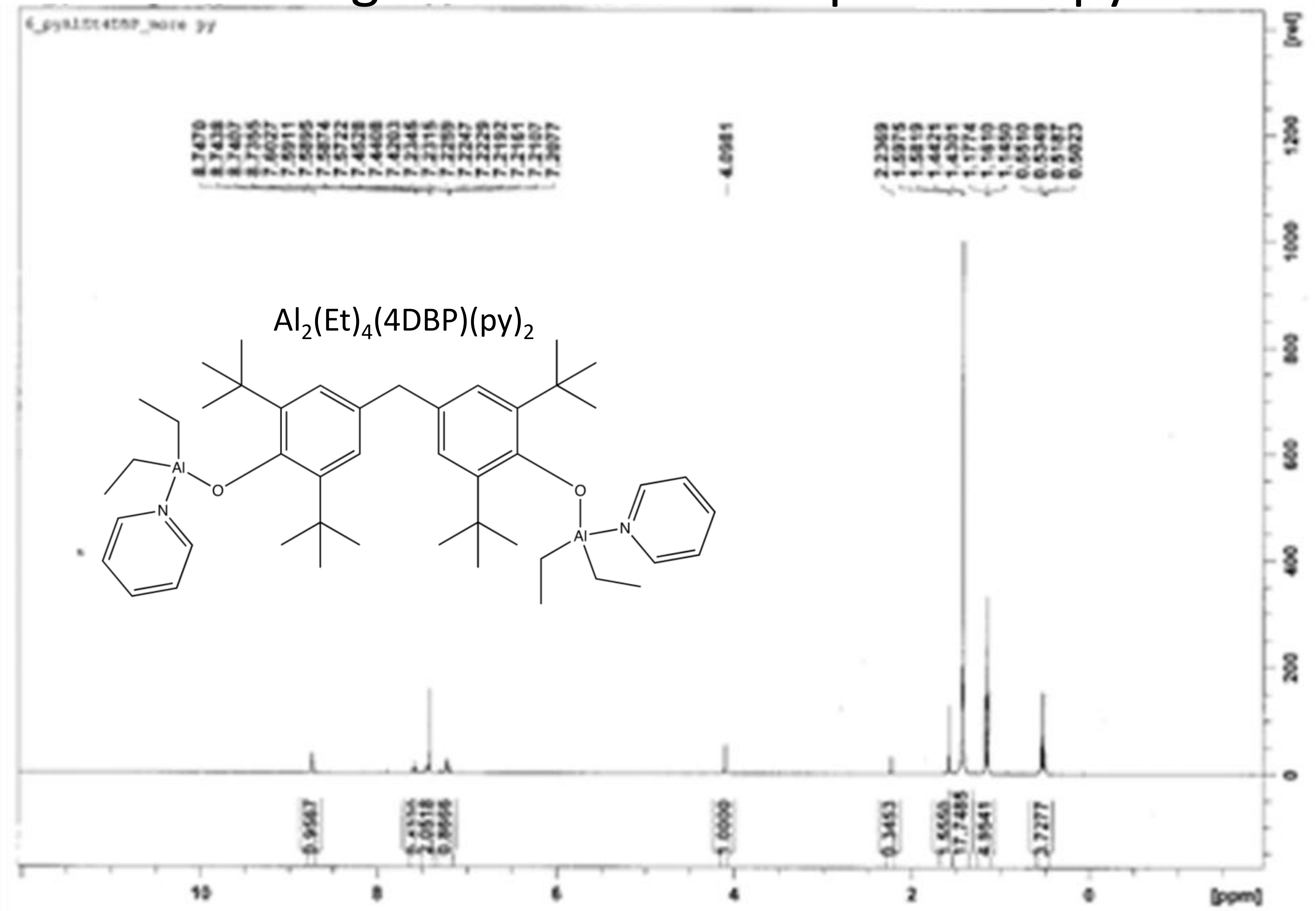
- Single source precursors will be applied for nanoparticle synthesis

