Metal Complexes Containing High Nitrogen Content Poly(tetrazolyl)metalate Ligands

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Workshop on "Synthesis of Advanced Energetic Materials-The Path Forward"
April 3-5, 2011

DEPARTMENT OF CHEMISTRY

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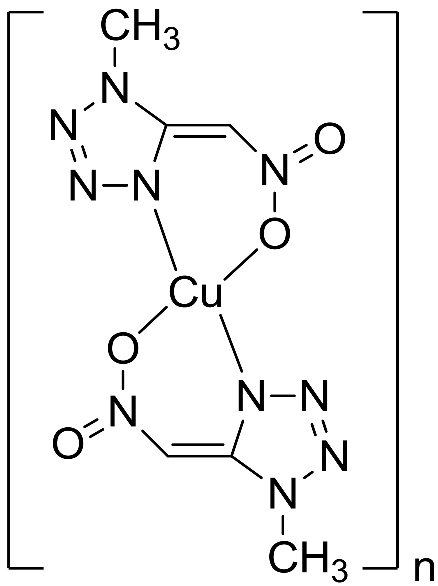
Outline

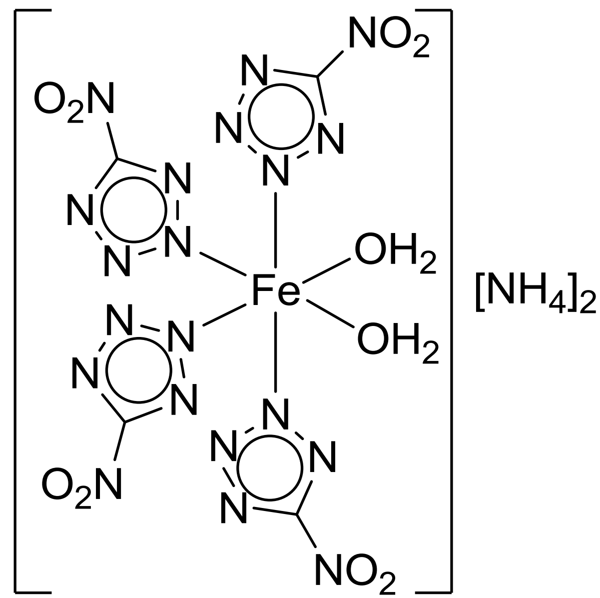
- Introduction
- Metal poly(tetrazolyl)borate ligands
- Poly(pyrazolyl)aluminate ligands
- Poly(tetrazolyl)aluminate ligands
- Summary and conclusions

Our Overall Goal: Prepare metal complexes containing as many nitrogen atoms as possible

Metal-Based Energetic Materials



1-methyl-5-nitriminotetrazolate



nitrotetrazolate

- Use of non-toxic or low toxicity metal ions such as copper, zinc, iron, and others → *green explosives*
- Tetrazole-based ligands have been used due to high endothermicity, high nitrogen contents, tunable sensitivity, and low smoke formation

Klapötke, T. M. *Eur. J. Inorg. Chem.* **2007**, 4743-4750
Hiskey, M. A. *PNAS* **2006**, *103*, 5409-5412

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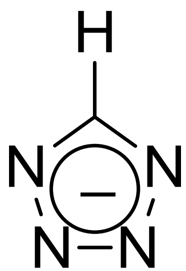
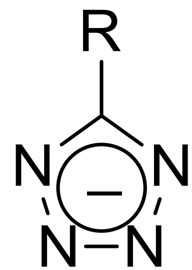
Equivalents of N_2 per Negative Charge



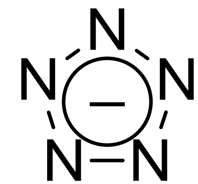
tetrazolate

2 N_2/negative charge



R = nitrogen-based

>2 N_2/negative charge



pentazolate

2.5 N_2/negative charge

- Ligand charge determines stoichiometry in metal complexes
- Highest possible nitrogen content desired
- Tetrazolate and even pentazolate have modest nitrogen contents
- Nitrogen-based carbon substituents in tetrazolates can boost nitrogen and gaseous product contents

Klapötke, T. M. *Angew. Chem. Int. Ed.* **2008**, *47*, 3330-3347
Christe, K. O. *Angew. Chem. Int. Ed.* **2002**, *41*, 3051-3054

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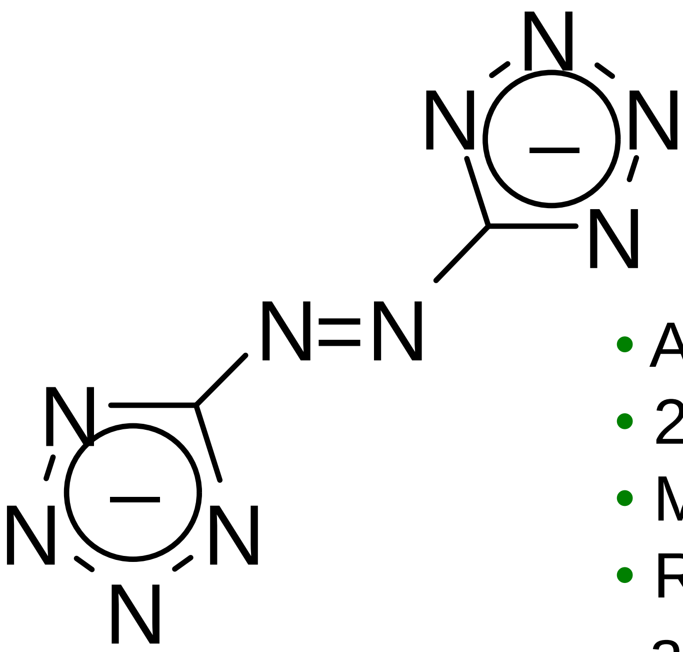
Azobis(tetrazolate) Complexes



- A frontier of nitrogen-rich ligands
- 2.5 N_2/negative charge
- Metal salts known
- Relatively stable when hydrated; shock and friction sensitive when anhydrous

Klapötke and Shreeve Laboratories
Inorg. Chem. **2009**, *48*, 9918-9923
Eur. J. Inorg. Chem. **2002**, *4*, 834-845
Chem. Mater. **2008**, *20*, 1750-1763

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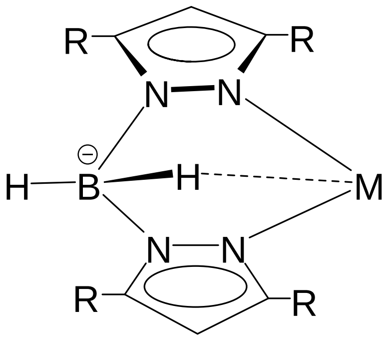
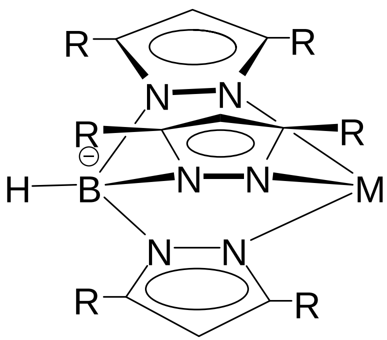
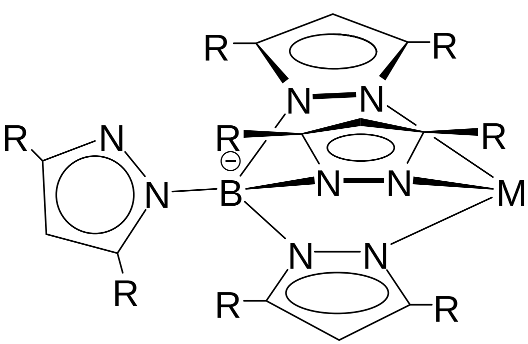
Poly(pyrazolyl)borate Complexes



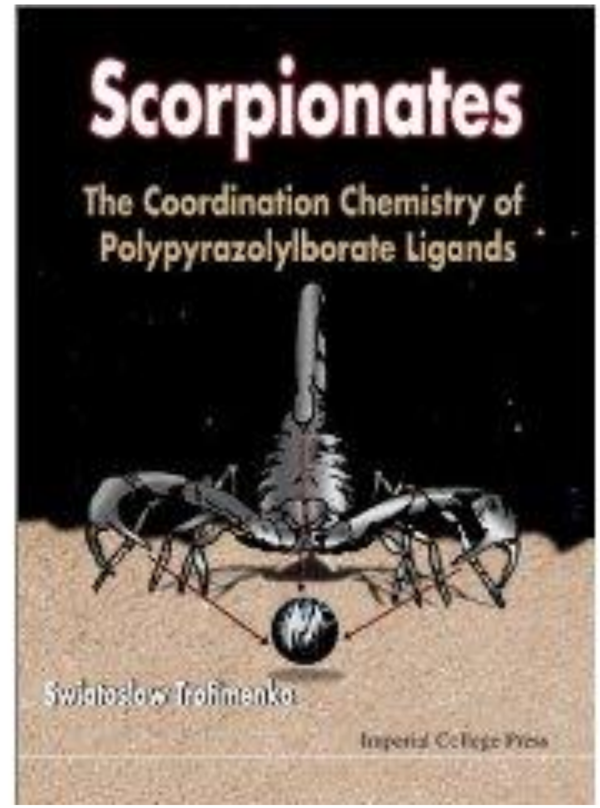
Bis(pyrazolyl)borate (Bp)



Tris(pyrazolyl)borate (Tp)



