

# Bifunctional Electrolytes for Lithium-ion Batteries

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ES068

# Overview

## Timeline

- **Start Date:** April 2009
- **End Date:** May 2013
- **Percent Complete:** 30%

## Budget

- **Total Project Funding**  
\$798K
- **FY09** - \$199.5 K
- **FY10** - \$199.7 K

## Barriers

- Barriers addressed  
**Abuse tolerance**

## Partners

Novolyte Technologies,  
Independence, OH

# Objectives

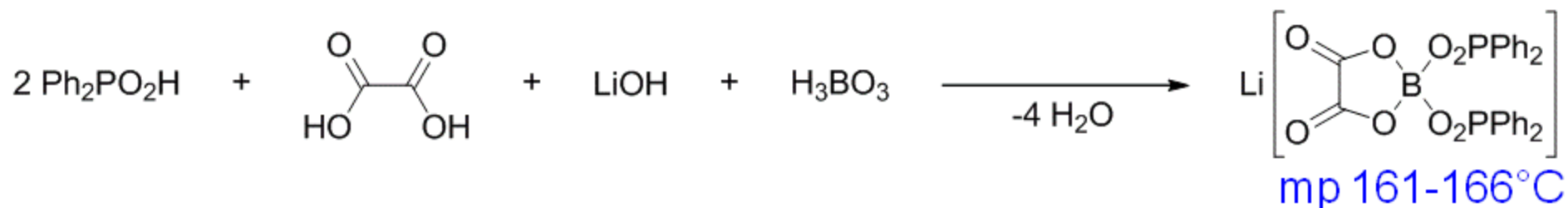
- Design, synthesize, and characterize physical and electrochemical properties of functionalized Li salt anions containing phosphorous and boron moieties known to impart materials with flame retardant properties (Flame Retardant Ions or **FRIONS**) and thus improve device safety.
- Gain insight into the overall chemical and electrochemical behavior, including reactivity of these novel bifunctional electrolytes toward Li-ion charged anodes using a combination of electrochemical and in situ spectroscopic techniques.
- Develop structure-function relationships that will guide further search of optimized FRIONS and other species that contribute to enhance abuse tolerance.

Month/Year	Milestones
Dec-09	<ul style="list-style-type: none"> <li>▪ Synthesize first generation <u>F</u>lame <u>R</u>etardant <u>I</u>ons (FRIONS)</li> <li>▪ Complete design of spectroelectrochemical cell for in situ Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) for measurements involving highly reactive Li-based systems.</li> <li>▪ Initiate contacts with Novolyte Technologies to undertake testing of materials developed at Case in actual coin cells.</li> </ul>
April-10	<ul style="list-style-type: none"> <li>▪ Complete full characterization of first FRION including preliminary charge-discharge curves in actual coin cells.</li> <li>▪ Complete construction of in situ ATR-FTIR cell.</li> </ul>
Nov-10	<ul style="list-style-type: none"> <li>▪ Submission of paper on first FRION for publication</li> <li>▪ Initiate and complete <i>in situ</i> spectroscopic and impedance measurements with the first FRION.</li> <li>▪ Synthesize and <i>fully</i> characterize second generation FRIONS.</li> </ul>
April-11	<ul style="list-style-type: none"> <li>▪ Initiate and complete <i>in situ</i> spectroscopic and impedance measurements with the second generation FRIONS.</li> <li>▪ Synthesize and <i>fully</i> characterize third generation FRIONS.</li> </ul>

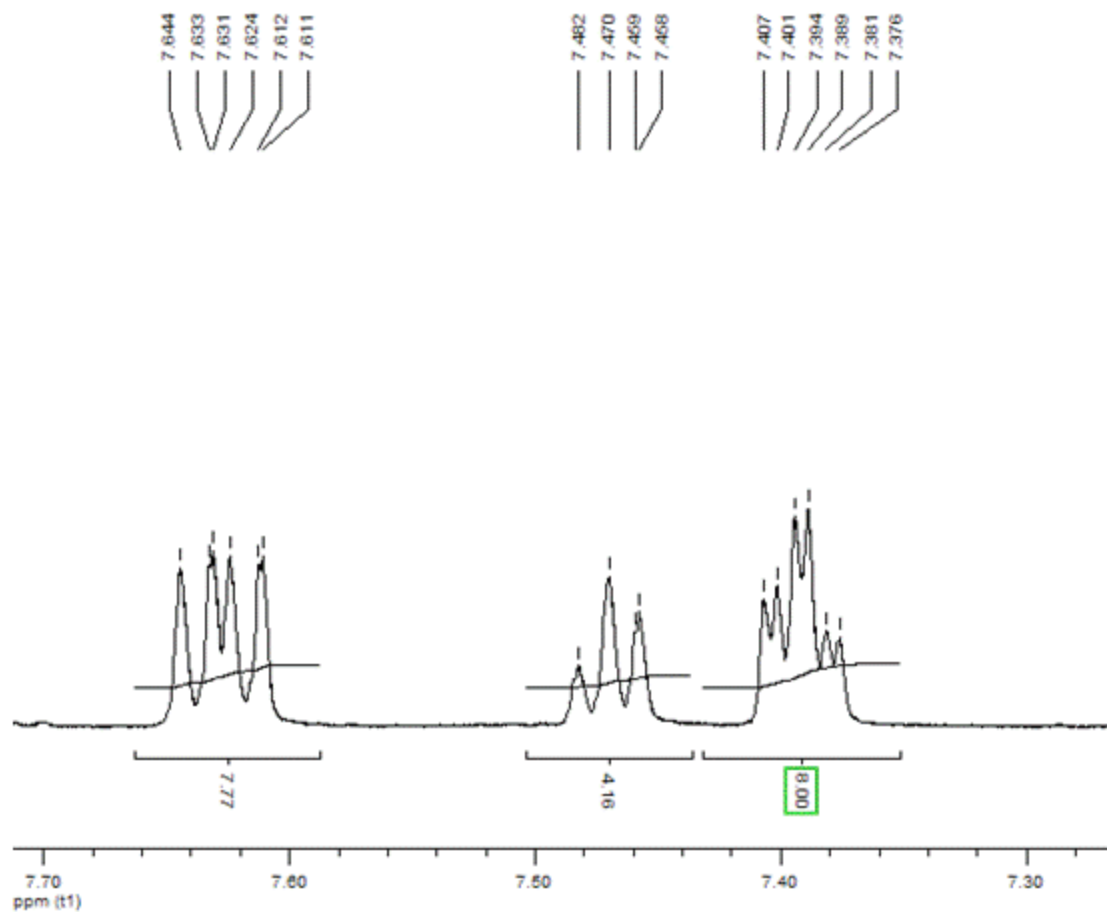
# Approach/Strategy

- Incorporate flame retardant and overcharge protection chemical groups to anionic species that display good transport properties and use these materials as salts or as additives to more conventional electrolytes.
- Gain insight into modifications to the structural and physico-chemical properties of the passive on Li-ion anodes using a combination of attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and conventional electrochemical techniques including impedance spectroscopy.
- Build up knowledge bases that could afford rational guidelines for the search of novel materials displaying required properties to enhance abuse tolerance of high energy density high power density Li batteries.

