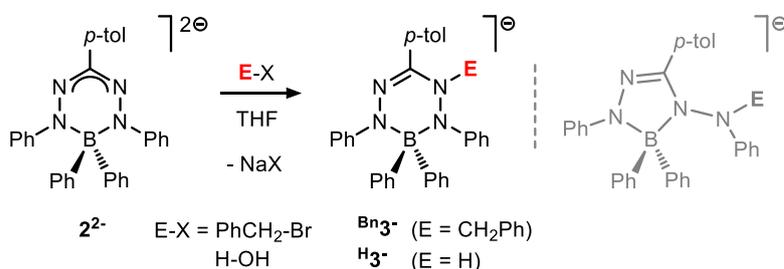


# REACTIVITY OF 2-ELECTRON REDUCED FORMAZANATE BORON COMPOUNDS WITH ELECTROPHILES: FACILE N-H/N-C BOND HOMOLYSIS DUE TO FORMATION OF STABLE LIGAND RADICALS

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The majority of synthetic molecular catalysts change their oxidation state by changing the formal oxidation state of the central metal atom. In contrast, Nature often uses metalloenzymes in which there is a redox-active organic moieties which accumulate redox equivalents that can subsequently be used by the metalloenzyme to perform challenging multi-electron transformations.<sup>[1]</sup> Inspired by these enzymatic systems, there is increasing interest in the chemistry of synthetic catalysts with redox-active ligands.<sup>[2]</sup> Herein, we have explored the reactivity of a boron complex with redox-active formazanate ligand, LBPh<sub>2</sub> (L = PhNNC(*p*-tol)NNPh). Two-electron reduction of this main group complex generates the stable dianion [LBPh<sub>2</sub>]<sup>2-</sup>, which is susceptible to electrophilic attack by BnBr and H<sub>2</sub>O and yields products that derive from ligand benzylation and protonation, respectively (scheme 1). The resulting complexes are anionic boron analogues of leucoverdazyls. N-C and N-H bond homolysis of these compounds was studied by exchange NMR spectroscopy and kinetic experiments. The weak N-C and N-H bonds in these systems derive from the stability of the resulting borataverdazyl radical, in which the unpaired electron is delocalized over the four nitrogen atoms in the ligand backbone. We thus show the ability of this system to store [2e-/E<sup>+</sup>] on the organic ligand and convert it to E<sup>•</sup> radicals, reactivity that has implications in energy storage applications such as hydrogen evolution.



Scheme 1. Synthesis of compounds **Bn3•** and **H3•**.

## References

- 1) J. W. Whittaker, *Chem. Rev.* **2003**, *103*, 2347.
- 2) W. I. Dzik, J. I. van der Vlugt, J. N. H. Reek, B. de Bruin *Angew. Chem. Int. Ed.* **2011**, *50*, 3356.