SAND2014-16273PE

Synthesis of Metal Boranes

Kathryn F. Kasky, Timothy J. Boyle, Eric Sivonxay
Org. 1815 Advanced Materials Laboratory
1001 University Boulevard SE
(505) 720-9596
ktkasky@gmail.com

AML
Advanced Materials Laboratory

STAR PROGRAM™

LOS LUNAS HIGH SCHOOL

ASP

Sandia National Laboratories
Advanced Materials Laboratory
1001 University Boulevard, SE
Albuquerque, NM 87106
ktkasky@gmail.com
(505)720-9596

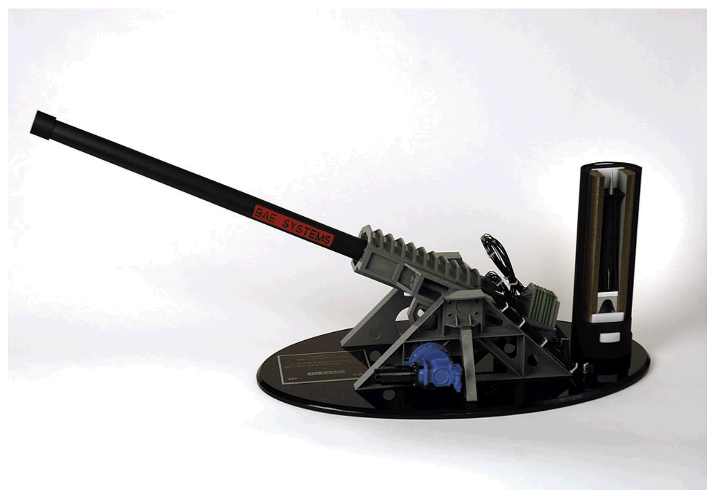
This work is partially supported by the Sandia STAR Program. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. Thanks also for the grateful use of the Bruker X-ray diffractometer purchased via the National Science Foundation CRIF:MU award to Prof Kemp of the University of New Mexico (CHE04-43580).

Major GOAL: synthesize single source precursors (SSP) to Group (IV) metal borides.

Metal Borides: metal bound by boron atoms (i.e., TiB_2, ZrB_2, HfB_2)

Uses of Group 4 metal diborides are varied:

Satellite thrusters

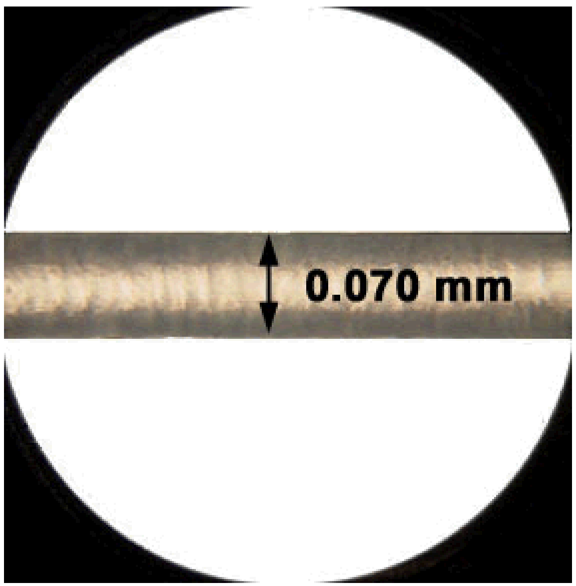


Rail Gun

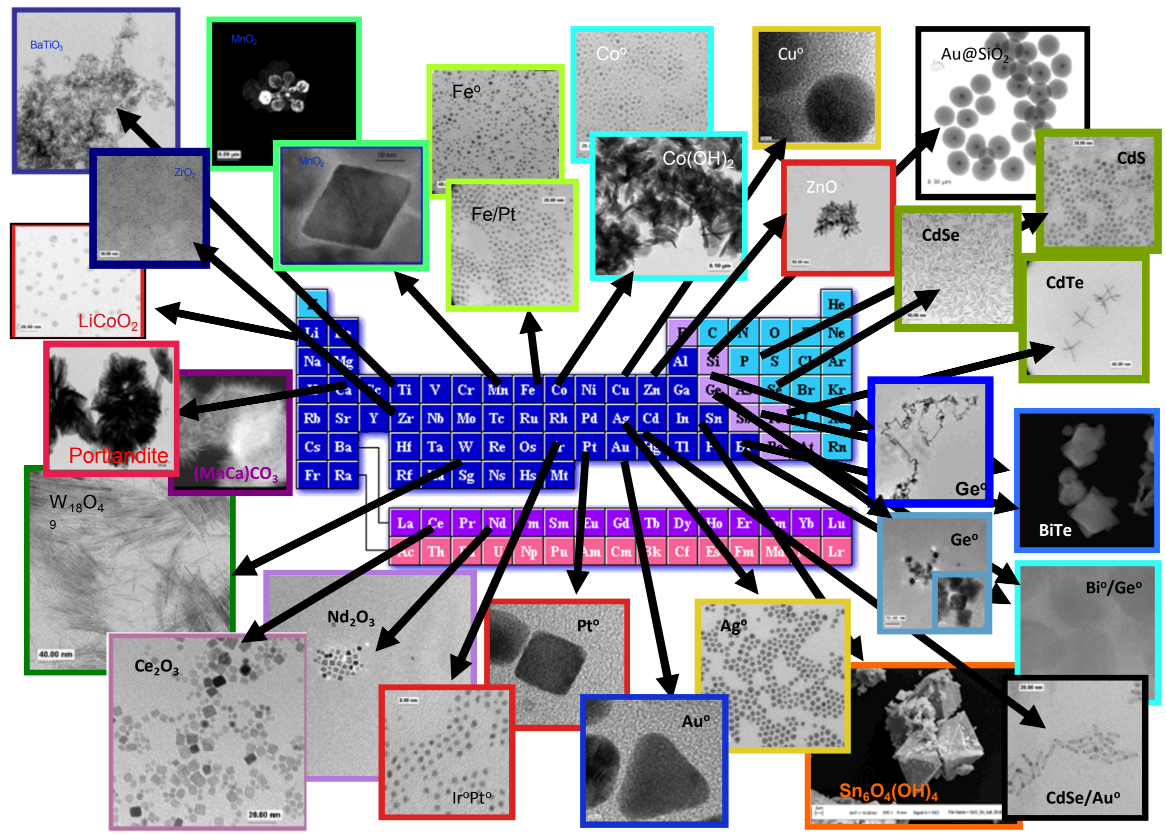
Wear Resistant coatings (Saw Blades)