Tetrakis(pyrazolyl)borate



ISBN-13: 978-1860941726

>3000 crystal structures of Bp and Tp complexes

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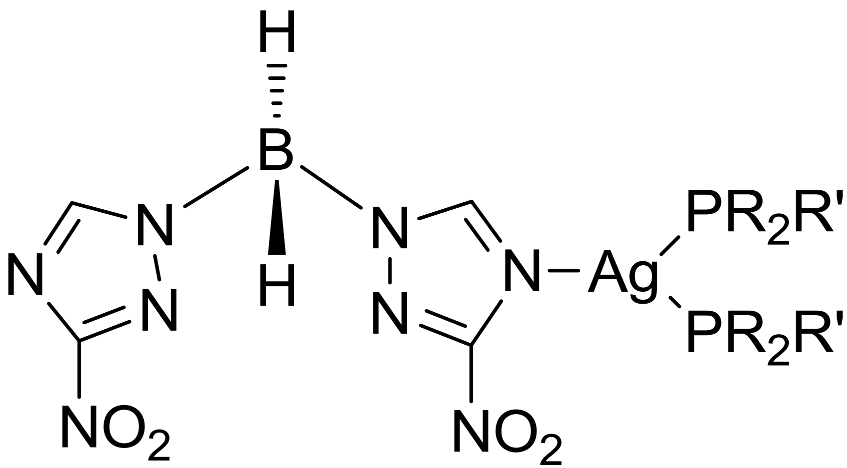
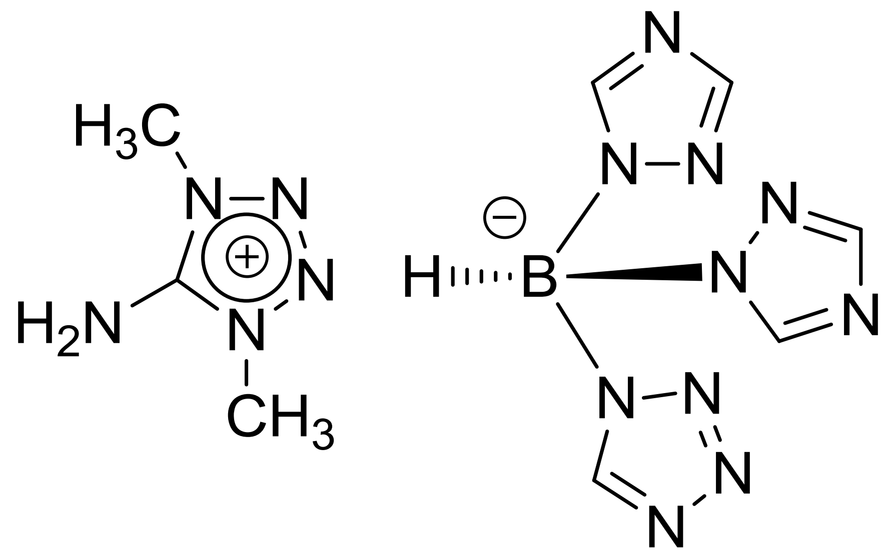
Energetic Tris(1,2,4-triazoyl)borate-Containing Materials





- Bis- and tris(1,2,4-triazolyl)borate ligands are well known
- 1,2,4-triazole heat of formation = 109 kJ/mol
- Nitro groups or energetic cations affords energetic species

Shreeve, J. M. *Organometallics* **2007**, *26*, 1782-1787
Santini, C. *Inorg. Chim. Acta* **2007**, *360*, 2121-2127

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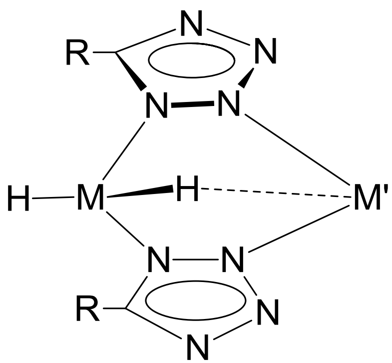
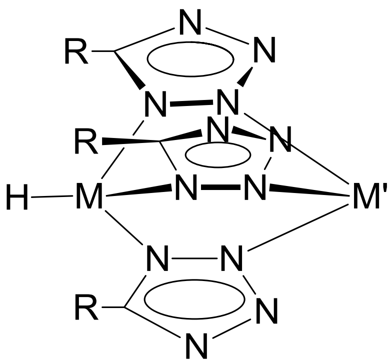
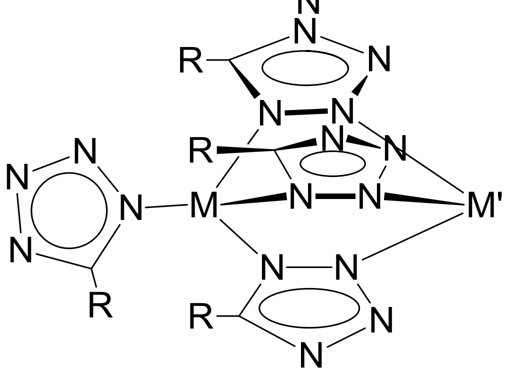
What About Poly(tetrazoyl)metalate Complexes (M = B, Al)?



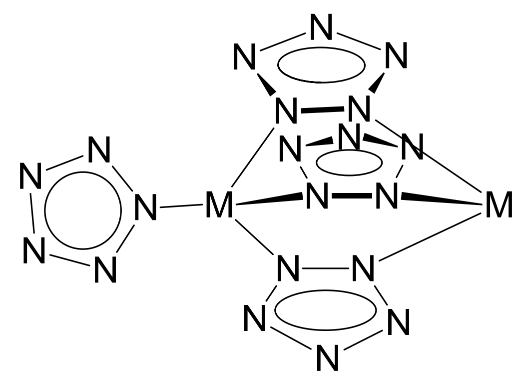
Bis(tetrazolyl)borate
4 N_2/negative charge



Tris(tetrazolyl)borate
6 N_2/negative charge

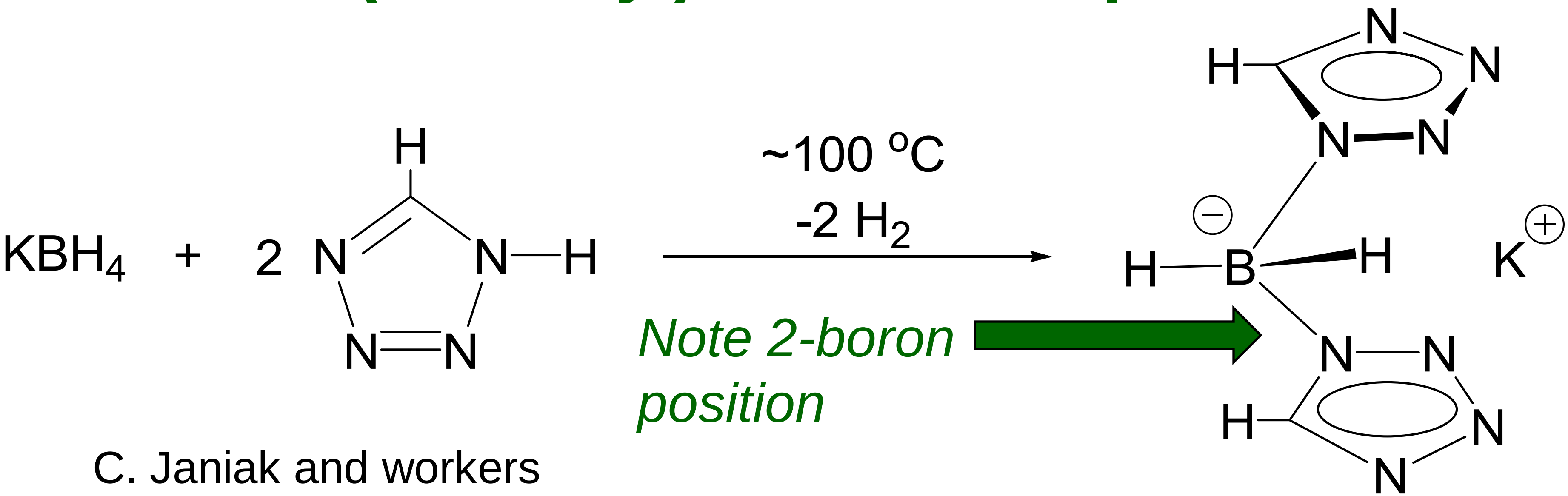


Tetrakis(tetrazolyl)borate
8 N_2/negative charge



Tetrakis(pentazolyl)borate
10 N_2/negative charge

Bis(tetrazoyl)borate Complexes



74-83%

C. Janiak and workers

M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II)

Z. Naturforsch. **1993**, *48b*, 394-396

J. Chem. Soc., Chem. Commun. **1994**, 545-547

Chem. Ber. **1995**, *128*, 323-328

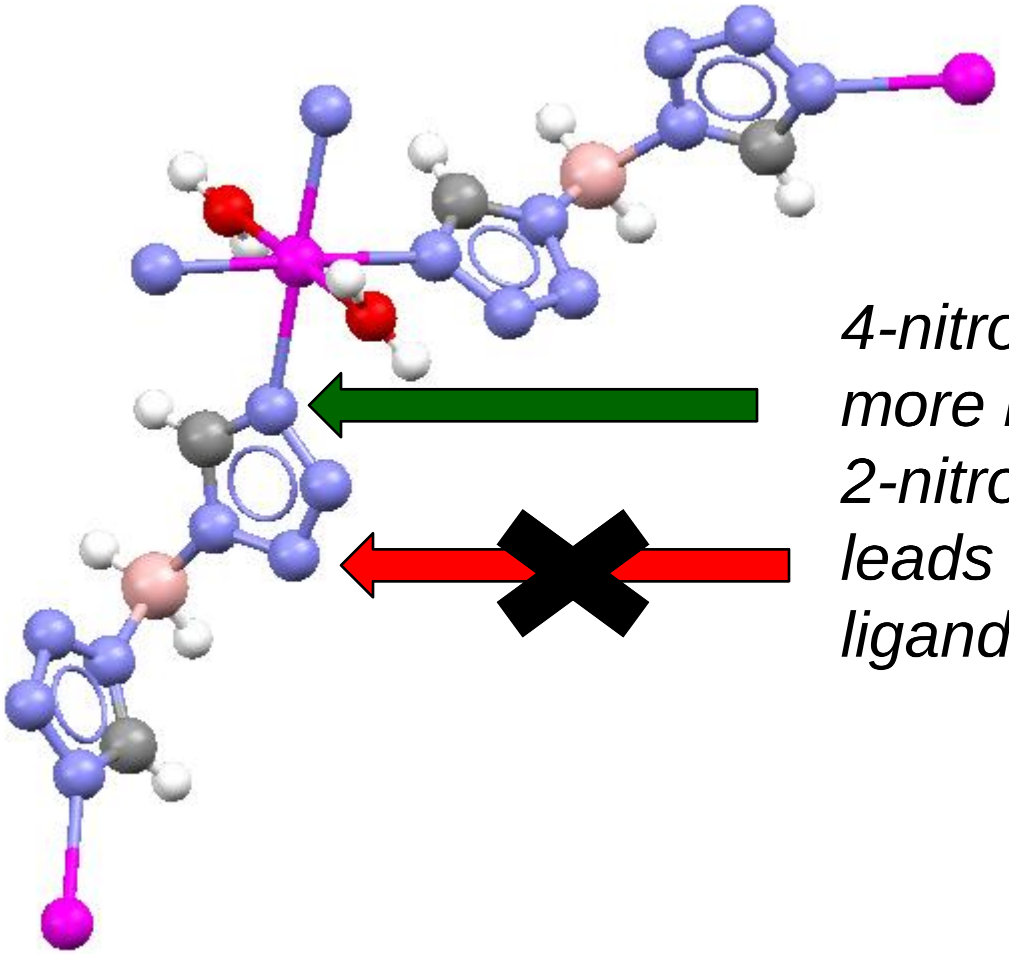
Chem. Eur. J. **1995**, *1*, 637-644

5-aminotetrazolyl analogs:

T. J. Groshens

J. Coord. Chem. **2010**, *63*, 1882-1892

Crystal Structures of $M(BH_2(CHN_4)_2)_2(H_2O)_2$ (M = Mn, Fe, Co, Zn, Cd)



4-nitrogen atom more basic than 2-nitrogen atom; leads to bridging ligands

Janiak, C. *Chem. Ber.* **1995**, *128*, 323-328

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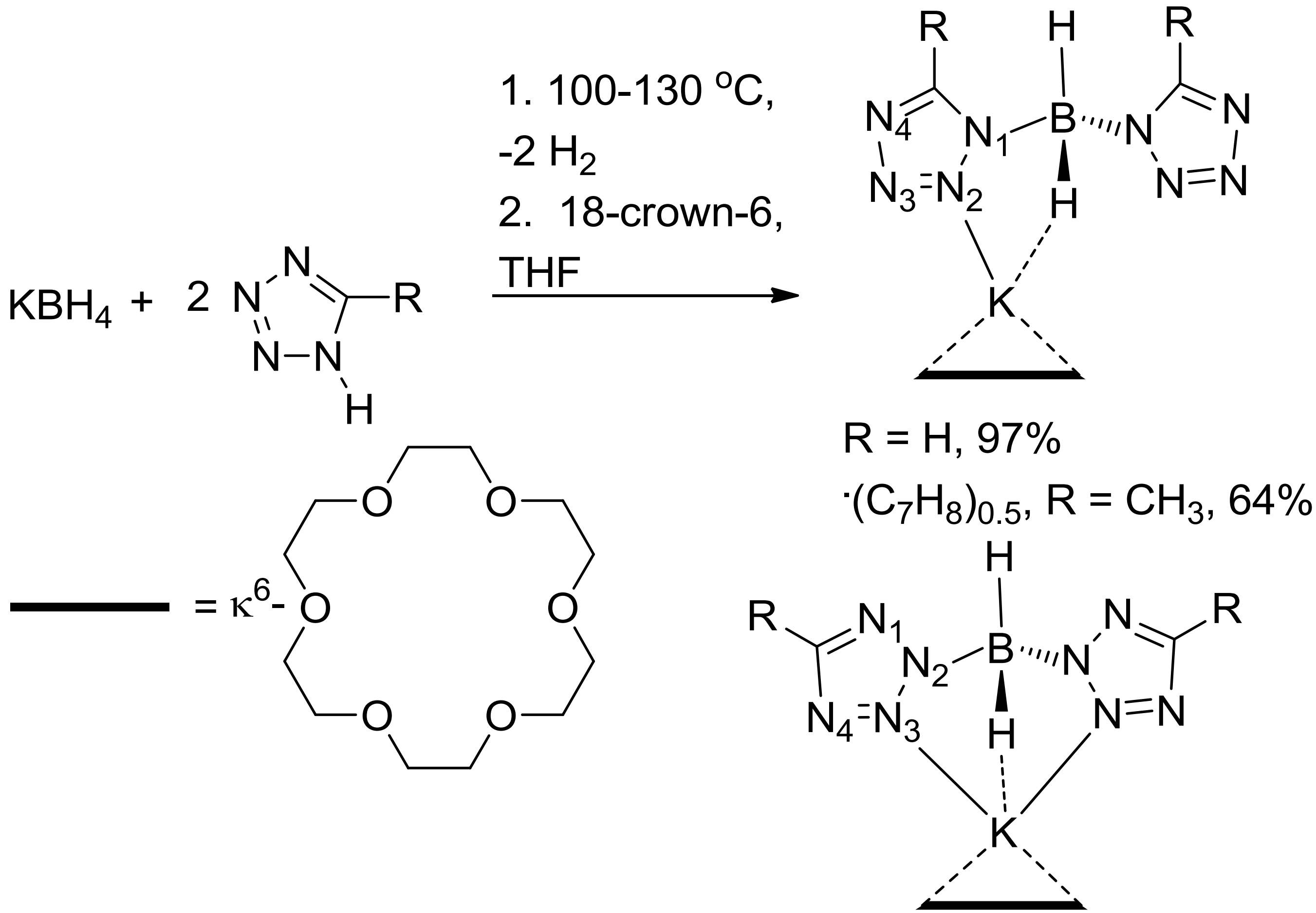
Synthesis of $[K(18\text{-crown-6})]^+$ Complexes Containing Bis(tetrazolyl)borate Ligands



R = $N(CH_3)_2$, 77%
R = $N(CH(CH_3)_2)_2$, 80%

Lu, D.; Winter, C. H.
Inorg. Chem. **2010**, *49*, 5795-5797

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Comments

- 18-Crown-6 complexes synthesized to simplify the coordination chemistry and focus on ligand bonding modes
- Crystal structures determined for all four complexes
- Like Janiak's complexes, bis(tetrazolyl)borate and bis(methyltetrazolyl)borate complexes show B-N formation to the 2-nitrogen atoms and exhibit bridging coordination modes
- By contrast, bis(dimethylaminotetrazolyl)borate and bis(diisopropyltetrazolyl)borate complexes show B-N formation to the 3-nitrogen atoms and exhibit chelating coordination modes

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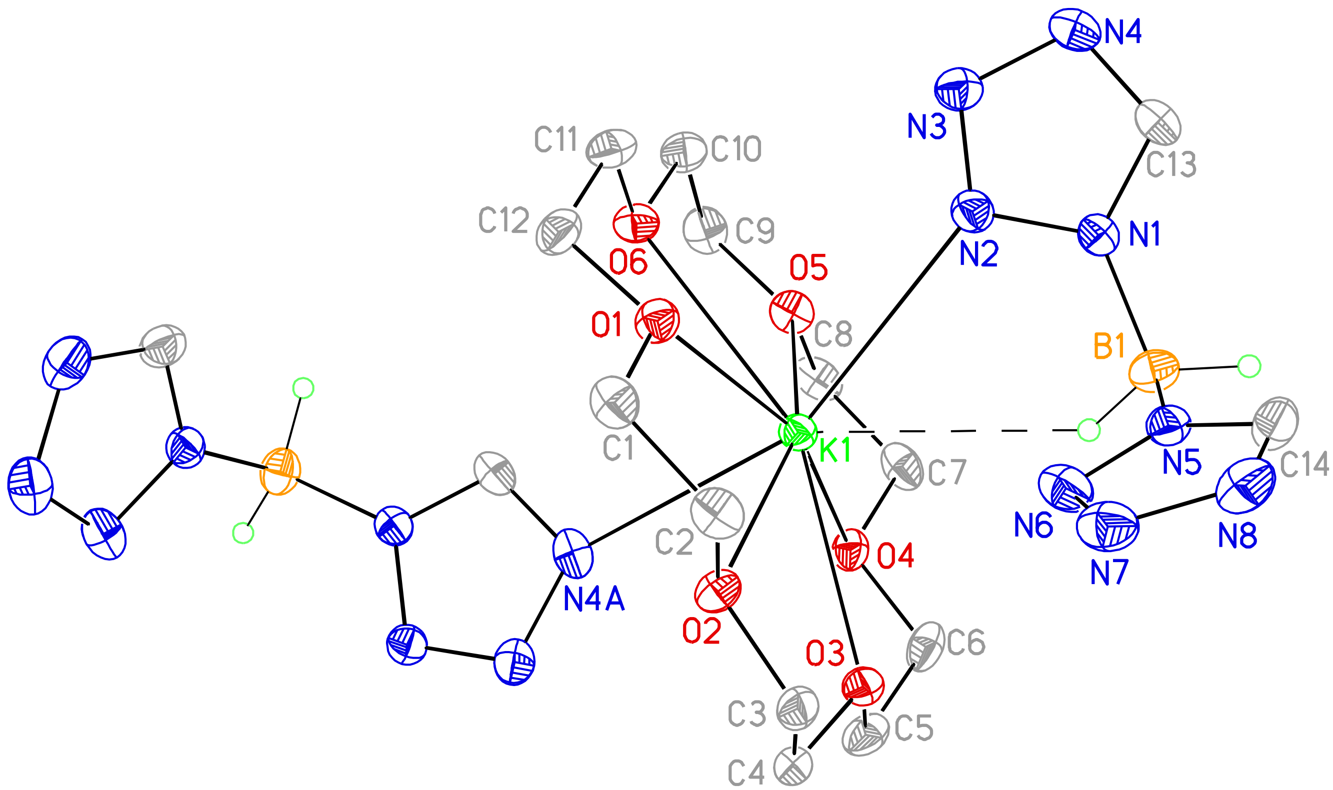
Crystal Structure of $[K(BH_2(HCN_4)_2)(18\text{-crown-6})]$



- Polymeric structure through K-N bonds to N(2) and N(4)’
- Coordination to N(2) (N_2) not seen in Janiak’s complexes
- *B-N bonds to tetrazolyl N_1 atoms*