Extra Slides

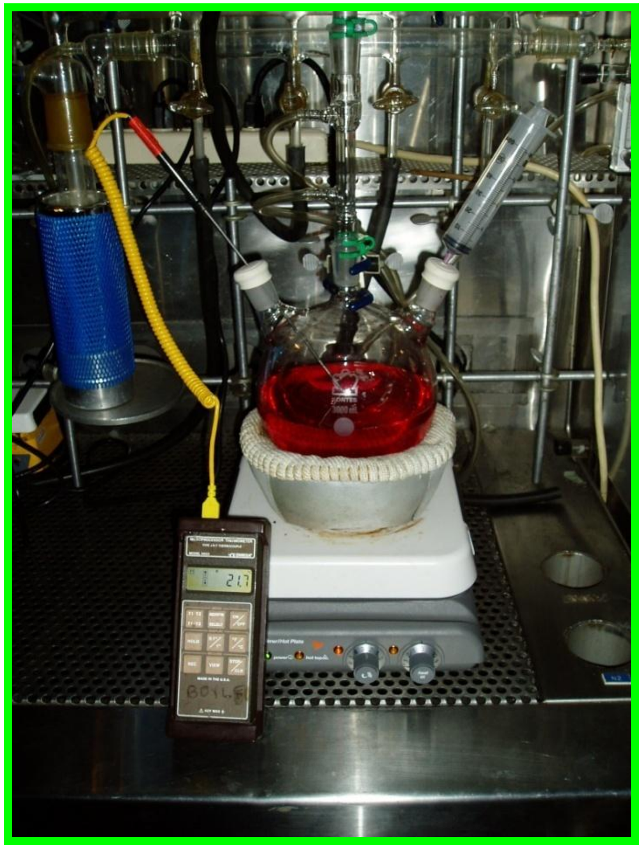
Nuclear Magnetic Resonance Spectroscopy Data



Nuclear Magnetic Resonance Spectroscopy Data

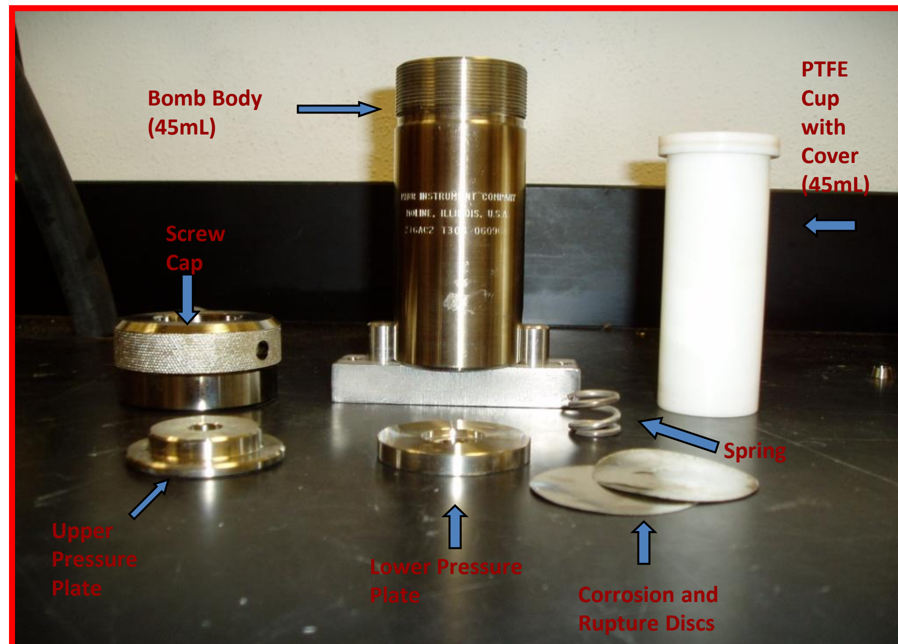


Pending Mixed Metal Results, Nanoparticles are to be Synthesized



Solution Precipitation route

Parr Digestion Bomb



Solvothermal route