

The efficient storage of renewable electricity derived from intermittent sources such as solar and wind is a key chemical challenge for the 21st century. One promising approach to this challenge involves the conversion of excess electricity into energy dense chemical fuels. The linchpin for this strategy is the development of efficient catalysts capable of using electrical potentials to drive energy storing fuel production reactions such as hydrogen evolution or CO₂ reduction. Traditionally, scientists have looked to transition metals to fill this role, owing to their rich chemistry and redox activity. We have begun to pursue alternate materials in which conjugated hydrocarbons doped with boron atoms provide the requisite redox chemistry and chemical reactivity to promote energy storing reactions. In particular, we have focused on the molecule 9,10-diboraanthracene (DBA) as a small molecule platform with multielectron redox capacity and the ability to activate small molecules of energy consequence (Figure 1).

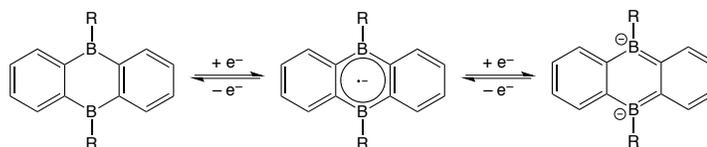


Figure 1. 9,10-dihydro-9,10-diboraanthracene (DBA, left) and its reduction by two electrons to give a stable dianion.

In the previous reporting period, we disclosed two new approaches to stabilizing reduced DBA units. In one approach, we developed a new ligand, B₂P₂, which uses phosphine donors to bind a transition metal near the diboron core of DBA. This ligand enabled us to prepare the first example of a molecular auride complex which undergoes reduction at a potential ~500 mV positive of the metal free analogue (Figure 2).¹ In the current reporting period, we have extended this chemistry in several directions. First, we explored the chemistry of B₂P₂ with the remaining coinage metals copper and silver. In this study we sought to understand the extent to which gold may be unique in stabilizing redox chemistry at DBA. We found that although the copper and silver complexes of B₂P₂ were redox active, their one-electron reduction products were unstable, and we could not observe a two-electron reduced product. These results highlight the unique properties of gold and its redox-active s-orbital, a consequence of relativistic effects on its electronic structure. This manuscript was published in *Inorganic Chemistry*.²

We have also begun to explore other boron heterocyclic complexes as ligands. We used a previously reported ligand based on borafluorene to prepare its nickel(0) complex and compare it to the related complex (B₂P₂)Ni (Figure 3).³ Although

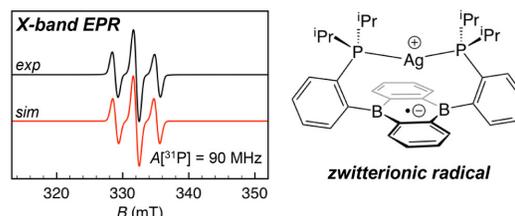


Figure 2. The zwitterionic radical prepared by reducing [(B₂P₂)Ag]⁺ (right) and its room temperature X-band EPR spectrum (left) showing both the experimental and simulated spectra. The hyperfine structure is due to coupling of the electron spin to the two equivalent ³¹P nuclei.

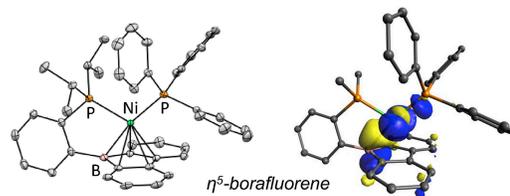


Figure 3. A pentahapto Ni(0) complex of a phosphine tethered borafluorene ligand.

neither of these species exhibit the rich redox chemistry of the gold system described above, they have helped us delineate the design principles for such compounds in the future. The key insight in this regard is the presence of an accessible empty orbital on the metal that is capable of engaging the boron p-orbitals in a bonding fashion. In the case of gold, this is the 6s orbital. Future studies will target earlier transition metals with low d-electron counts.

Finally, we have begun to explore the reactivity of the $[(B_2P_2)Au]$ system (Figure 4).⁴ We found that the anionic species can be protonated by mild acids to give a reactive borohydride that is capable of reducing CO_2 to formate. The formate can subsequently be released either by protonation or reduction to close the cycle. The anionic complex also reacts directly with CO_2 to effect its reductive disproportionation to CO and carbonate. These reactions represent rare examples of the redox transformation of CO_2 mediated at boron and demonstrate the overall feasibility of the goals outlined above. Collectively, these reactions constitute a closed synthetic cycle for the reduction of CO_2 to either formic acid or CO with protons and electrons, processes generally carried out by transition metals.

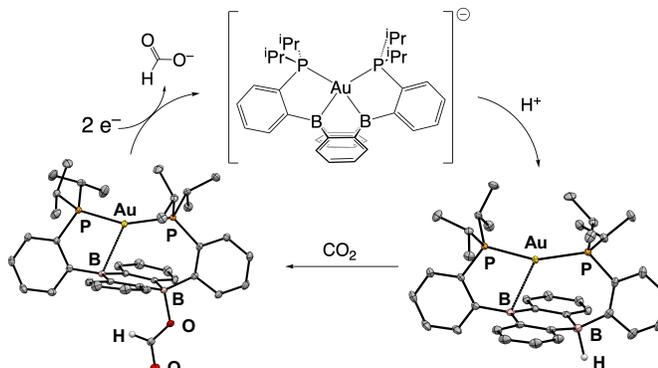


Figure 4. Reduction of CO_2 to formate with protons and electrons mediated by $[(B_2P_2)Au]$.

Support for this project from the American Chemical Society Petroleum Research Fund has been instrumental in the career development of both the PI and his students. The DNI grant provided funding during a time in which the PI's startup funds were nearly expended, and in the subsequent year, the PI was awarded an NSF Faculty Early Career Development award (NSF CAREER) on the basis of this project. The supported students were able to focus on their research full time, and the primary student supported by the grant, Jordan Taylor, was recently awarded the UCR Dissertation Year Fellowship, a competitive, campus-wide award for graduate students in their final year. Jordan graduated this May and is now doing a postdoctoral fellowship in the lab of Prof. Richard Schrock.

¹ Taylor, J. W.; McSkimming, A.; Moret, M.-E.; Harman, W. H. A Molecular Boroauride: a Donor-Acceptor Complex of Anionic Gold. *Angew. Chem. Int. Ed.* **2017**, *56*, 10413–10417.

² Taylor, J. W.; McSkimming, A.; Moret, M.-E.; Harman, W. H. Copper and Silver Complexes of a Redox-Active Diphosphine-Diboranthracene. *Inorg. Chem.* **2018**, *57*, 15406–15413.

³ Essex, L. A.; Taylor, J. W.; Harman, W. H. Nickel Complexes of Phosphine-Appended Benzannulated Boron Heterocycles. *Tetrahedron* **2019**, *75*, 2255–2260.

⁴ Taylor, J. W.; McSkimming, A.; Essex, L. A.; Harman, W. H. CO_2 Reduction with Protons and Electrons at a Boron-Based Reaction Center. *Chem. Sci.* **2019** *ASAP Article*.