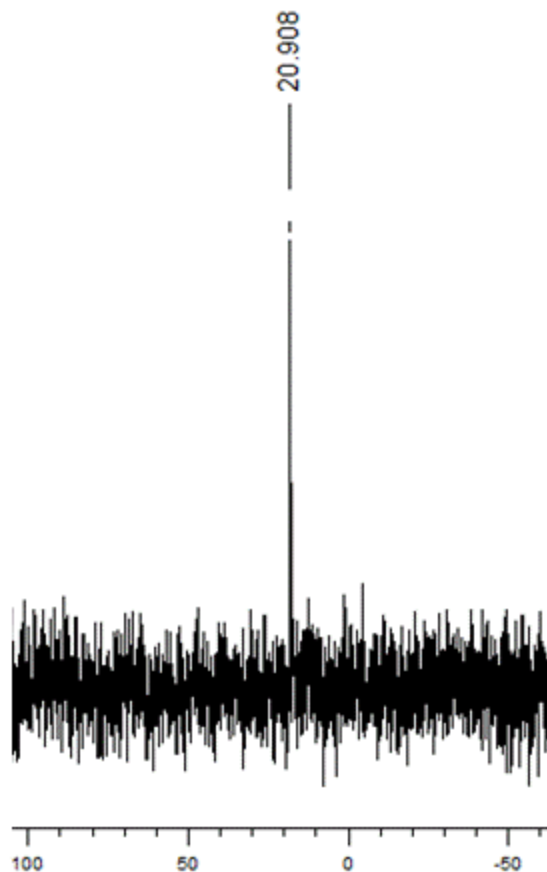
# Al. Synthesis and NMR Characterization of Li[OxB(OP)<sub>2</sub>]



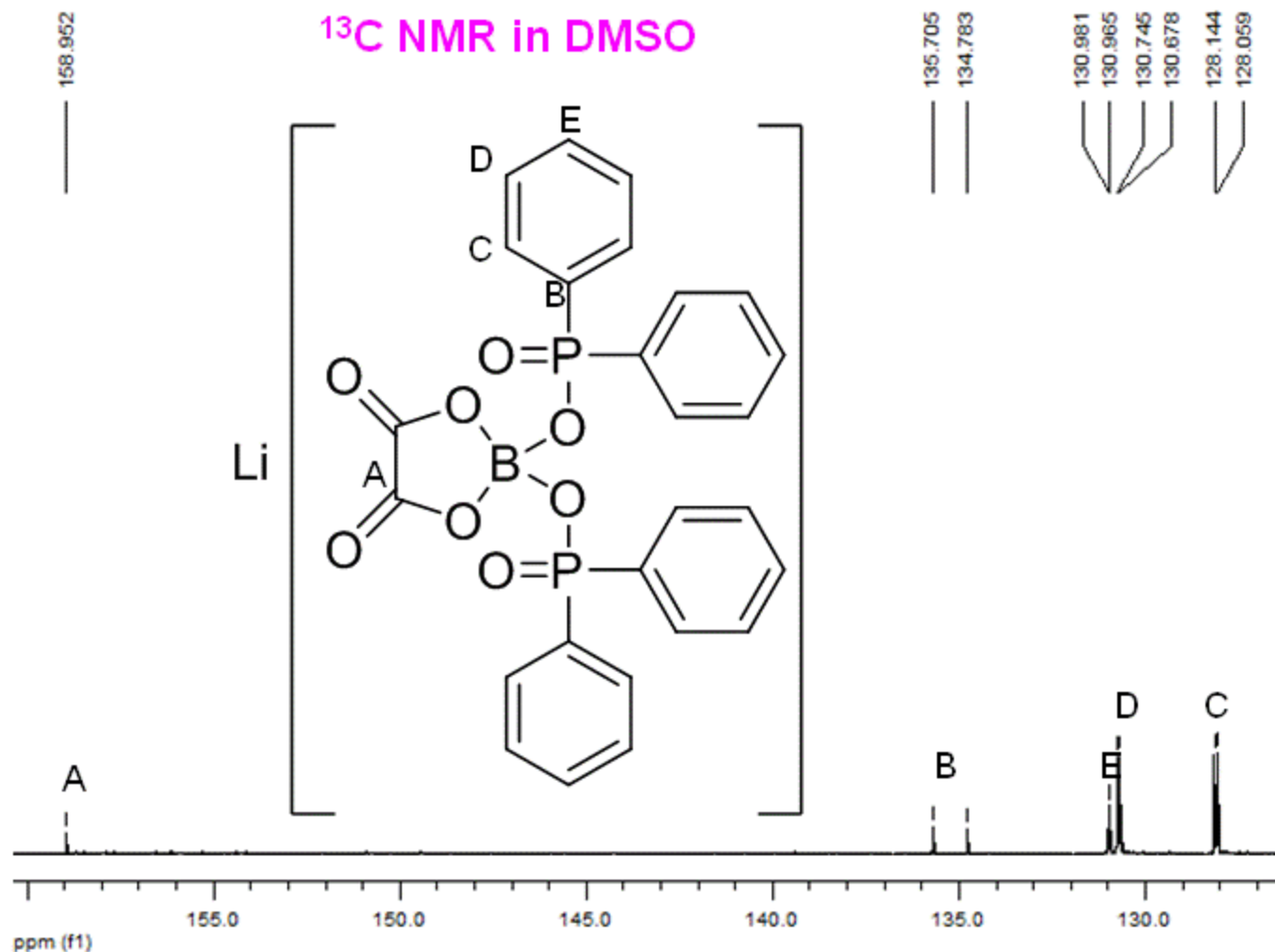
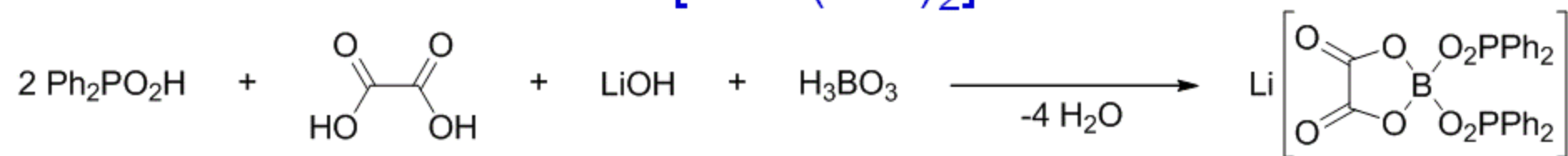
## <sup>1</sup>H NMR in DMSO