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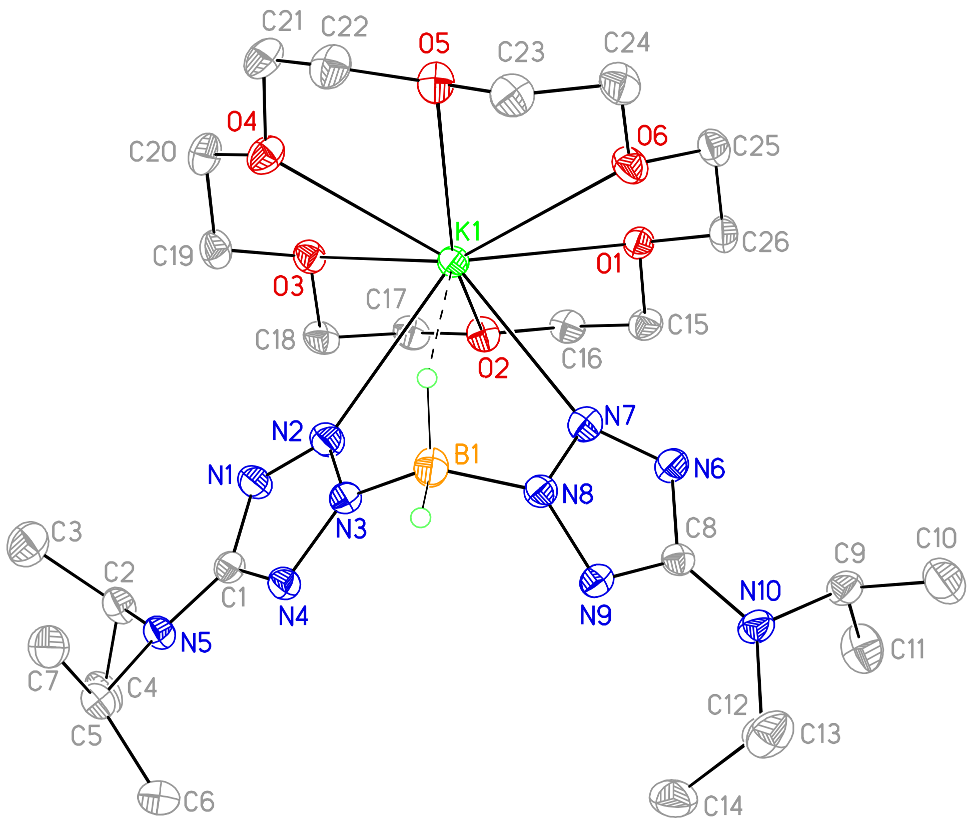
Crystal Structure of $[K(BH_2(NiPr_2CN_4)_2)(18\text{-crown-6})]$



- Monomeric structure through K-N(2), K-N(7), and K-HB bonds
- *B-N bonds form to tetrazolyl N_2 atoms*
- Isomeric B-N bonds probably steric in origin

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Comments on Structures

- Bridging ligands adopt κ^2-N,H- and μ_2-N,N-coordination modes
- Chelating ligands adopt κ^3-N,N,H-coordination modes
- The bridging ligand modes do a poor job of saturating the coordination spheres of metals, which requires non-energetic neutral ligands such as water to achieve saturation and stability
- Chelating κ^3-N,N,H-coordination mode does a much better job of saturating the metal coordination spheres, which should reduce or eliminate coordination of non-energetic neutral ligands
- *The coordination chemistry of the chelating κ^3-N,N,H-ligands should resemble that of well developed bis(pyrazolyl)borate ligands*
- *Many potentially energetic complexes possible*

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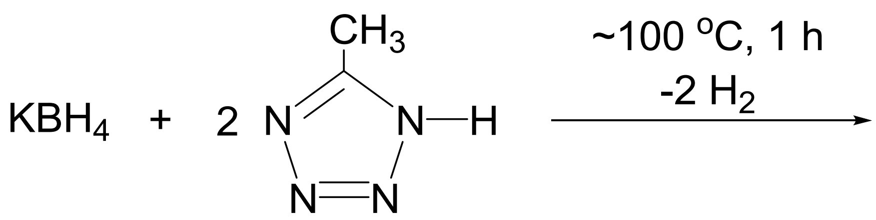
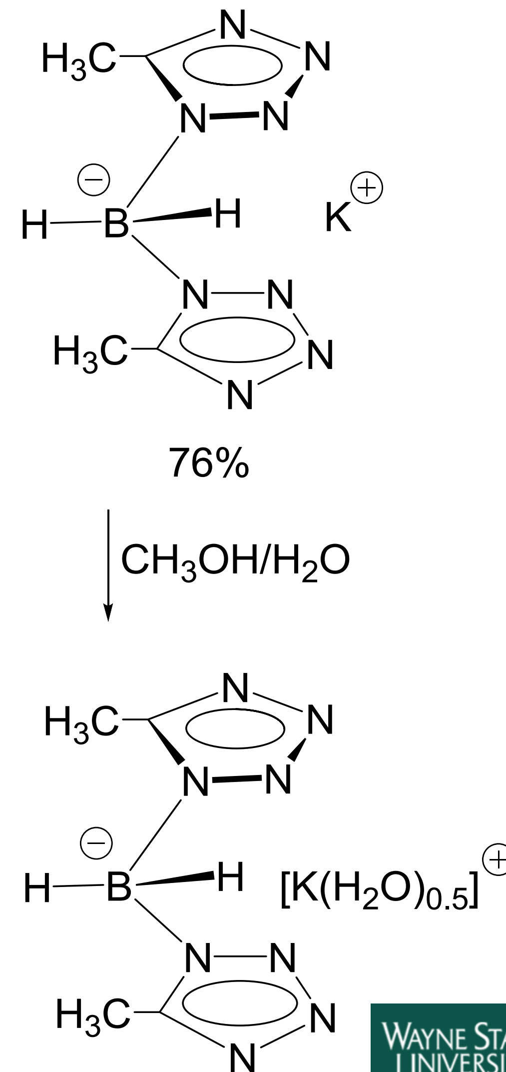
Energetic Properties

- None is highly sensitive, probably due to lack of electron-withdrawing groups on the tetrazolyl core carbon atoms and the non-energetic 18-crown-6 ligands
- All melt without decomposition in 2 ºC ranges between 111 and 158 ºC; stable to >250 ºC by TGA
- No explosions upon being struck hard with a hammer on an aluminum block
- Deflagrated with little smoke upon burning in a Bunsen burner flame
- Sparks from a Tesla coil did not lead to explosion; no explosion upon being scraped across 200-grit emery cloth with a spatula

Synthesis of $K(BH_2(CH_3CN_4)_2)$





- KBH_4 and methyl tetrazole were ground together and then heated as a solid mixture
- D. Lu, M.J. Heeg, C.H. Winter, manuscript in preparation
- Other substituted derivatives also prepared and characterized
- Energetic properties same as the 18-crown-6 complex

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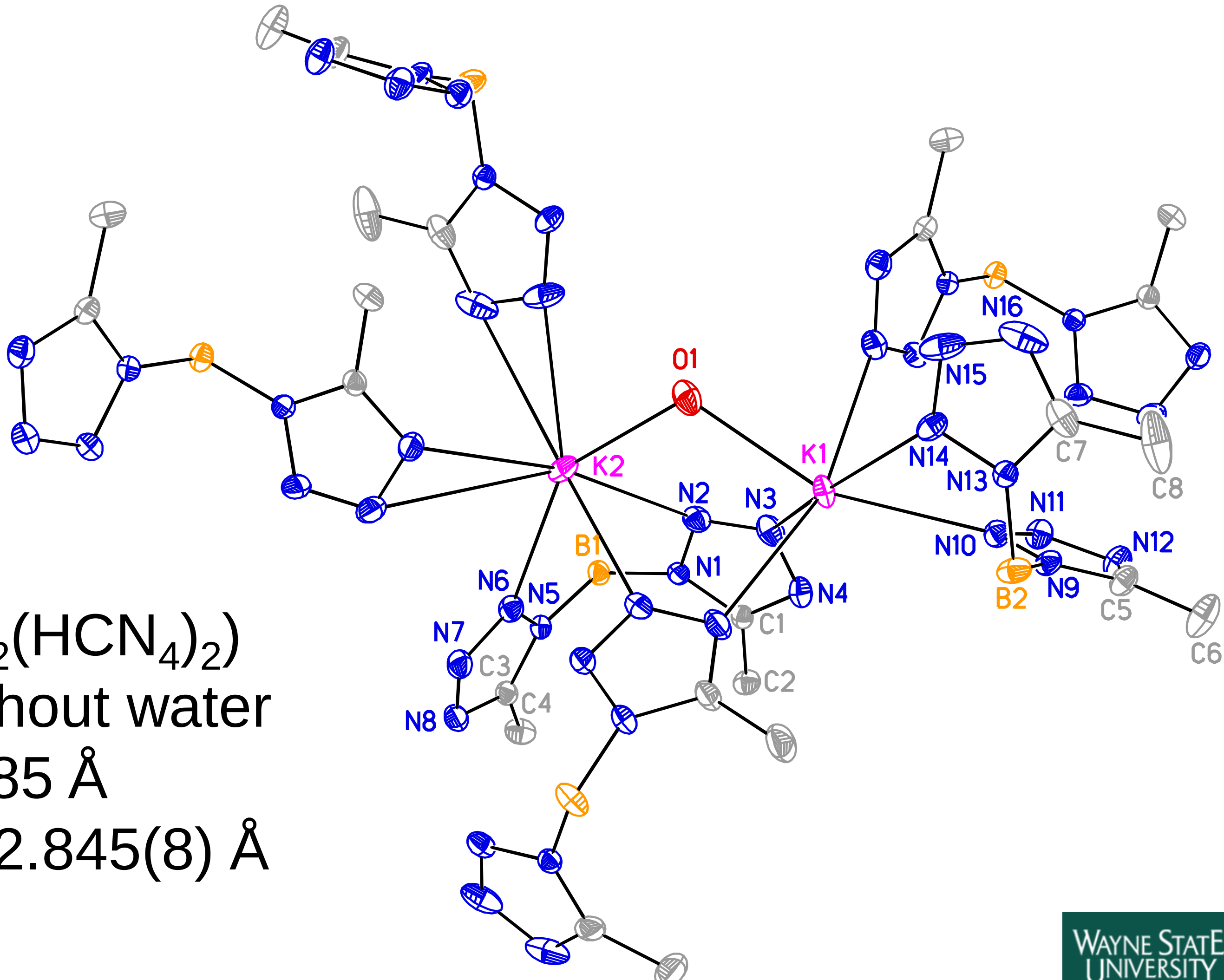
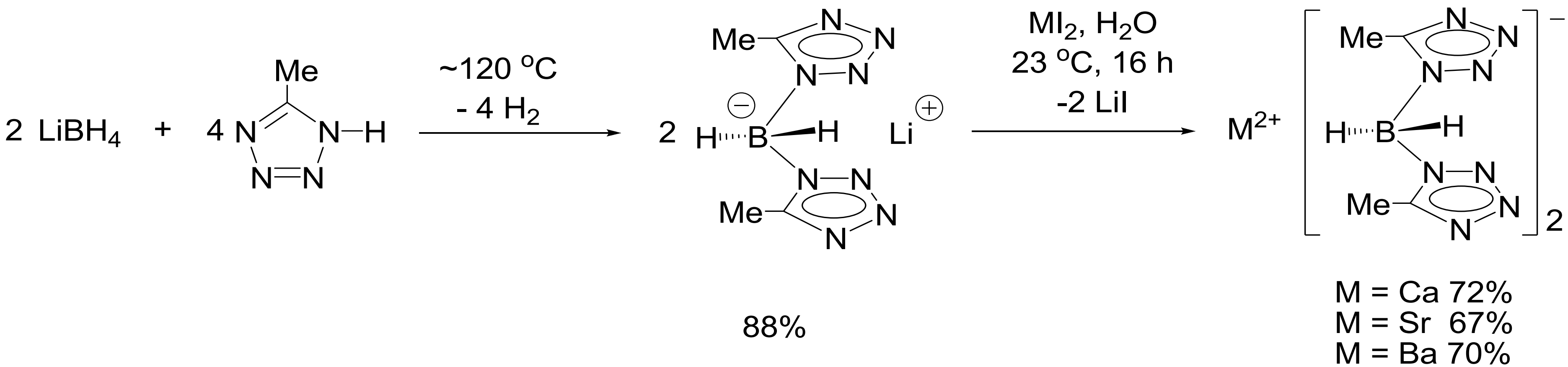
X-Ray Crystal Structure of $K[BH_2(CH_3CN_4)_2]\bullet(H_2O)_{0.5}$



