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Effect of Spiroconjugation on the Stability of Spirocyclic Group 13, 14, and 15-Centered Redox Mediators

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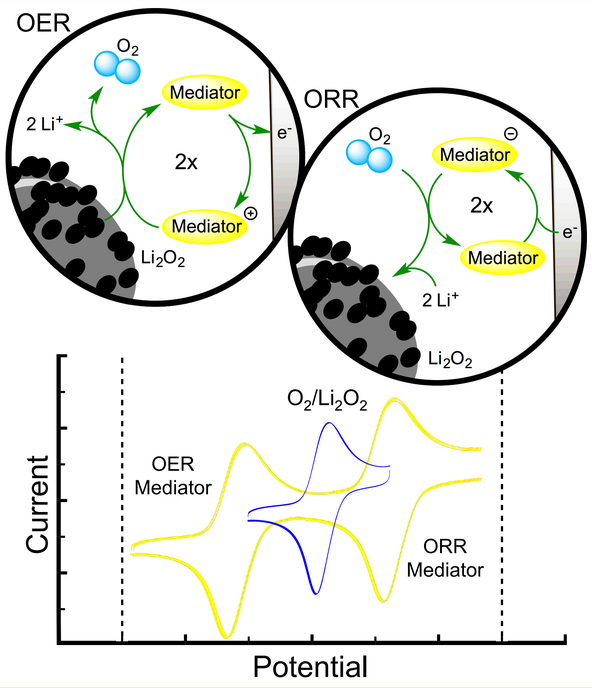
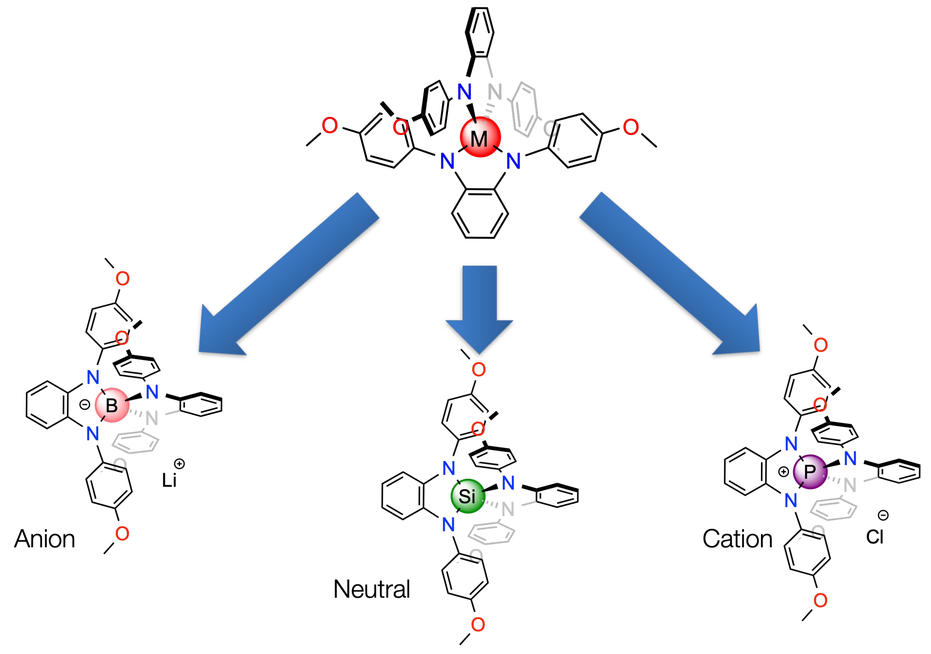
Abstract and Hypothesis

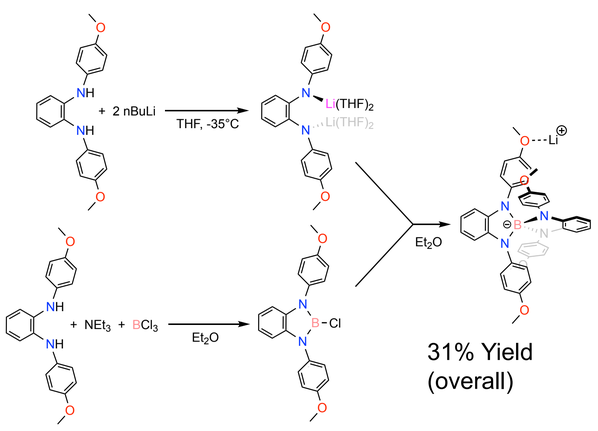


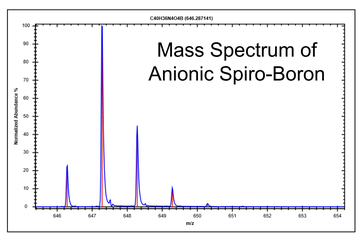
Interfaces between liquid, solid and gas can inhibit the movement of charge in electrochemical systems. In batteries, optimum performance and maximum capacity can be maintained when transferring charge across these barriers through the use of redox mediators: molecular species that act as an intermediary in the electrochemical reactions. This presentation will describe the development and electrochemical studies of isostructural Group 13, 14, and 15 spirocyclic redox-active compounds. Spiroconjugation is evident in this series of compounds, however it is modulated by bond lengths and other structural factors leading to highly variable stability and redox activity despite the superficial similarities. The preliminary results are put into the context of a metal-air battery, examining the reactivity with gaseous oxygen.