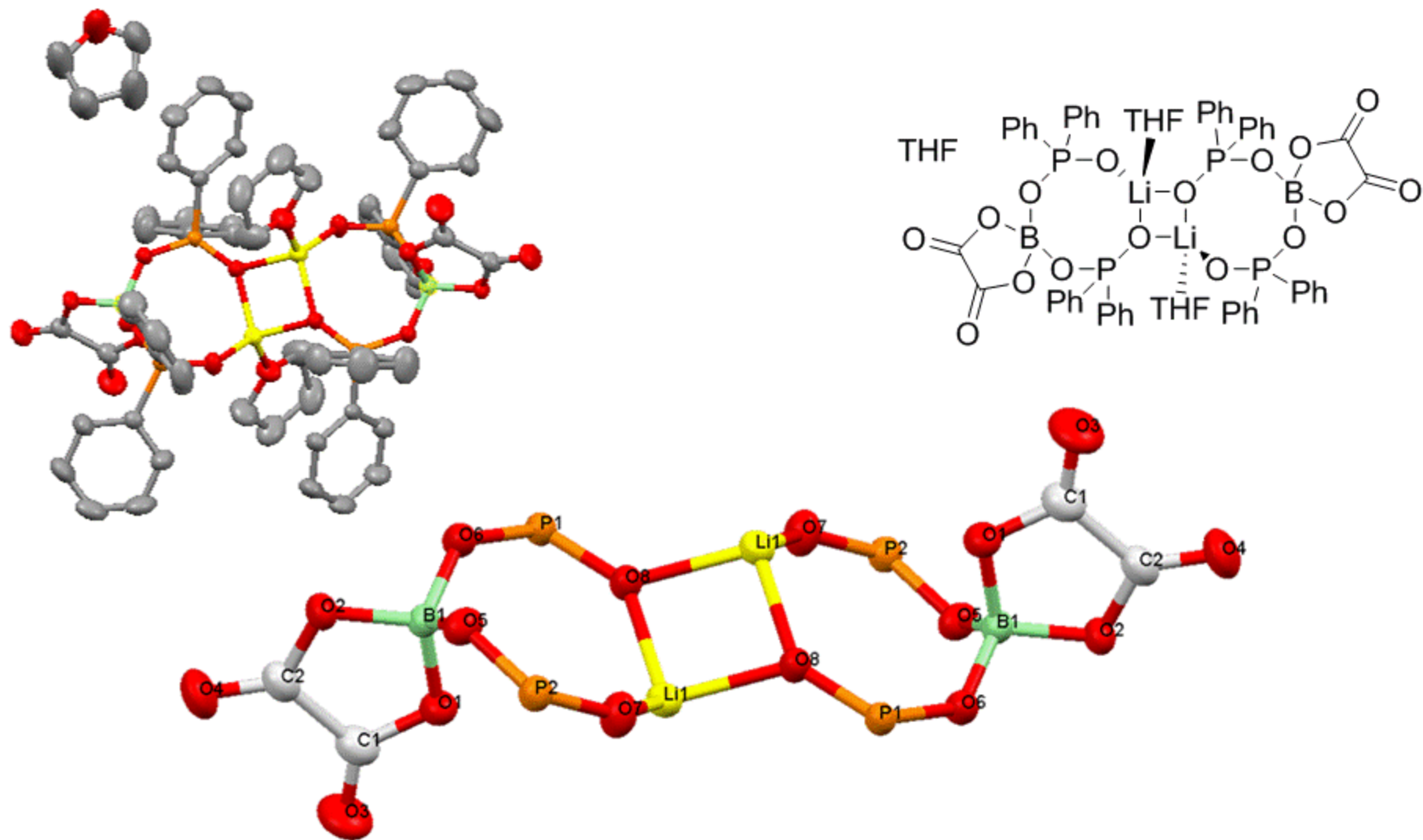
## <sup>31</sup>P NMR in DMSO



## A.II. Synthesis and NMR Characterization of $\text{Li}[\text{OxB}(\text{OP})_2]$



## A.III. X-ray Crystal Structure of (THF)Li[OxB(OP)<sub>2</sub>] Dimer

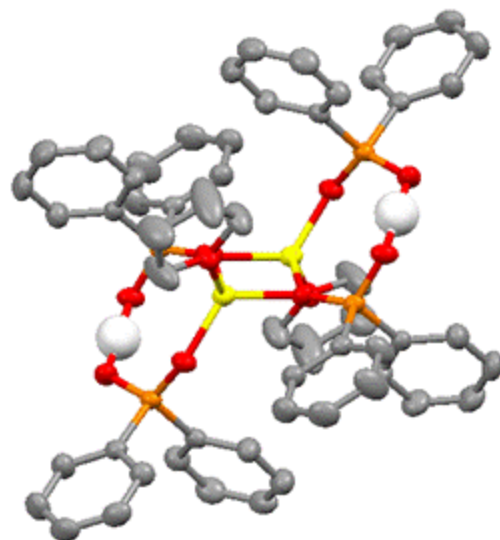
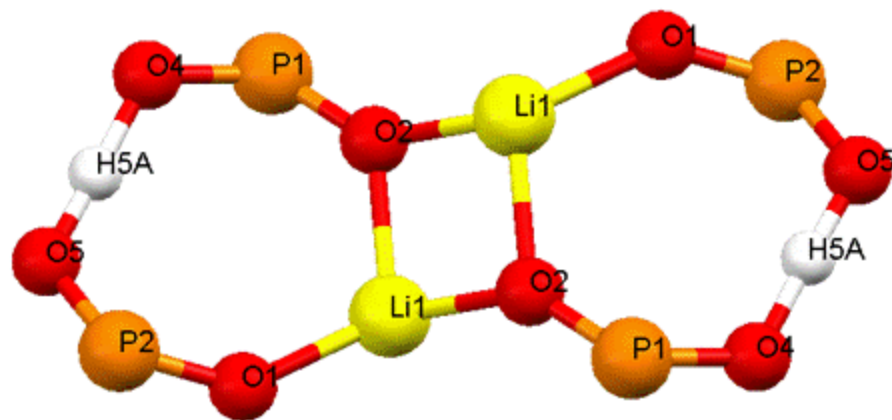
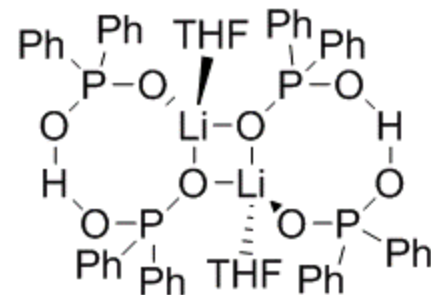


Core Section of (THF)Li[OxB(OP)<sub>2</sub>] dimer.  
Phenyl rings and THF molecules are omitted for clarity.