- Janiak's $K(BH_2(HCN_4)_2)$ crystallized without water
- K-N 2.804-2.885 Å
- K-O 2.689(8), 2.845(8) Å

Synthesis of Group 2 Metal Bis(5-methyltetrazolyl)borate Complexes



- Lithium salt was used to carry out the metathesis with group 2 metal iodides to form the corresponding bis(tetrazolyl)borates; LiI is soluble in THF with 5% water added, whereas the complexes are not
- $Ca[BH_2(CH_3CN_4)_2]_2\bullet(H_2O)_4$, $Sr[BH_2(CH_3CN_4)_2]_2\bullet(H_2O)_5$, and $Ba[BH_2(CH_3CN_4)_2]_2\bullet(H_2O)_5$ were structurally characterized
- The complexes are air stable and insensitive toward shock, friction, and electrical discharge, but deflagrated upon burning with bright flame; *deflagration more violent than K^+ salts*
- D. Lu, C.H. Winter, manuscript in preparation

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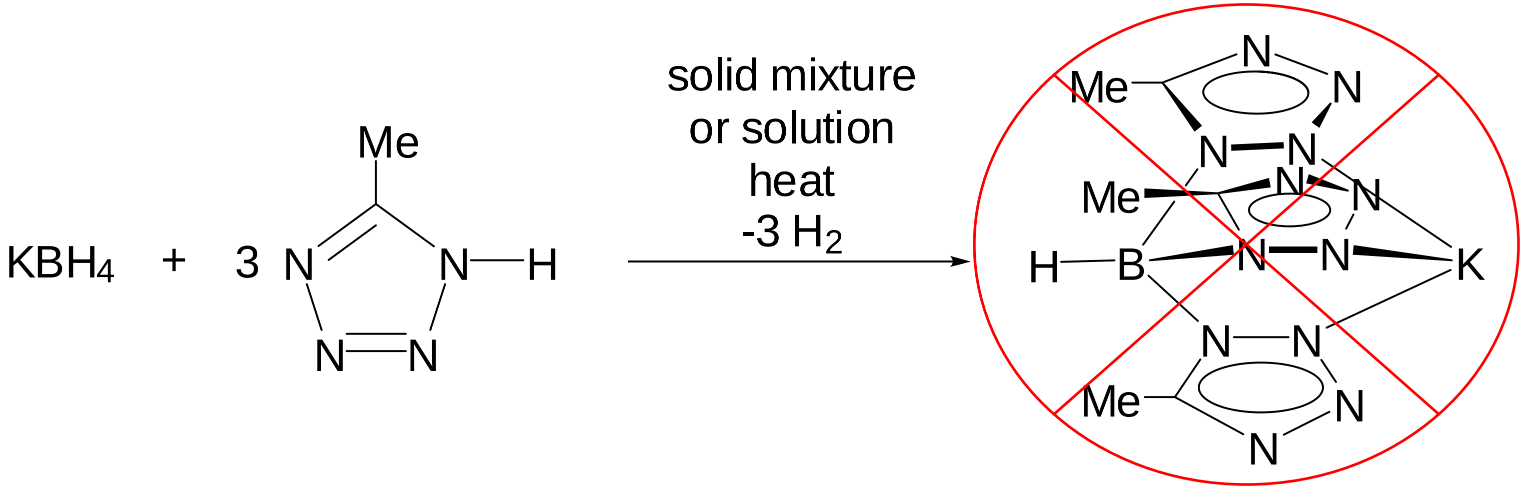
Attempts to Prepare Tris(tetrazoyl)borate Ligands by Thermolysis



- Heating solid and solution mixtures tried under a variety of conditions
- *$K[BH_2(CH_3CN_4)_2]\cdot(H_2O)_{0.5}$ was isolated in all cases*
- Probably requires higher temperatures, but tetrazoles decompose between 170-200ºC
- *Experiments are ongoing*

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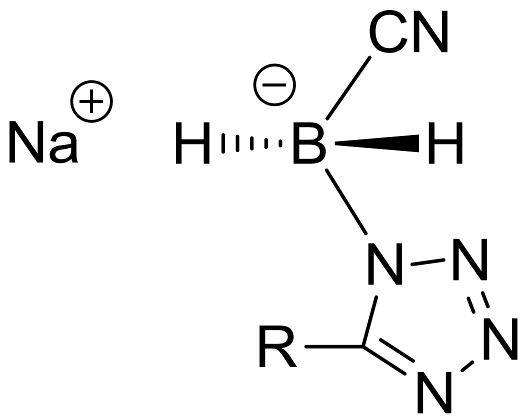
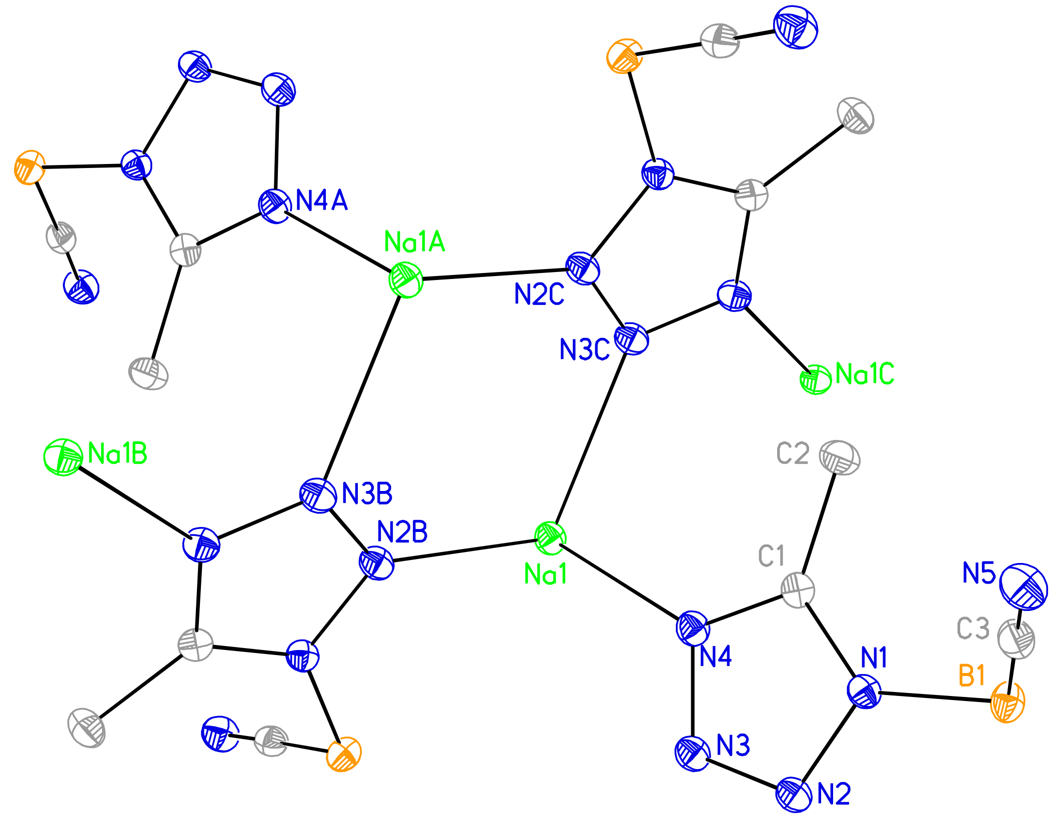
Other Related Complexes



R = H, CH_3



- Only one tetrazolyl group incorporated under all conditions
- Polymeric, metalorganic framework structure!
- $[BH_3(N_3)]^-$ has been claimed in the patent literature
- D. Lu, C.H. Winter, manuscript in preparation