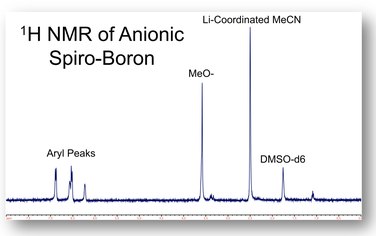


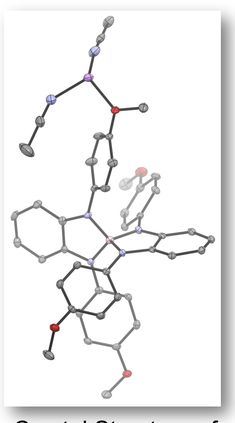
Methods and Results

Group 13 (Boron and Aluminum)

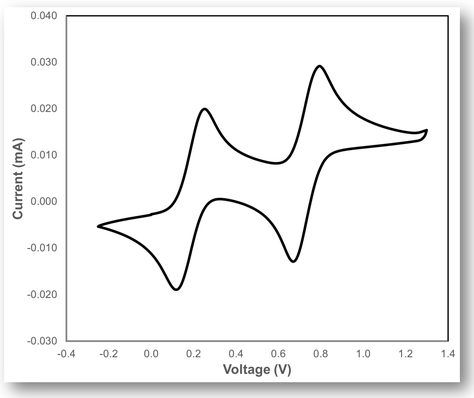






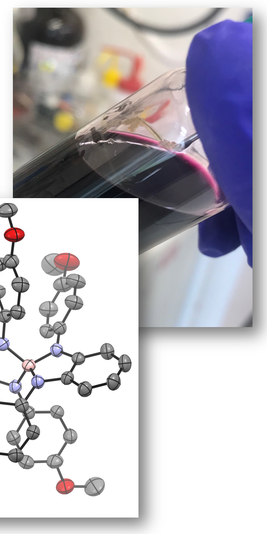


Crystal Structure of Anionic Spiro-Boron

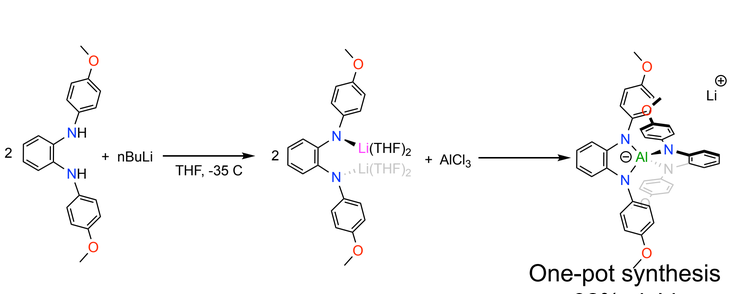


Using cyclic voltammetry, we determined molecular oxygen could oxidize this complex.

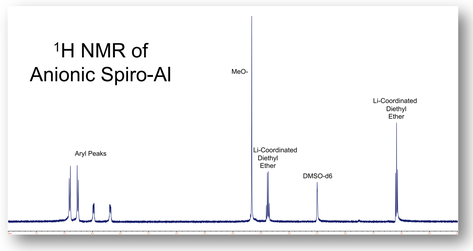
When subjected to molecular oxygen, a solution in CH_2Cl_2 turns a distinctive **Purple** color.

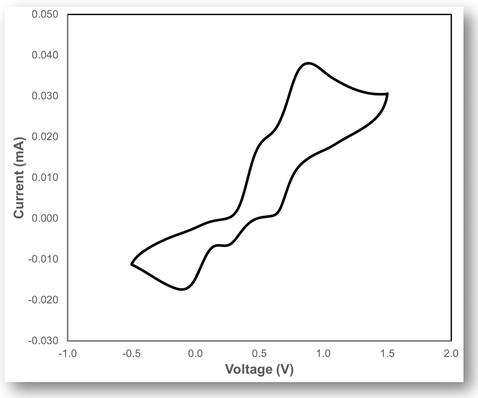


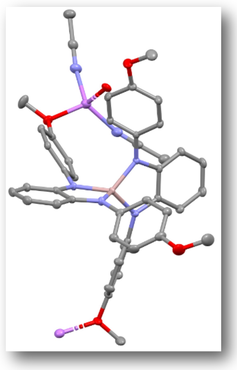
Calculations of Neutral Spiro-Boron performed by Prof. Neil Tomson at University of Pennsylvania show that it should exist as a radical spread across the **π**-orbitals of both of the diamine ligands, linked by the overlap of the p-orbitals on the nitrogens. The Boron does not interact with this **π**-system. The SpiroB cation should exist as a diradical!