Nanomaterials are of interest since they have exploitable properties that are different from bulk materials

- A nanomaterial is a particle between 1 and 100 nanometers.
- That's one billionth of a meter (10^{-9})!

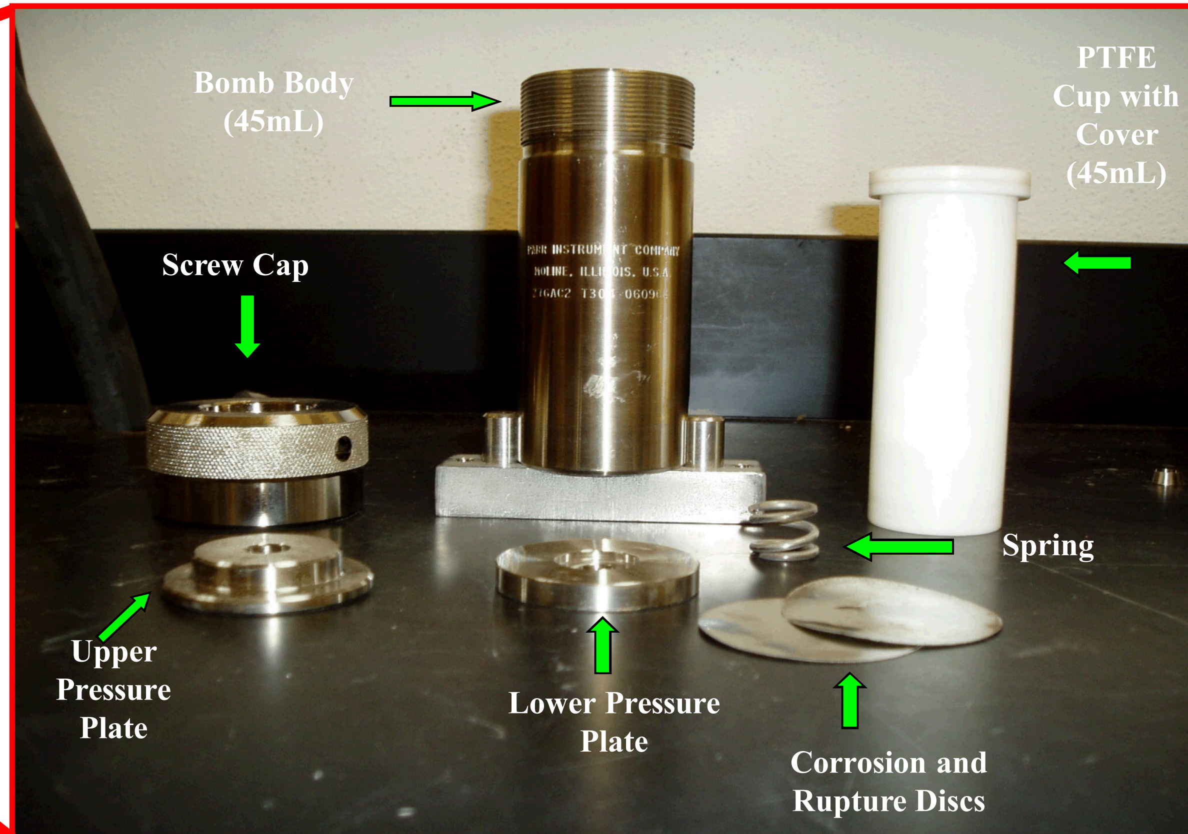


The Periodic Table of Elements for Nanomaterials



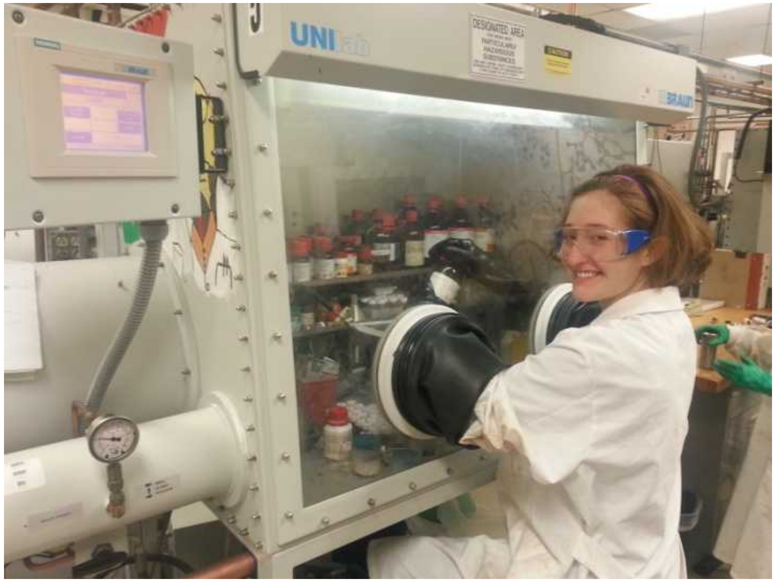
- Nanomaterials come in all sizes (below 100 nm), shapes, and compositions.
- Typically solution routes are used to synthesize these nanomaterials.

One of the routes used to make nanomaterials is the solvothermal process using a Parr Bomb.



The Teflon™ liner contains the sample (usually dissolved in a solvent), the bomb is sealed, and the unit is heated for a pre-selected amount of time.

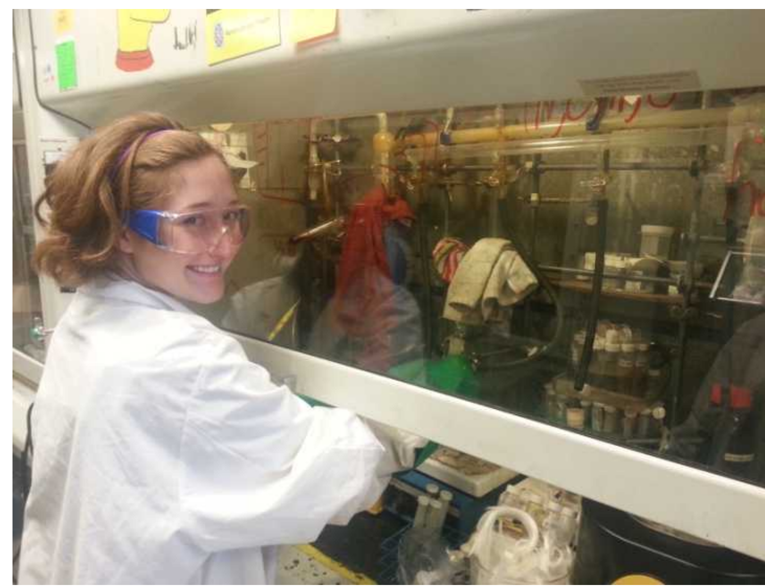
Safety is top priority.



Working in a glove box.

- Training
  - •paper work, paper work,
  - •paper work at SNL, AML, 104, 228-9
- Introduction to the Lab
  - •shoulder to shoulder, line of sight, line of shout, in-lab, free reign.
- Safety Culture

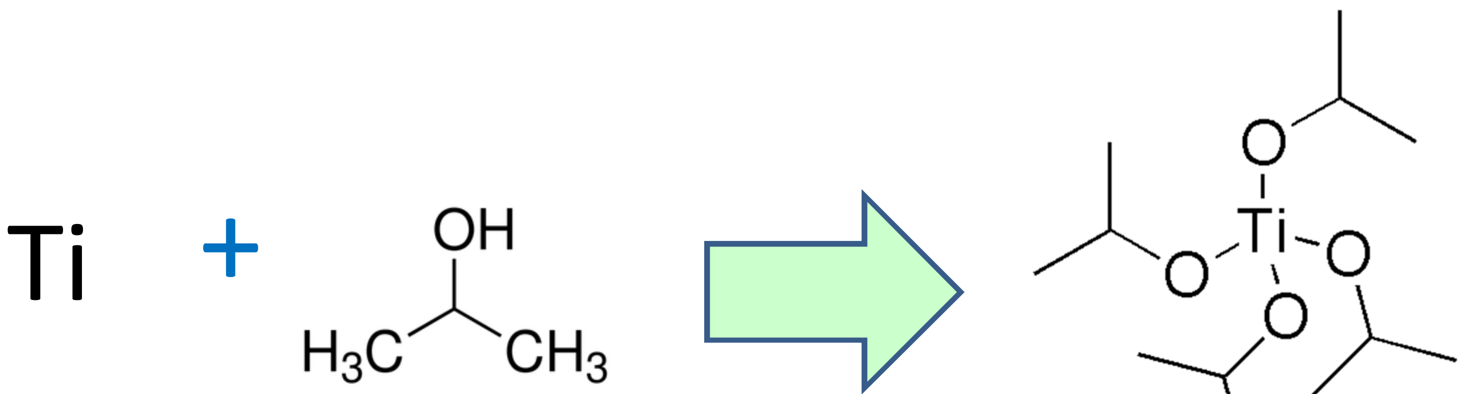
- PPE
- Common Sense
- Equipment
  - Glovebox
  - Schlenk Line



Working in a fume hood.