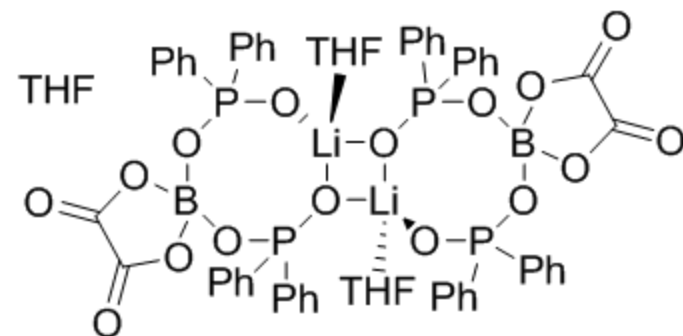
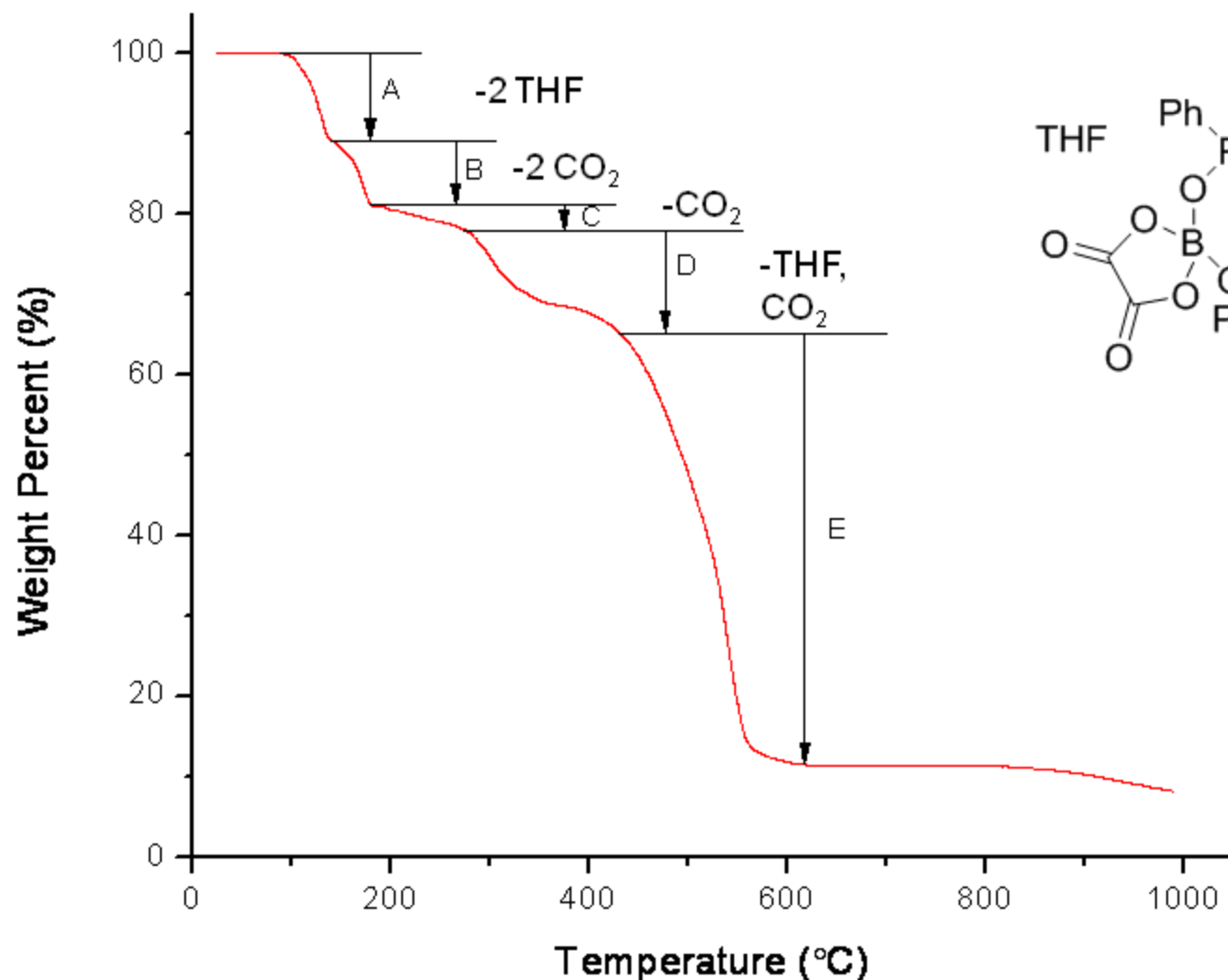
## A.IV.Competing Byproduct in $\text{Li}[\text{OxB}(\text{OP})_2]$ Synthesis

$\{(\text{THF})\text{Li}(\text{O}_2\text{PPh}_2)(\text{HO}_2\text{PPh}_2)\}_2$  arises from the reaction of  $\text{Ph}_2\text{PO}_2\text{H}$  and  $\text{Ph}_2\text{PO}_2\text{Li}$ , which is generated in situ by deprotonation of the parent compound by  $\text{LiOH}$ . The byproduct contains the same core structure as the  $(\text{THF})\text{Li}[\text{OxB}(\text{OP})_2]$  dimer except for substitution of oxalato-borate component for a hydrogen.



Core Section of  $\{(\text{THF})\text{Li}(\text{O}_2\text{PPh}_2)(\text{HO}_2\text{PPh}_2)\}_2$   
Phenyl rings and THF molecules are omitted for clarity.

# A.V. Thermogravimetric Analysis of $\text{Li}[\text{OxB(OP)}_2]$

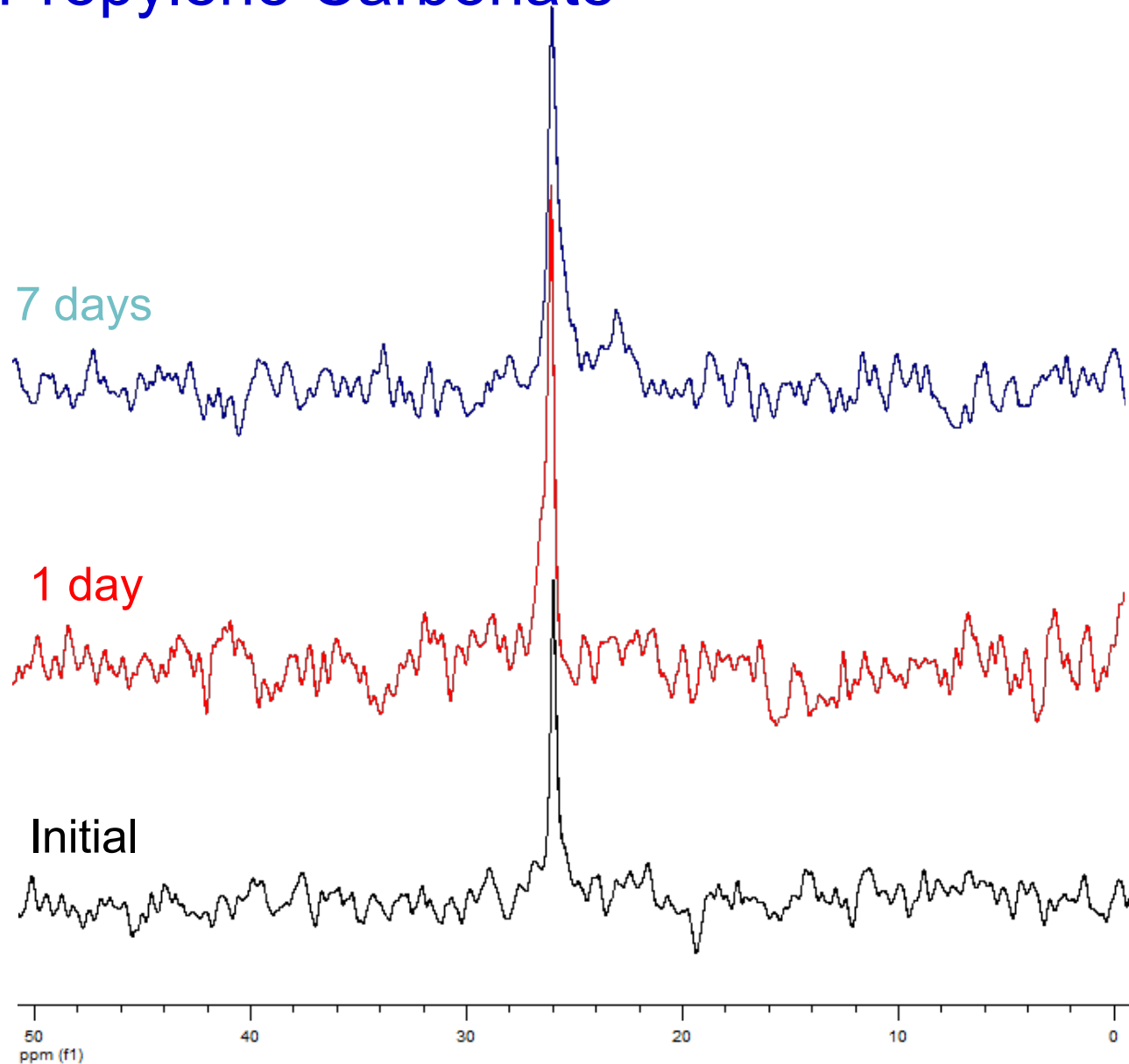


Event	T (°C)
A	94.5
B	155.4
C	179.2
D	249.5
E	343.6

$\text{Li}[\text{OxB(OP)}_2]$  is stable up to temperatures slightly higher than 150°C.