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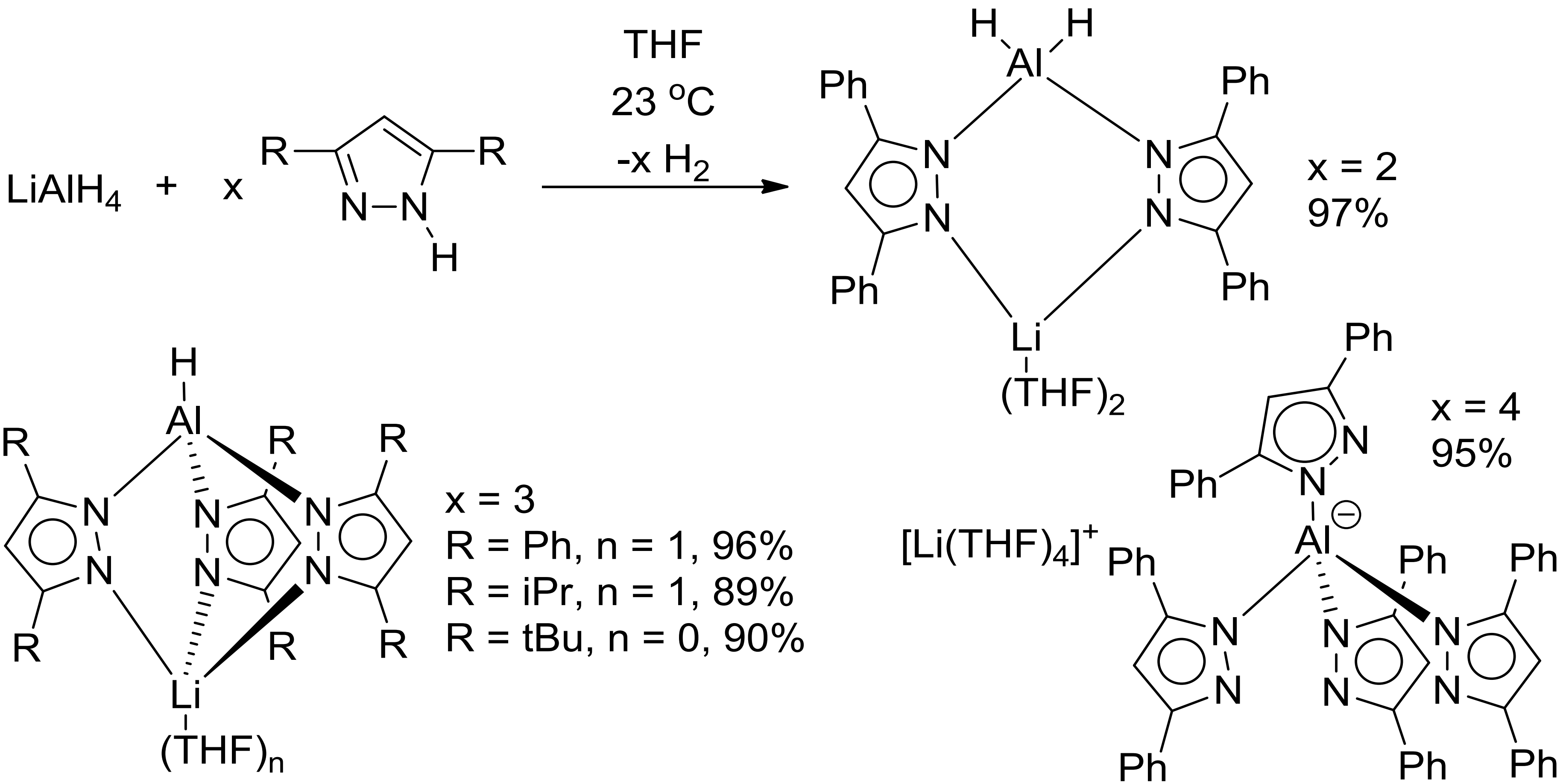
Poly(pyrazolyl)aluminate Complexes



- C.J. Snyder, M.J. Heeg, C.H. Winter, manuscript in preparation
- These ligands have not been previously reported

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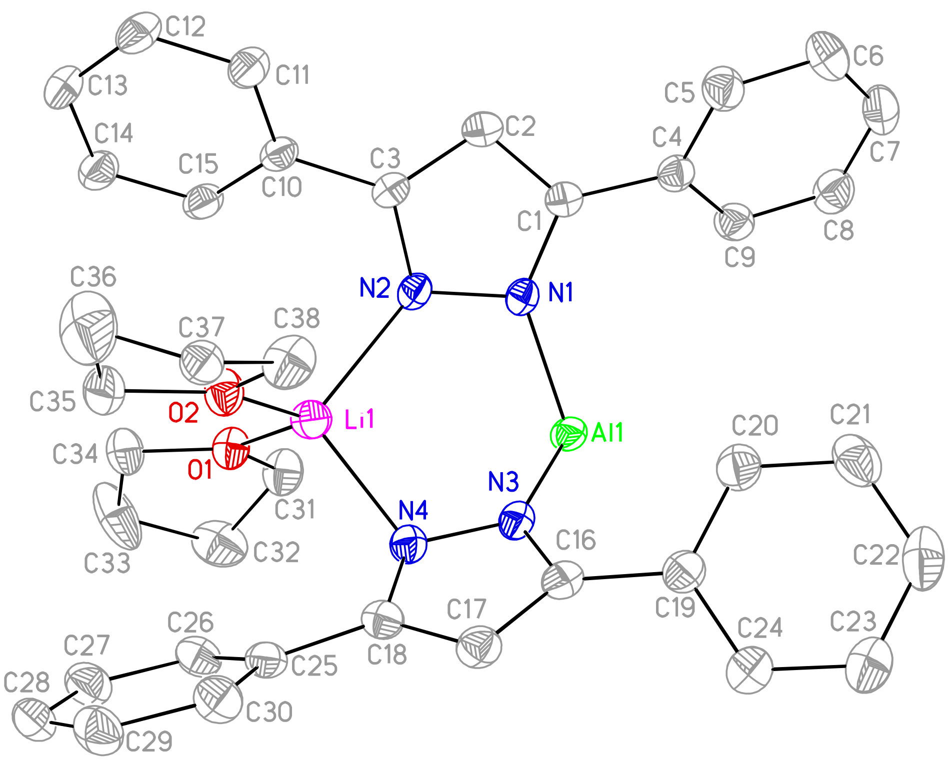
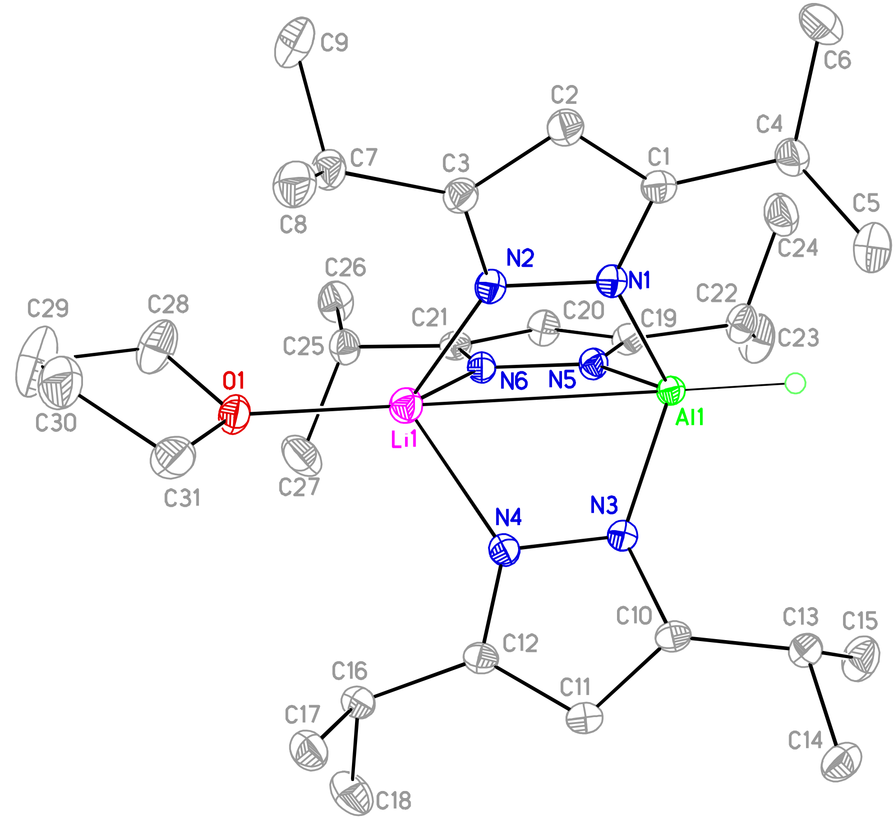
X-Ray Crystal Structures