Metal alkoxides are the precursor of choice for production of ceramic oxide nanomaterials (in the Boyle group) .

An alcohol is any organic compound whose molecule contains one or more hydroxyl groups attached to a carbon atom (H-OR).



titanium

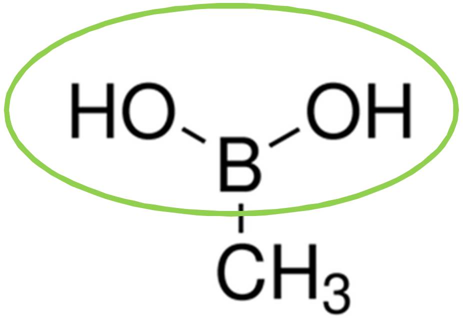
iso-propanol

titanium (iv) iso-propoxide

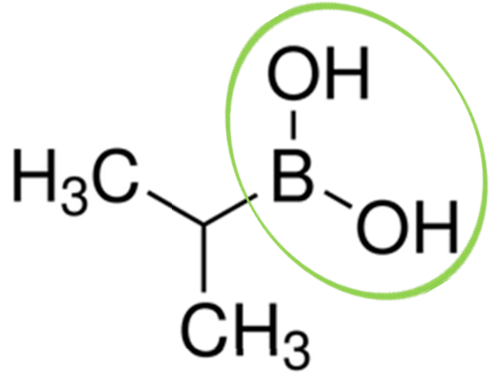
NO boron atoms present – can't possibly make the MB_2 nanomaterials with these $M(OR)_4$.

- Metal alkoxide – alcohol with the H replaced by a metal (M-OR).

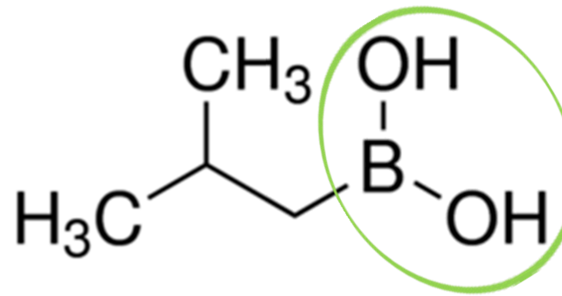
Boronic acid derivatives of $M(OR)_4$ will be explored as a SSP to MB_2 nanomaterials