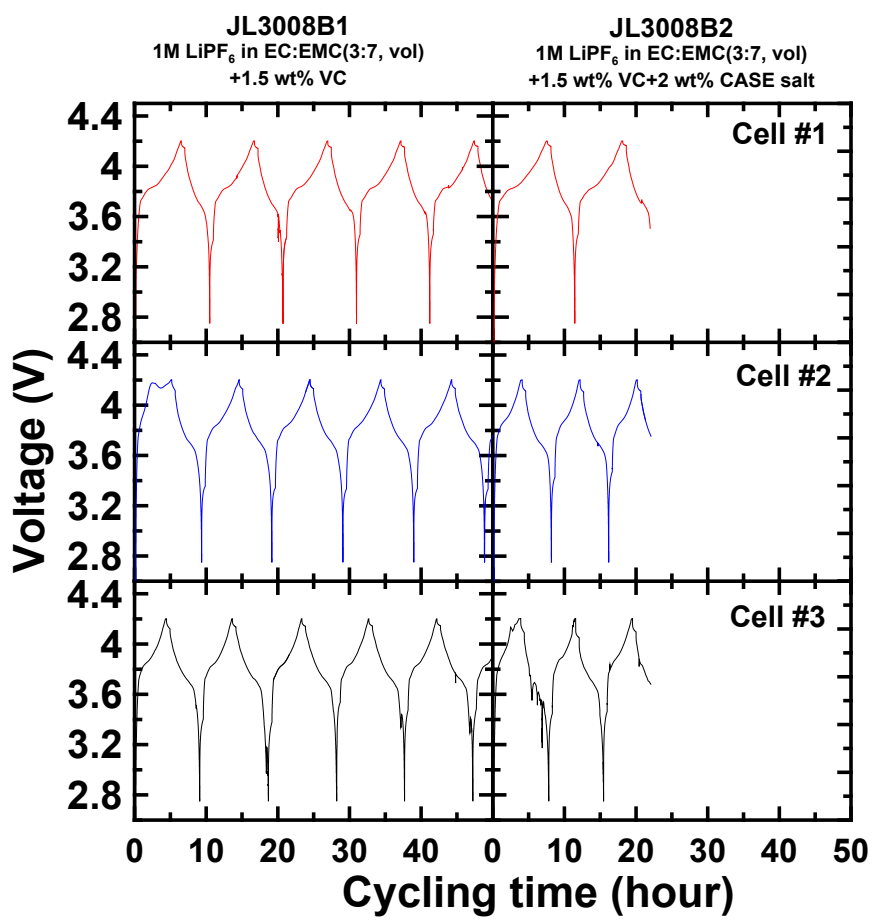
## A.VI. Thermal Stability of $\text{Li}[\text{OxB}(\text{OP})_2]$ in Propylene Carbonate

$\text{Li}[\text{OxB}(\text{OP})_2]$  and propylene carbonate were heated in a Teflon sealed container, to  $70^\circ\text{C}$  for 1 week and monitored via  $^{31}\text{P}$  NMR spectroscopy (singlet at 25.8 ppm). After one week, no visible decomposition was detected.



# A. VII. Comparison of Charge/Discharge Curves Recorded in a 2032-type Coin Cell with (Left) and Without Li[OxB(OP)<sub>2</sub>] (Right)

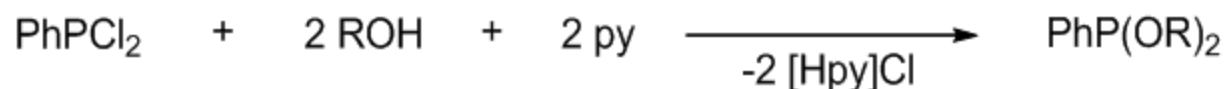
Positive Electrode:  
LiCoO2  
Positive Electrode:  
Synthetic Graphite



Cycling Protocol  
1 mA between  
4.2 and 2.75 V.  
C/5 Rate

Data collected by Novolyte Technologies, Independence, OH  
Addition of Li[OxB(OP)<sub>2</sub>] does **not** adversely affect battery performance.