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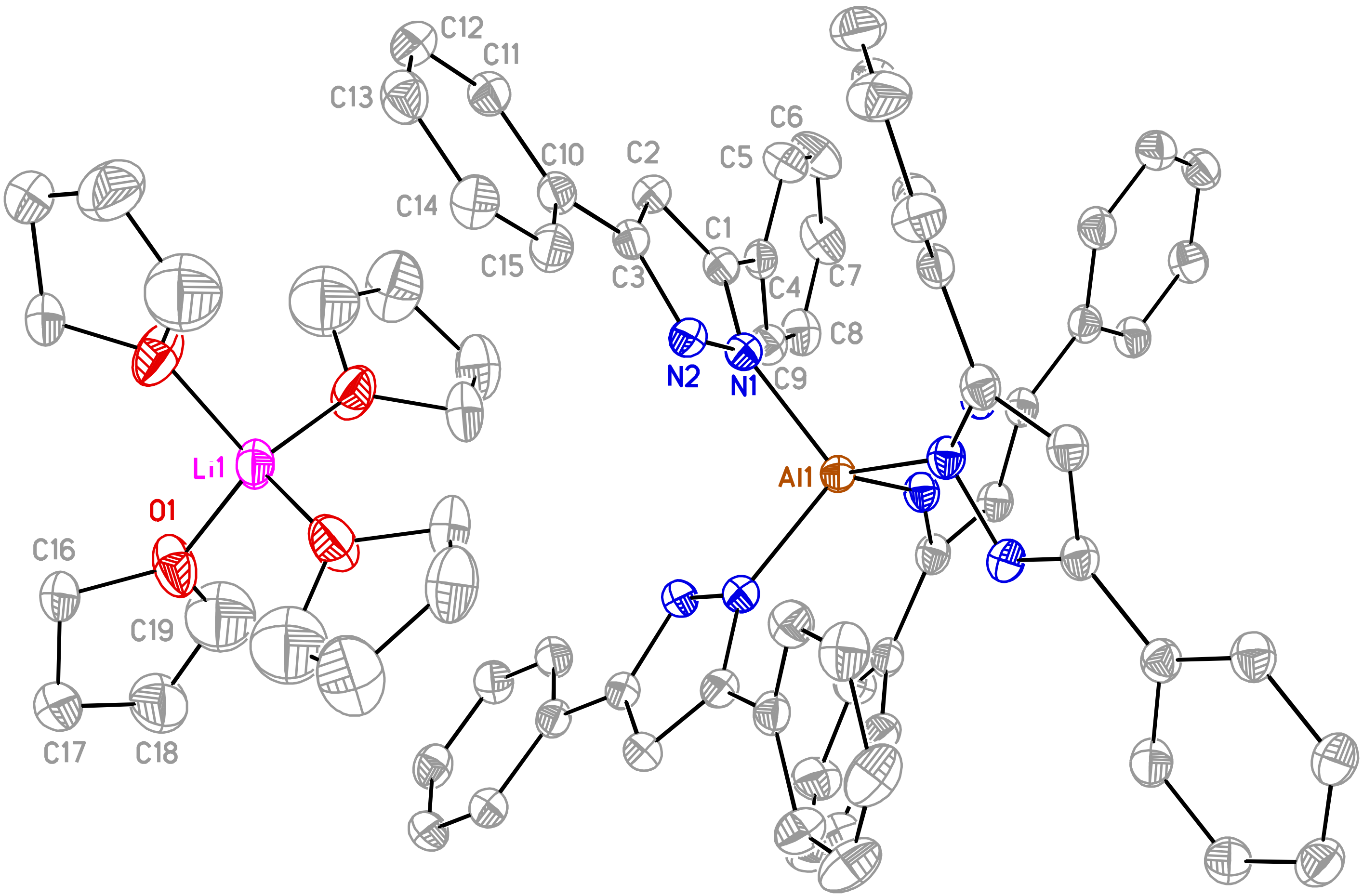
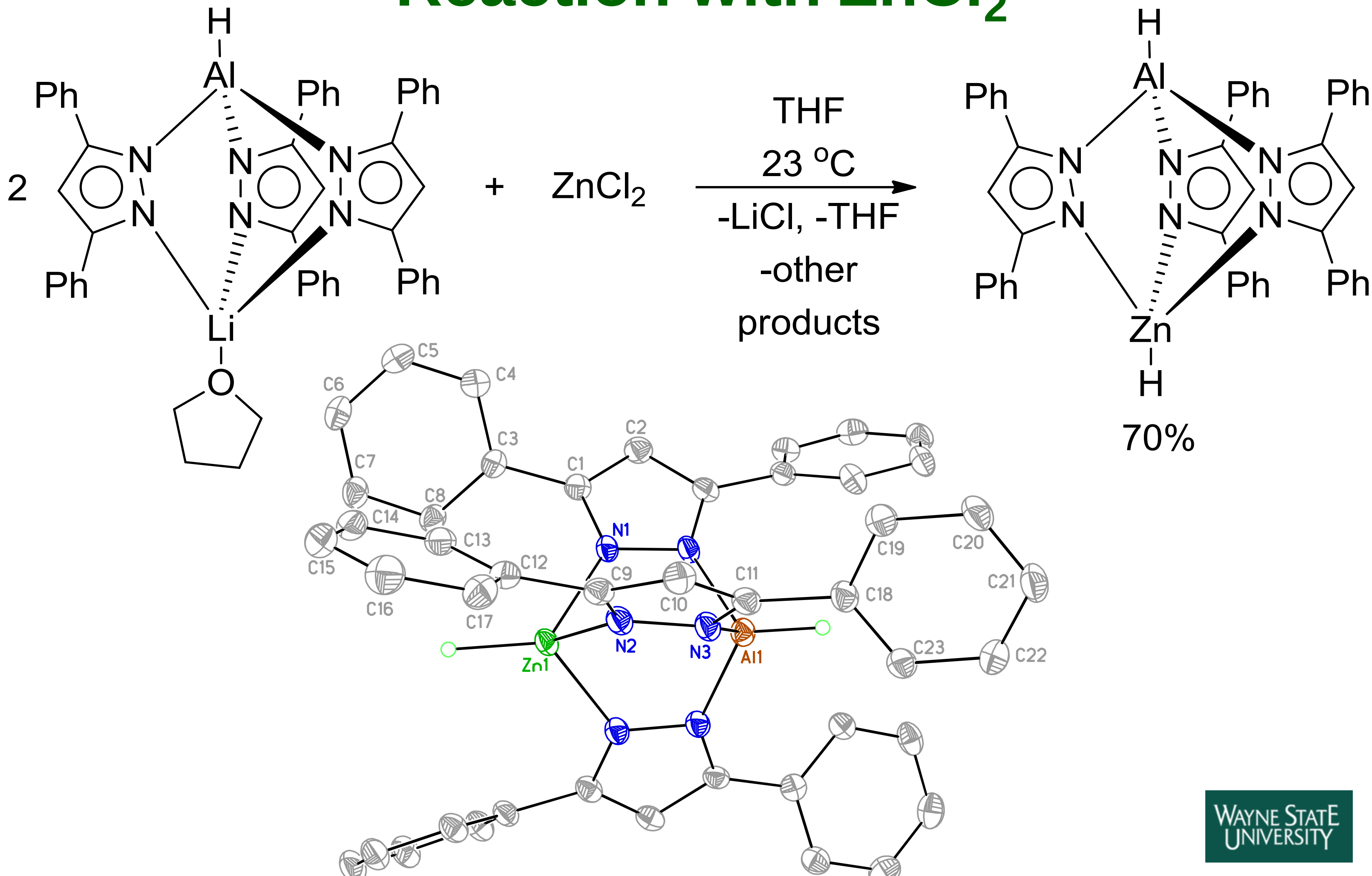
X-Ray Crystal Structure



Ligand and HydrideTransfer Reaction with $ZnCl_2$



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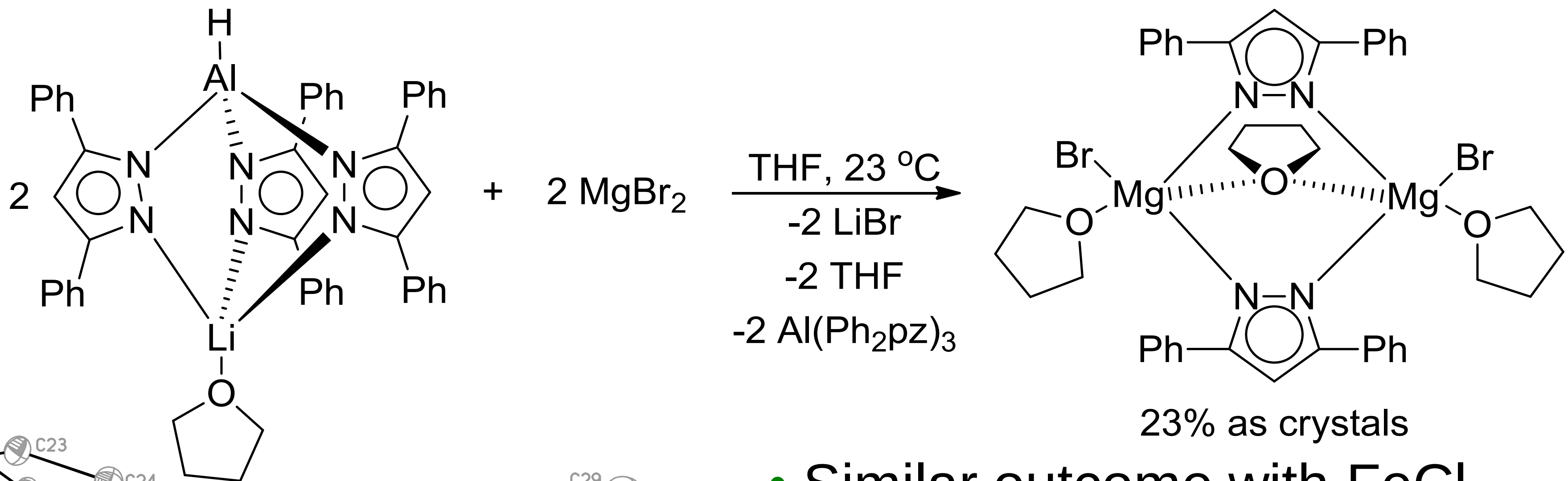
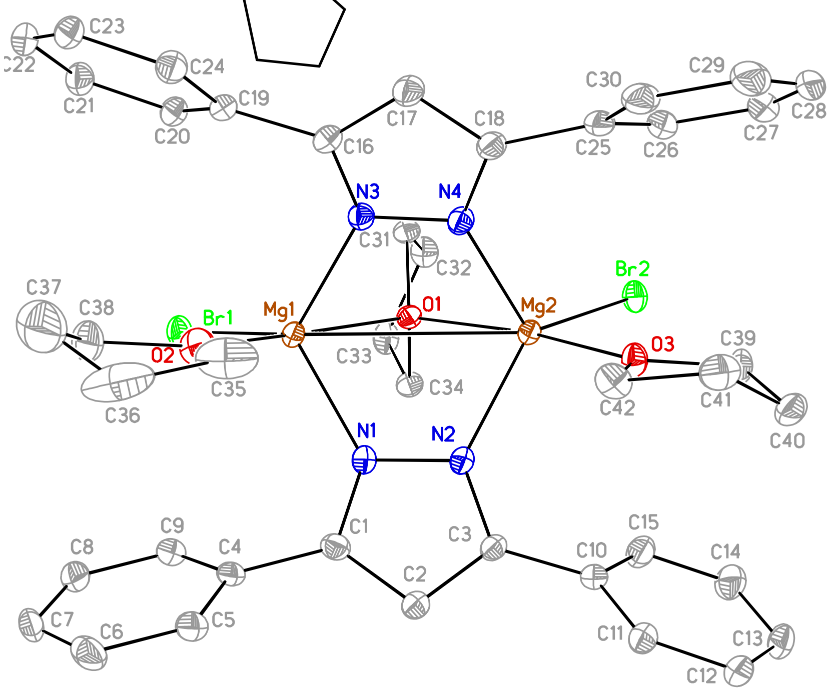
Pyrazolate and HydrideTransfer Reactions with MBr_2