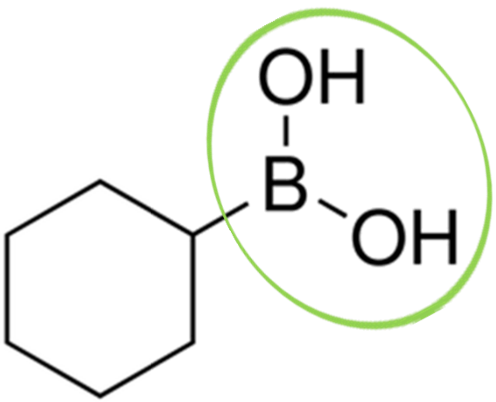
Methylboronic acid



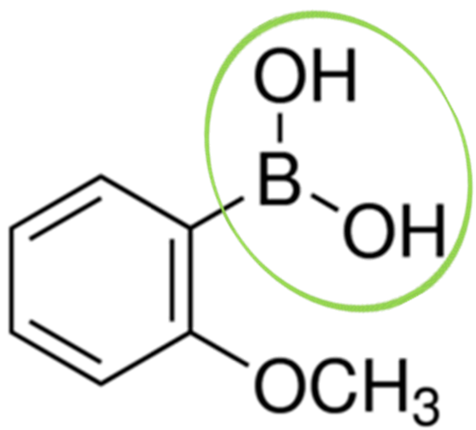
Isopropyl boronic acid



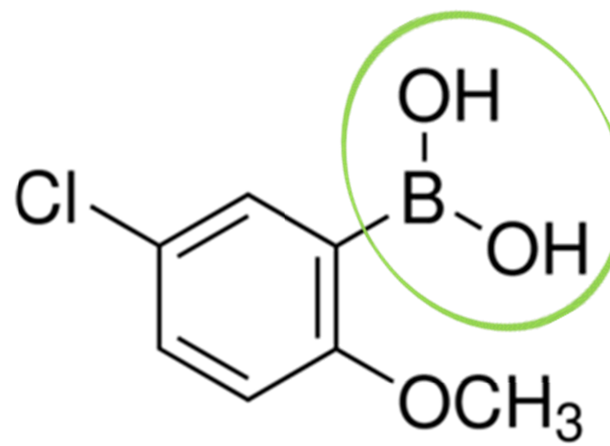
(2-Methylpropyl) boronic acid



Cyclohexyl boronic acid



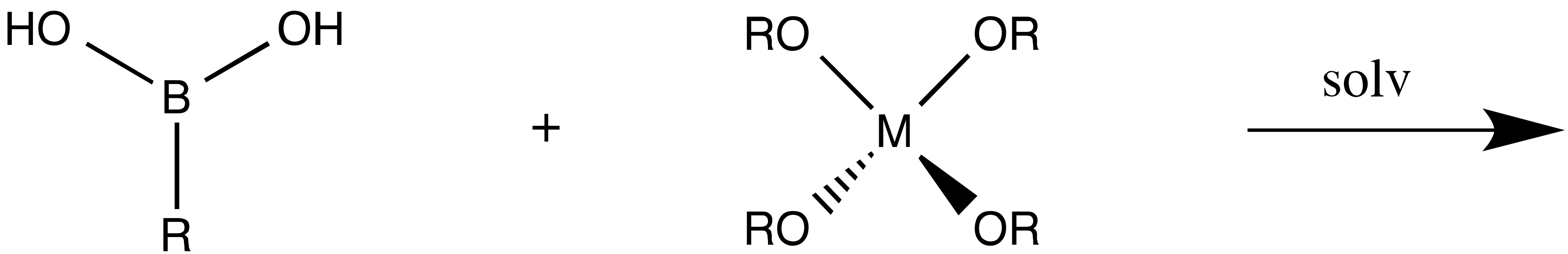
2-Methoxyphenyl boronic acid



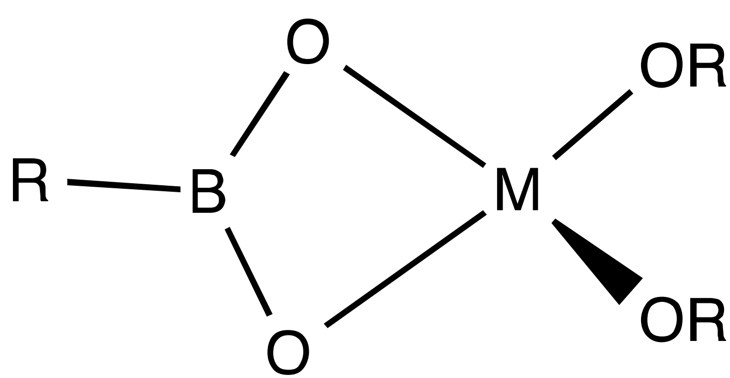
5-Chloro-2-Methoxyphenyl boronic acid

The reaction of a series of boronic acids with a set of $M(OR)_4$ was started.

General reaction:



- Inert atmosphere synthesis conditions •(I did the reaction in a glovebox)
- Small scale synthesis to minimize waste •(Ran it in vial to save $$)