# B.I. Synthesis of Anion Precursors



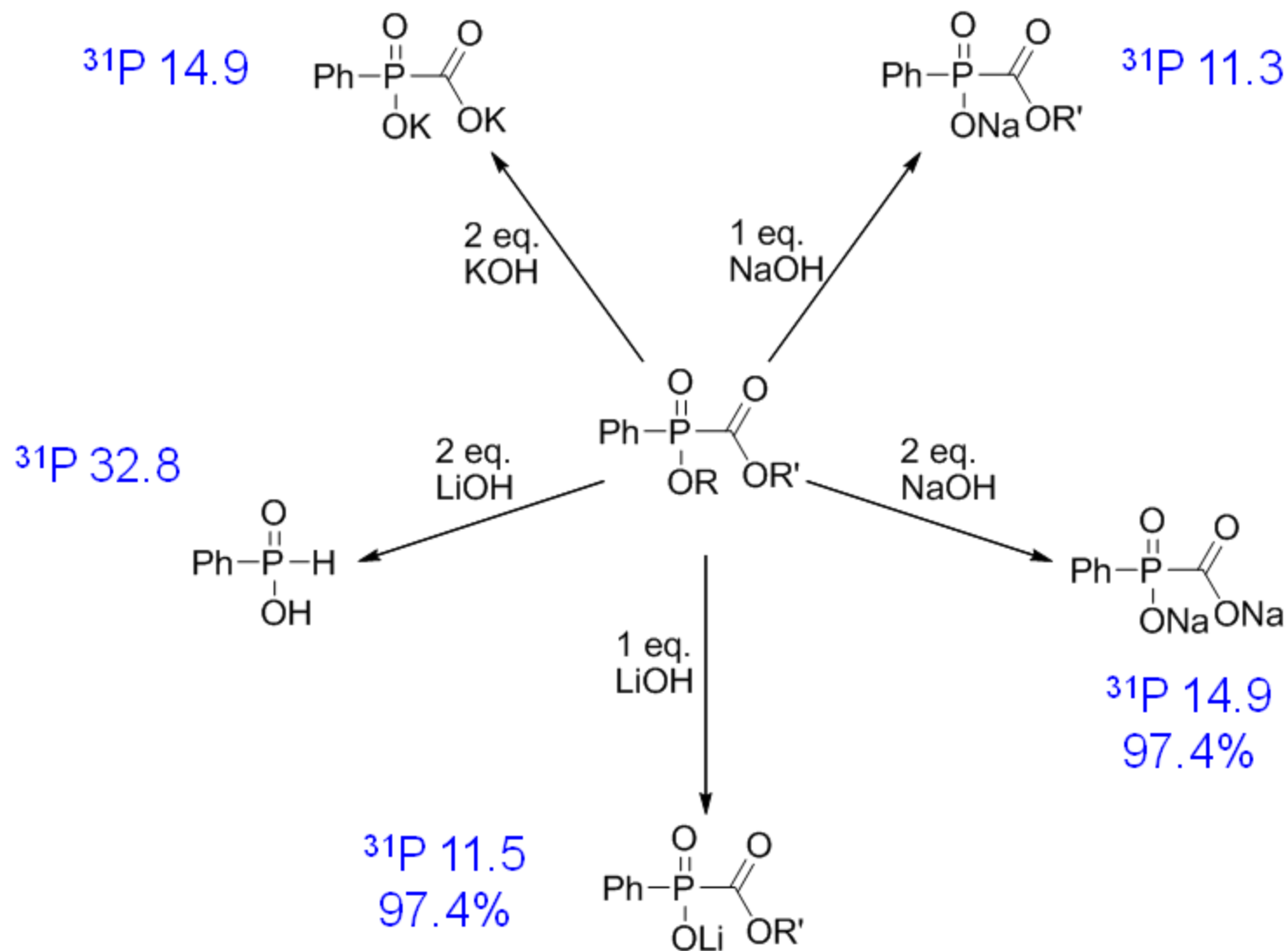
R = CH<sub>2</sub>CH<sub>3</sub> 80.0%

CH(CH<sub>3</sub>)<sub>2</sub> 77.8%

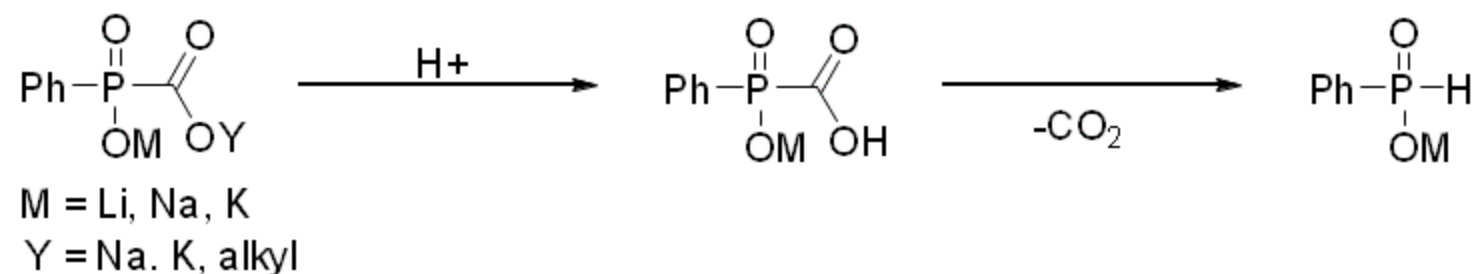
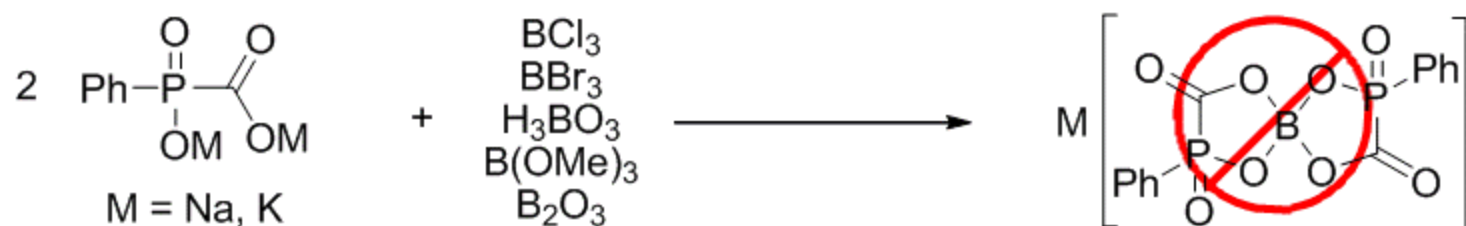
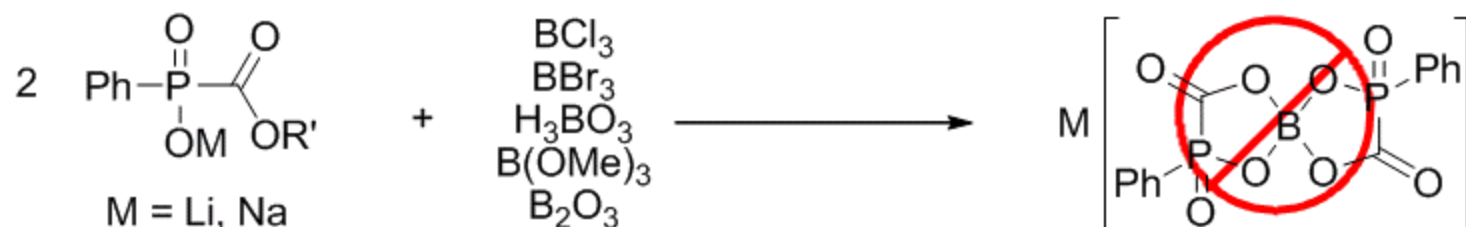


R	R'	<sup>31</sup> P Shift	% Yield
CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	16.4	70.4%
CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	16.5	62.1%
CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>2</sub> CH <sub>3</sub>	16.6	58.4%