One-pot synthesis
92% yield

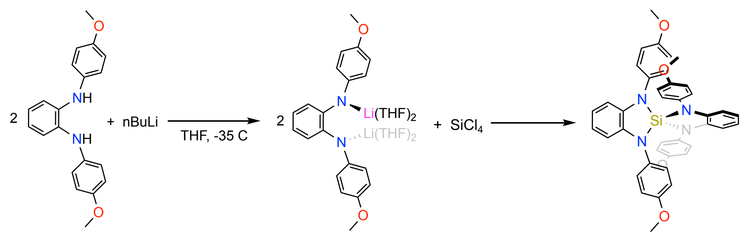


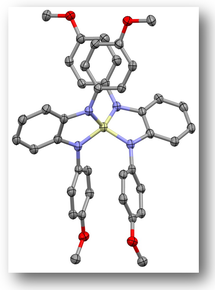




The cyclic voltammogram of the anionic Spiro-Aluminum shows additional features in the oxidative direction, which leads us to believe that this material is not stable to oxidation. Oxygenated samples are purple, similar to boron compounds.

Group 14 (Silicon)

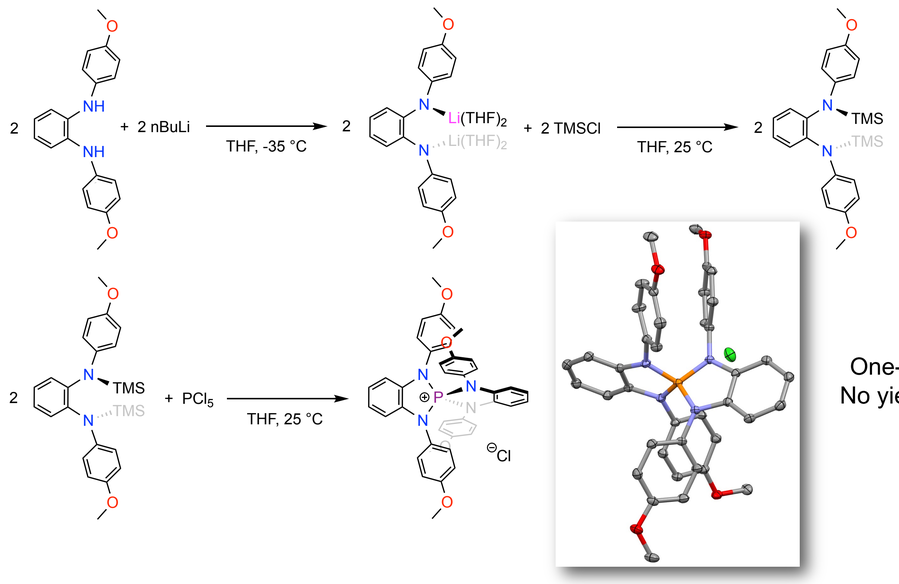




Synthesis of aluminum complex proceeded cleanly, analogously to the aluminum complex. This compound was crystallized (right) showing similar features to the other three structures previously obtained.

Electrochemical data show decomposition upon oxidation, similar to aluminum.

Group 15 (Phosphorus)



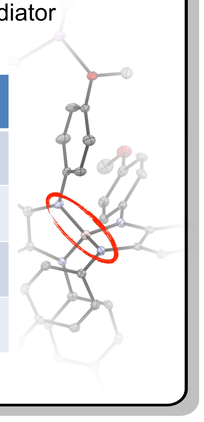
One-pot synthesis
No yield determined

These data are very preliminary, but the ^{31}P signal is at +16 ppm, in the range for an expected P(V) compound. The 1H NMR shows the expected signals for the diamino ligand with appropriate symmetry. In both NMR spectra, there are no other signals present leading us to conclude that this one-pot reaction is clean and straightforward. The reaction mixture was layered with hexanes to afford crystals suitable for X-ray crystallography (above).

Conclusions

Measuring avg. M-N and avg. N-N (opposite ligand) bond distances gives us one aspect to judge the extent of spiroconjugation. B-N is shortest, as expected, and the elements of Period 3 show the expected decrease in M-N distance based on periodic trends. Stability of the mediator should follow from this data, narrowing the search for mediator candidates for future studies.

Mediator	M-N Distance (Å)	N-N Distance (Å)
Boron	1.544	2.642
Aluminum	1.849	3.172
Silicon	1.722	3.097
Phosphorus	1.640	2.805



Future Work

Determine the stability of spiro compounds formed from different diamine, functionalized on the aryl substituent.

Study the utility of the spiroB in metal-air battery systems as well as flow battery systems.

Acknowledgements

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