- Boronic acid selected based commercial availability •(Easier to buy it)
- Solvent selected based on proper polarity •(Found something it would dissolve in)



Product characterization requires various instruments.


SCXD

Crystal structures very important for Product identification in Boyle group

- SCXD (Single Crystal X-Ray Diffraction)
- FTIR (Fourier Transform Infrared Spectroscopy)
- EA (Elemental Analysis)
- NMR (Nuclear Magnetic Resonance)

NMR

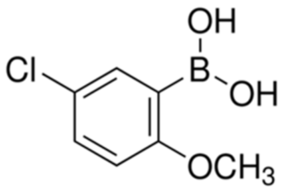

FTIR


EA

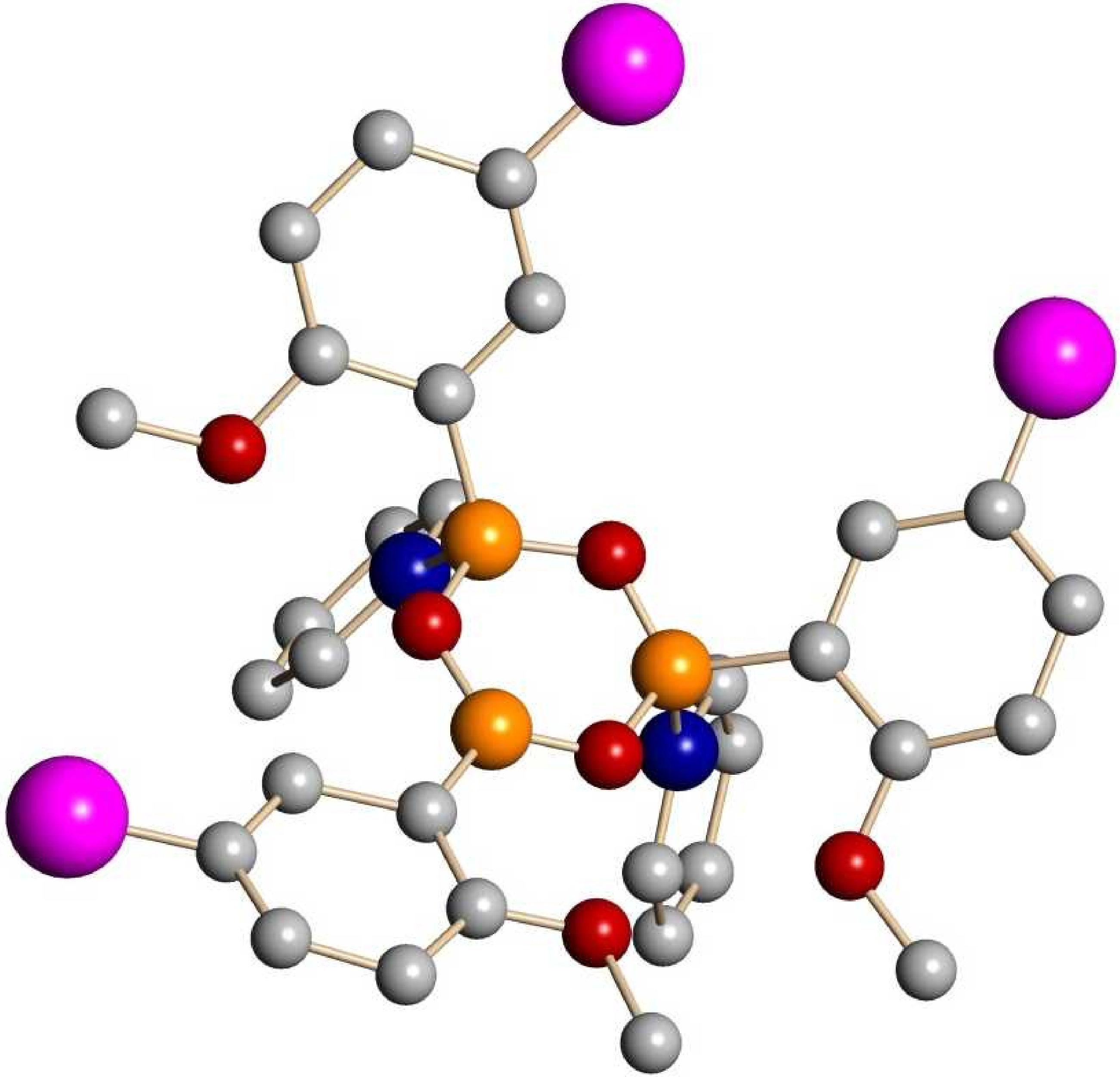
Initial synthesis efforts focused on exploring the reaction of $[Ti(OPr^i)_4]$ + $(OH)_2B$-R