## B.II.Salt Metatheses of Anion Precursors

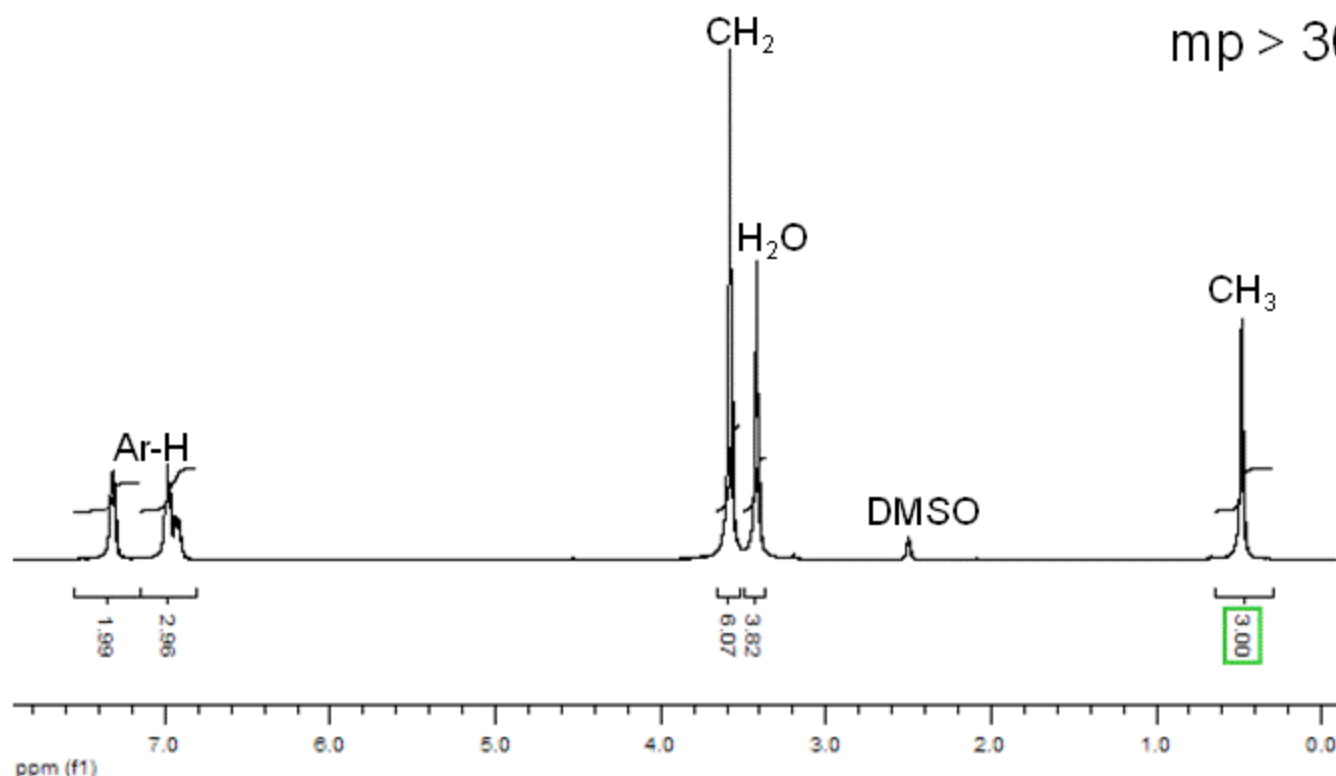
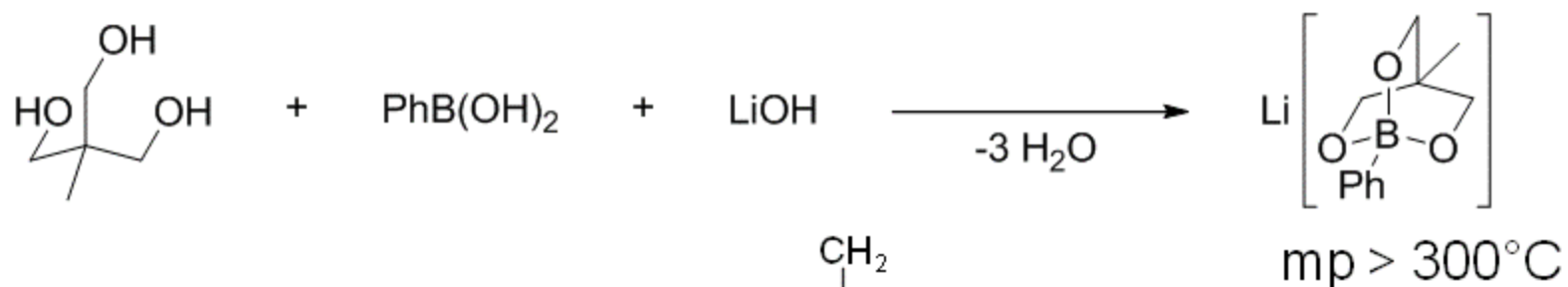


## B.III. Salt Metatheses of Anion Precursors



Upon addition of various boron reagents to the different salt precursors, decomposition was observed immediately, even at low temperatures. The decomposition product, phenylphosphinic acid, is formed via loss of CO<sub>2</sub>.

# C.I. Synthesis of $\text{Li}[\text{PhB}((\text{OCH}_2)_3\text{CCH}_3)]$

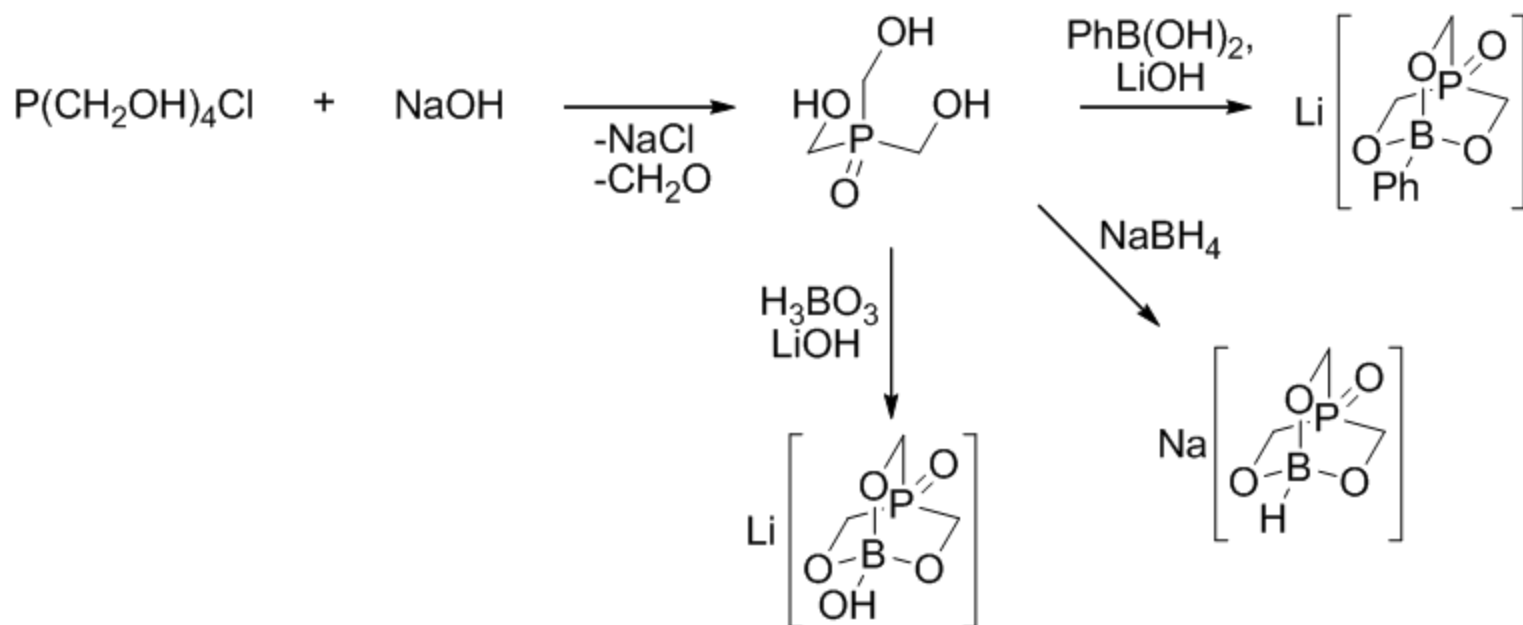


*Angew. Chem. Int. Ed.* **2008** 47, 928

Material is known but its electrochemical are yet to be determined



## C.II. Synthesis and Reactivity of TMPO



*J. Am. Chem. Soc.* **1963** 85, 79

When Li[PHB((OCH<sub>2</sub>)<sub>3</sub>P=O)] (TMPO) was reacted with phenyl boronic acid under the same reaction conditions as the carbon analog, no reaction was observed. TMPO is insoluble in toluene and a change in solvent has shown promising initial results. Other boron starting materials are being investigated with positive results.