- Similar outcome with $FeCl_2$ and $CoCl_2$
- Many transition metal MCl_2 gave metal powders, presumably through MH_2 formation
- *Pyrazolate and hydride transfers are facile*

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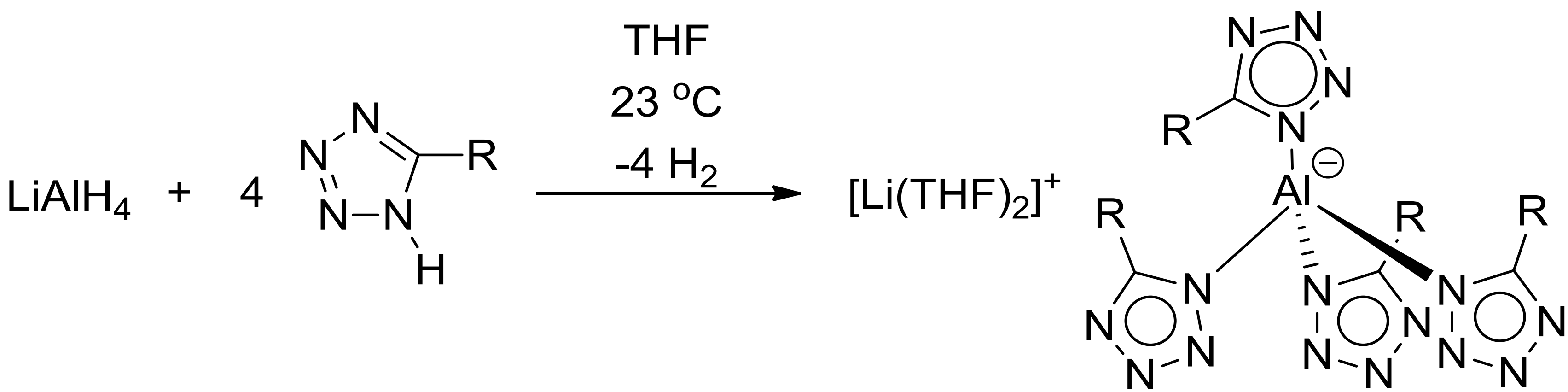
Lithium Tetrakis(tetrazolyl)aluminates?



- Reaction works for R = H, Ph, NMe_2, $NiPr_2$, tBu; yields ~90%
- Products precipitate from THF, except for R = tBu and $NiPr_2$, which are soluble; all are soluble in DMF and DMSO
- Solids lose THF upon standing → Li-N bond formation?
- R = H explodes upon burning, but does not explode upon being hit with a hammer, scraping across 100 grit sandpaper, or passing sparks through it with a Tesla coil

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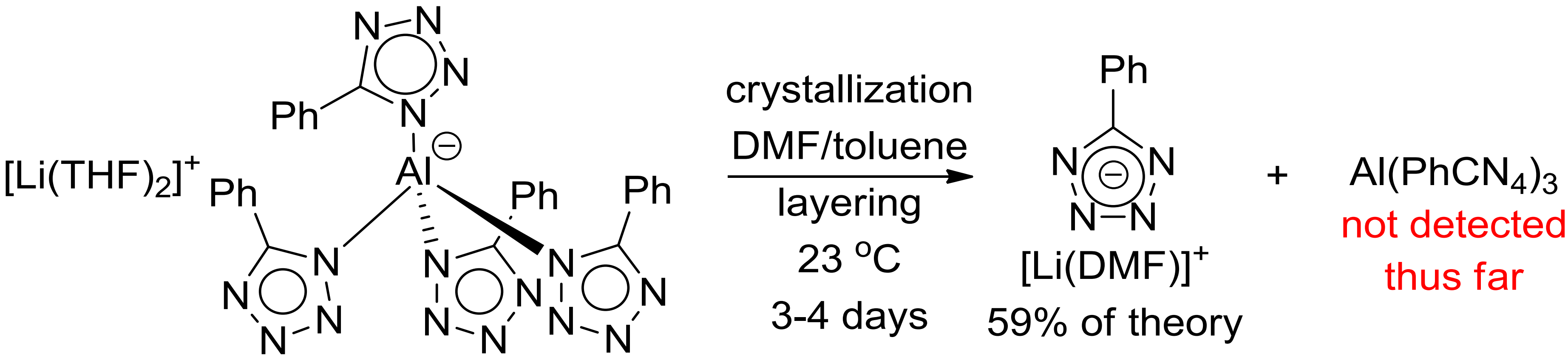
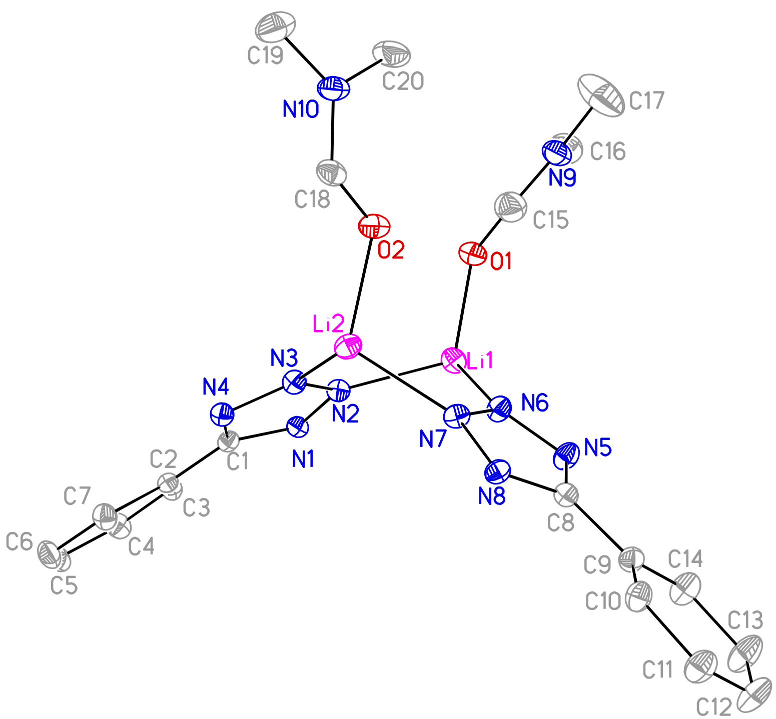
Attempted Crystallization of R = Ph





- Exists as a 3-dimensional polymer in solid state
- Dissociation may be driven by crystallization of Li tetrazolate
- Attempts to prepare neutral Al tetrazolates are ongoing

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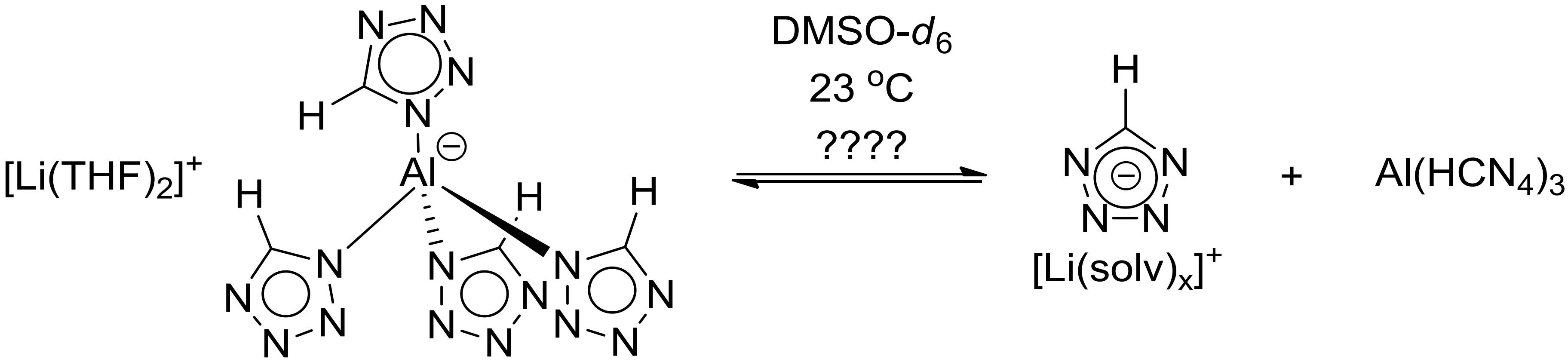
Probing Dissociation by ^{1}H NMR



- ^{1}H NMR $[Li(DMF)]^+[\textit{H}CN_4]^-$ δ 8.01 in DMSO-d_6
- ^{1}H NMR $[Li(THF)_2]^+[Al(\textit{H}CN_4)_4]^-$ δ 8.65, 8.60, 8.35, 8.07 in DMSO-d_6
- No evidence for $[Li(DMF)]^+[HCN_4]^-$, but ^{1}H NMR spectrum of $[Li(THF)_2]^+[Al(HCN_4)_4]^-$ is more complex than expected
- Experiment does not rule out $[Al(HCN_4)_4]^-$

Conclusions

- Bis(tetrazolyl)borate ligands are easily prepared; novel sterically-based ligand isomerism documented
- No routes thus far to tris(tetrazoyl)borate and tetrakis-(tetrazoyl)borate ligands
- Poly(pyrazolyl)aluminate ligands have been prepared and characterized for the first time; can serve as tripodal ligands, but pyrazolate and hydride transfer reactions can compete
- Salts of tetrakis(tetrazoyl)aluminate anions have been prepared and are under development → *hottest compounds we have prepared to date*
- Tetrazole-derived anion salts are energetic, and may lead to new types of high nitrogen content explosives and propellants

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Acknowledgments

Christopher J. Snyder

Dongmei Lu

Dr. Mary Jane Heeg

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N00014-07-1-0105

Program Officer: Dr. Cliff Bedford

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