Boronic Acid	Solvents	Heated	Results
Methylboronic acid	toluene	No	Crystallized
Isopropyl boronic acid	toluene	80 °C 10 min	Crystallized
(2-Methylpropyl) boronic acid	toluene/pyridine	80 °C 15 min	Gel
Cyclohexyl boronic acid	toluene	80 °C 10 min	Crystallized
2-Methoxyphenyl boronic acid	toluene	80 °C 20 min	Gel
5-Chloro-2-Methoxyphenyl boronic acid	toluene/pyridine	80 °C 10 min	Crystallized

H_2-CPB + $Ti(OPr^i)_4$ $\xrightarrow[\text{2. pyr}]{\text{1. tol}}$



H_2-CPB

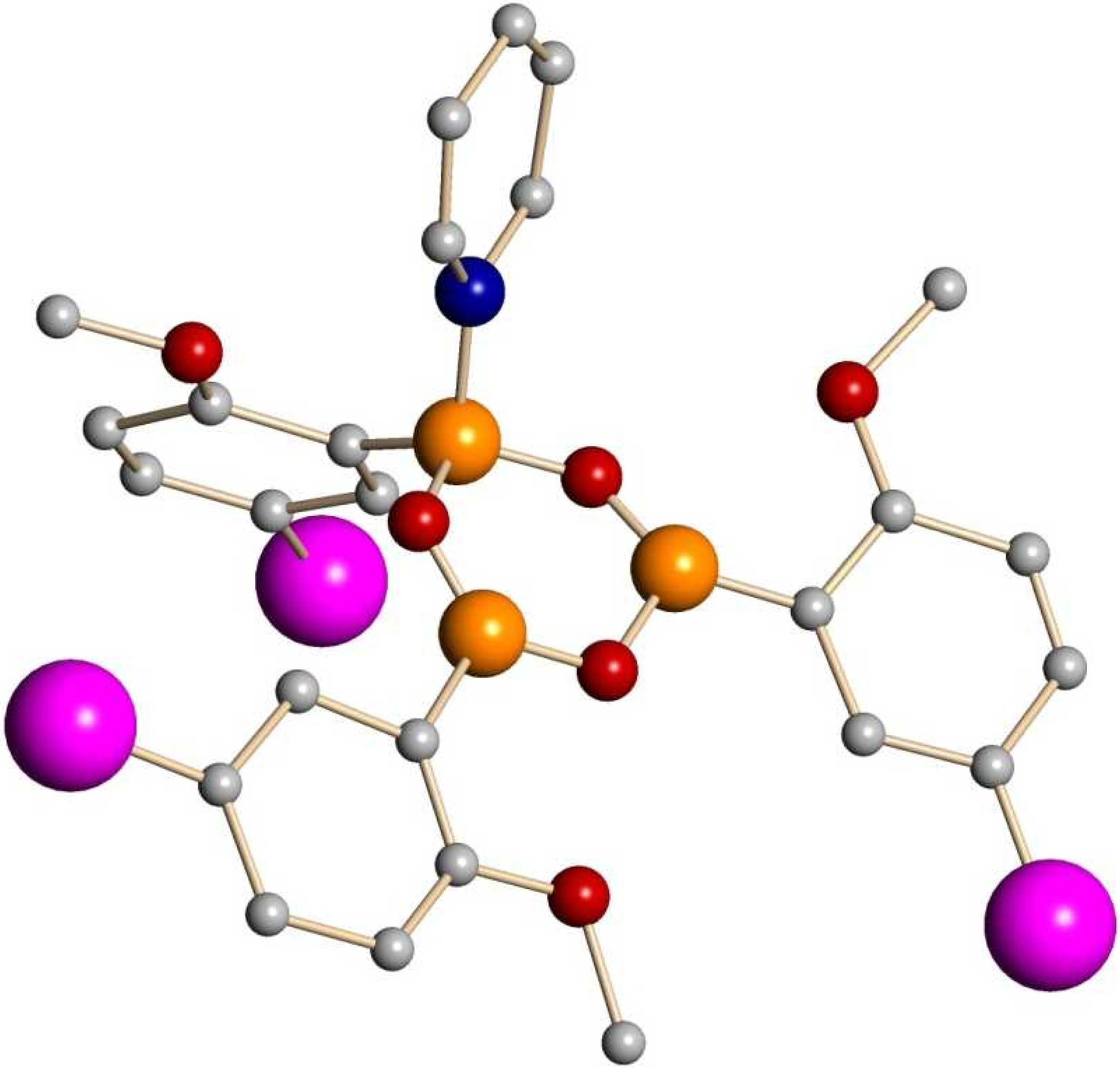


Orange	Boron
Red	Oxygen
Grey	Carbon
Pink	Chlorine
Blue	Nitrogen

The impact of increasing the steric bulk of the alkoxy ligand was investigated – $Ti(OBu^{t})_4$ Reactions.