## D. Spectroelectrochemical Cell for in situ Attenuated Total Reflection FTIR of Highly Reactive Interfaces

### Main Attributes:

Cell is filled directly from septum type electrolyte container without need of using a glove box.

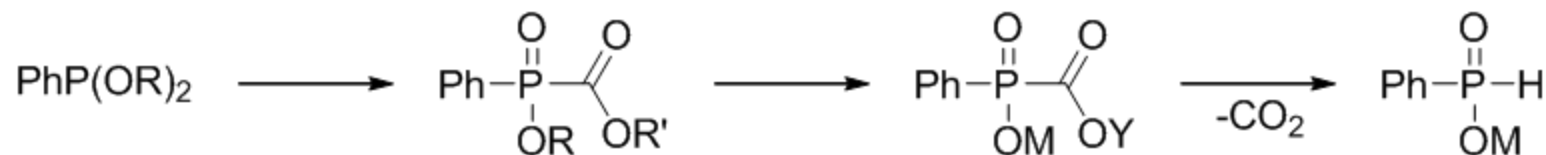
Anode is charged in situ avoiding exposure to the atmosphere in the glove box.

All operations within the cell are performed with custom made leak free manipulators including approach of the working electrode to the diamond window of the ATR-FTIR attachment.

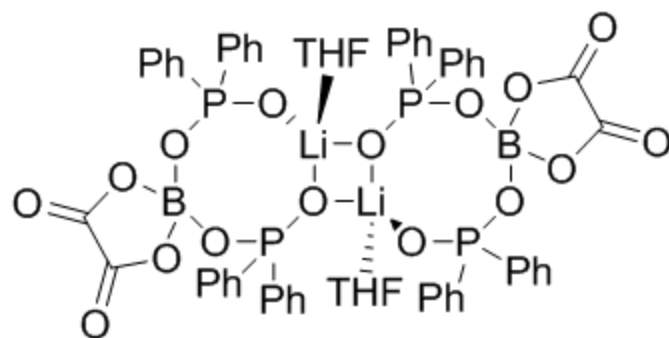


# Conclusions

- Several anion precursors and their corresponding alkali metal salt products were synthesized in moderate yields from inexpensive materials. However, these products undergo a loss of  $\text{CO}_2$  when reacted with a variety of boron reagents.



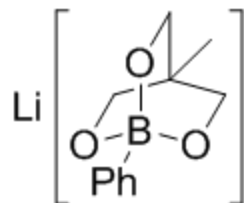
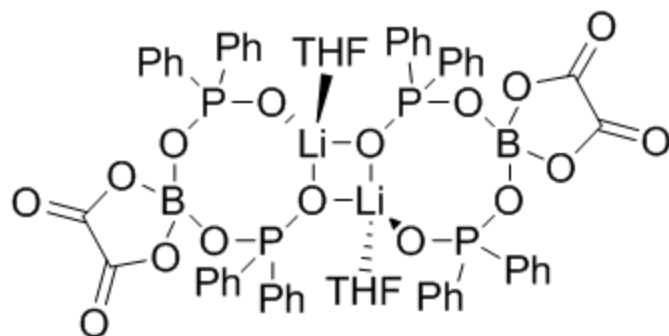
- $\text{Li}[\text{OxB(OP)}_2]$  was successfully synthesized from the dehydration of oxalic acid and diphenylphosphinic acid with boric acid. This compound displays water and air stability as well as no visible decomposition in propylene carbonate at elevated temperatures.



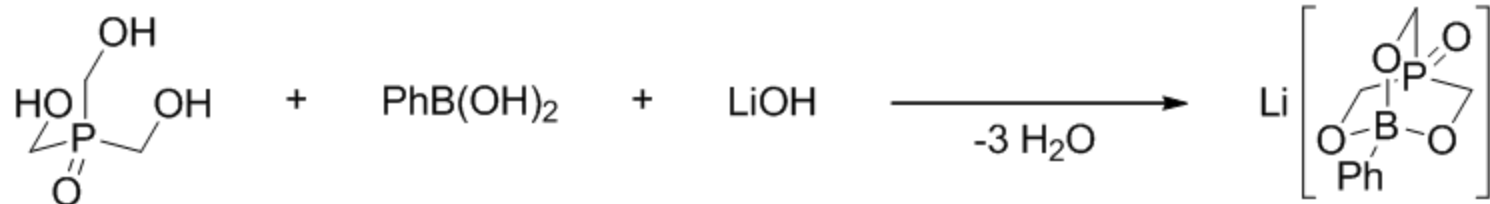
- The lithium analog of triol phenylborate has been isolated. Preparation of the phosphorus derivative has been recently undertaken.

# Future Work

- Scale up of  $\text{Li}[\text{OxB}(\text{OP})_2]$  and replacement of the phenyl rings from  $\text{Li}[\text{OxB}(\text{OP})_2]$  for lower molecular weight substituents
- Exploring the electrochemistry of  $\text{Li}[\text{OxB}(\text{OP})_2]$  and  $\text{Li}[\text{PhB}((\text{OCH}_2)_3\text{CCH}_3)]$



- Synthesis of cyclic borate phosphine oxides



# Collaborations with Other Institutions

Arrangements have been made with:

- i. Dr. Alexander Morgan of the Dayton University Research Institute in Dayton, OH has agreed to determine the inherent flammability of materials developed under this program by consumption calorimetry using their unique microscale combustion calorimeter. This organization is outside the VT program.
- ii. Novolyte Technologies of Independence, OH to conduct coin cell tests using materials developed under this program in combination with their specialty chemicals in actual coin cells. This company is outside the VT program.

# Proposed Future Work

- Continue design, synthesis, purification and full characterization of FRIONS and other safety enhancing bifunctional materials aimed at building knowledge base toward the rational search of materials that will enhance abuse tolerance without affecting adversely overall battery performance.
- Attention will be focused only on materials displaying optimized characteristics even if obtained in small yields leaving development of more effective synthetic routes to a second stage.
- Recent experimental results toward the synthesis of a new class of materials appear to be encouraging enough to warrant further research.
- Should a class of materials be found to be inferior to an earlier developed class, any further efforts will be abandoned and focus will be centered on the design and synthesis of new classes of yet unexplored materials.
- The results obtained with in situ ATR-FTIR will point to ways to improve the sensitivity and specificity of the instrumentation developed.
- Scale up of  $\text{Li}[\text{OxB(OP)}_2]$  and synthesis of functionalized derivatives

# Summary

- A 1<sup>st</sup> generation FRION,  $\text{Li}[\text{OxB}(\text{OP})_2]$ , was successfully synthesized from inexpensive, commercially available substrates and characterized using a wide array of techniques.
- $\text{Li}[\text{OxB}(\text{OP})_2]$  was shown to have excellent thermal stability in propylene carbonate for extended periods of time. Moreover, thermal gravimetric analysis data supports the relatively high stability of  $\text{Li}[\text{OxB}(\text{OP})_2]$ .
- The synthesis of cyclic borate-phosphine oxides is underway as a means of generating another entry point for the formation of FRIONs containing phosphorus and boron moieties.
- A unique spectroelectrochemical cell for performing in situ ATR-FTIR measurements of highly reactive systems was designed and constructed
- Additionn of  $\text{Li}[\text{OxB}(\text{OP})_2]$  to conventional electrolyte does not affect adversely battery performance.