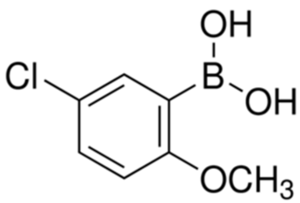
Boronic Acid	Solvents	Heated	Results
Methylboronic acid	toluene/pyridine	No	Gel
Isopropylboronic acid	toluene/ pyridine	No	Crystallized
(2-Methoxyphenyl) boronic acid	toluene/pyridine	No	Gel
Cyclohexyl boronic acid	toluene/ pyridine	No	Gel
(2-Methylpropyl) boronic acid	toluene	No	Gel
5-Chloro-2-Methoxyphenyl boronic acid	toluene/pyridine	No	Crystallized

H_2-CPB + $Ti(OBu^t)_4$ $\xrightarrow[\text{2. pyr}]{\text{1. tol}}$

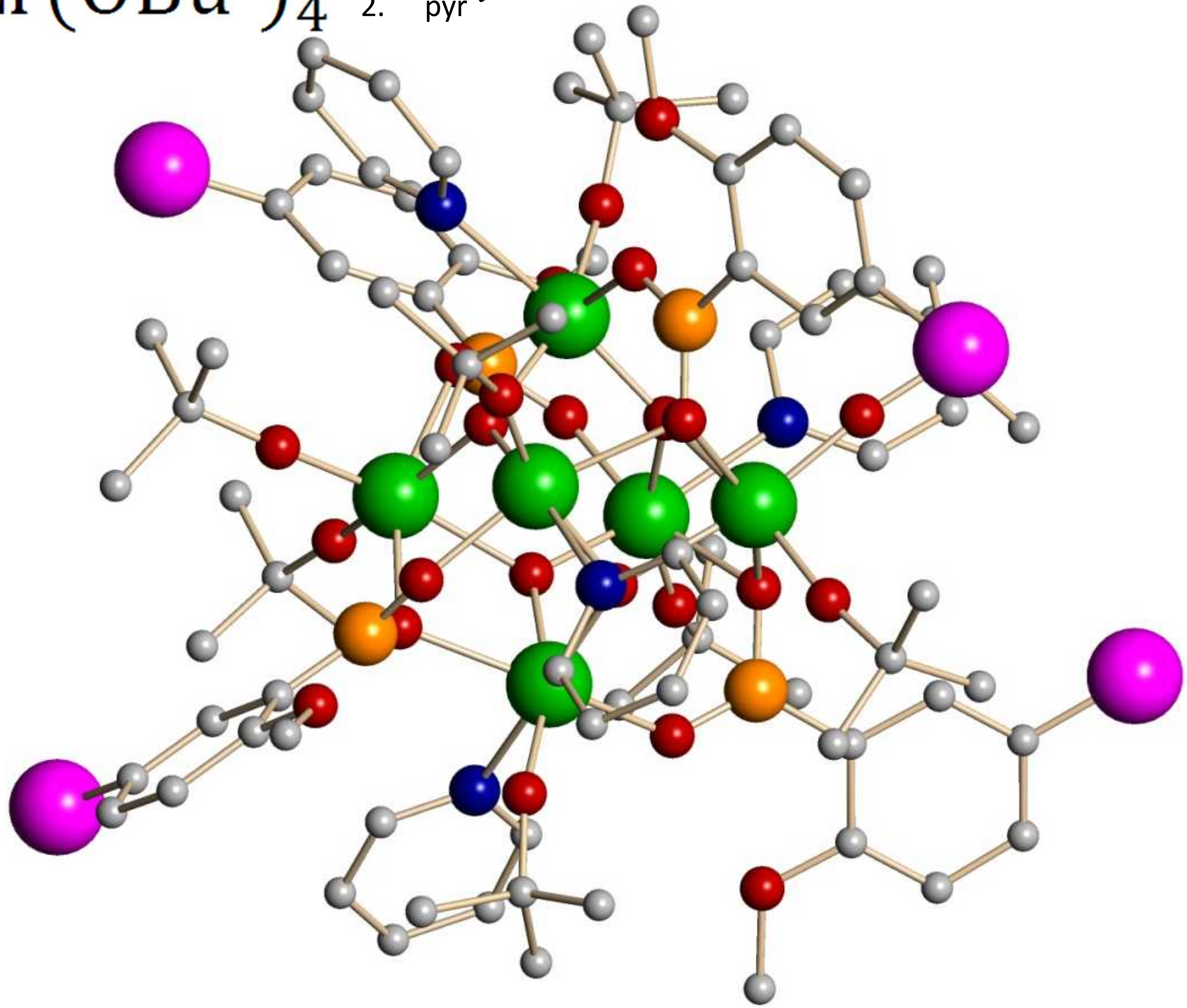


In order to test the effect of a heavier central atom, CPB was reacted with zirconium tert-butoxide.

$$H2\text{-}CPB + Zr(OBu^{t})_4 \xrightarrow[2.\quad pyr]{1.\quad tol}$$

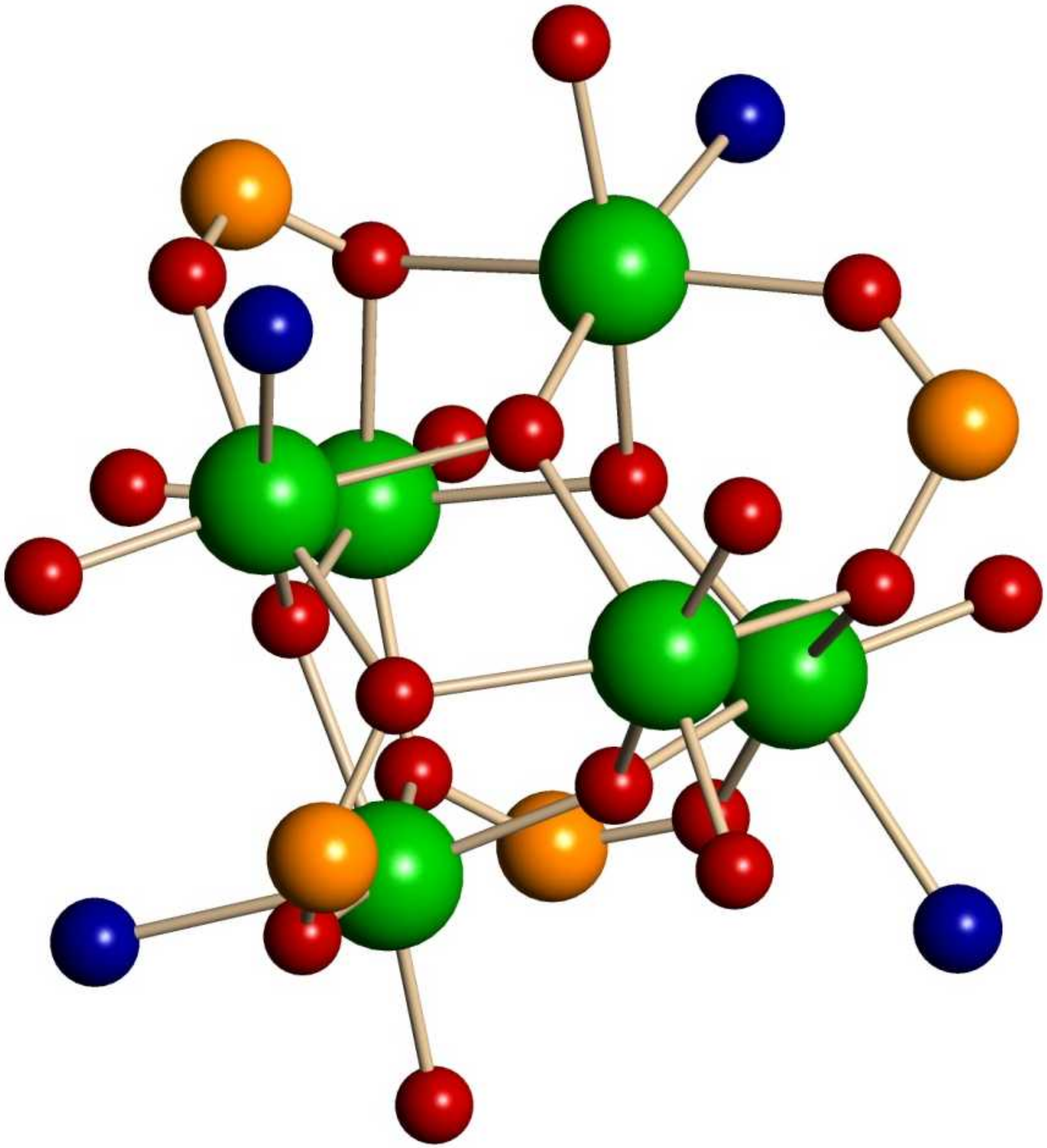


H_2-CPB



Orange	Boron
Red	Oxygen
Grey	Carbon
Pink	Chlorine
Blue	Nitrogen
Green	Zirconium

Core of Zirconium Structure



And now…

- Successfully synthesized a metal borane
- Characterization of Zirconium Tert-Butoxide and CPB compound decomposition
- Characterization of Diethyl Zinc Reaction
- 2-Pyridine methanol reactions in toluene dissolved in pyridine