In this project, my research group is investigating the possibility that late-metal silylamides, particularly those of base metals, can serve as precursors for nitrene-group transfer through a series of one-electron processes, as shown in Figure 1.

![Figure 1](image_url)

**Figure 1.** Possible catalytic cycle utilizing late-metal silylamides as protected nitrene-group sources

**Studies of (dtbpe)Ni Silylamides and their Redox Properties:** We previously developed a general route for synthesis of silylamido complexes of nickel supported by the 1,2-bis(di-tert-butylphosphino)ethane (dtbpe) ligand, shown below (Figure 2). All three complexes that have been prepared show a promising reversible Ni^{II}/Ni^{III} redox couple at more positive potentials than related complexes that have hydrogen rather than a trimethylsilyl substituent. These are useful complexes for exploring steps B and C.

![Figure 2](image_url)

**Figure 2.** Synthesis and structures of (dtbpe)Ni silylamides

We previously showed preliminary evidence that the 2,6-diisopropylphenyl (DIPP) silylamido complex could be reversibly oxidized, but we had difficulty isolating the product in clean form and the spectra were difficult to interpret. This summer we have honed the methodology, showing that both the DIPP and ‘Bu silylamido complexes can be oxidized cleanly to the corresponding cations (Figure 3). Efforts to obtain single crystals for analysis are currently underway, and we have moved to preliminary experiments attempting to remove the silyl group with fluoride (CsF, AgF, TASF) and oxide (e.g., alkoxide) nucleophiles. We are also beginning to explore alternative oxidation routes, particularly two-electron routes involving F^+ reagents that may allow formation of Ni(III) imido products via Me_3Si–F elimination.
Initial Studies on (dtbpe)Co Complexes: The work described above has focused primarily on nickel as a result of Hillhouse’s seminal work in this area. However, we are also interested to explore whether (dtbpe)Co can support imido complexes and, if so, whether the resulting complexes are capable of nitrene-group transfer in a manner similar to nickel. We had previously attempted to access [(dtbpe)CoCl]₂ through reduction of (dtbpe)CoCl₂ with strong reductants, but we inevitably obtained sparingly soluble material. Inspired by a recent report from Chirik showing that bis(phosphine) Co(I) dimers can be accessed easily through Zn reduction, we have pursued this route.

The precursor complex (dtbpe)CoCl₂ was easily prepared and crystallographically characterized. We have attempted Zn reductions of the complex. However, the presence of bulky, electron-rich tert-butyl groups makes the complexes considerably more difficult to reduce. Instead, we have begun performing the reductions in benzene to trap a formally Co(0) benzene adduct that we hope can be used to access Co(I) and Co(II) complexes relevant to the cycle in Figure 1. We have also explored this chemistry with the dcype ligand.

Future Work: During the remainder of the grant period, we intend to focus efforts on the following areas:

(a) Silyl-group removal strategies from Ni(I) and Ni(II) silylamides (step C)
(b) Accessing Co(I) and Co(0) complexes for comparative studies with Ni
(c) Preparing Co(II) imido complexes for comparative studies with Ni

The outcomes of this work will allow us to understand the differences in reactivity between Co and Ni, with the goal of focusing future efforts on metal/ligand combinations that are most likely to yield success in electrocatalytic nitrogen-group-transfer reactions.

Project Impacts: So far, this project has provided research opportunities for 6 undergraduate students, of whom four have graduated, with two enrolling in Chemistry Ph.D. programs (Princeton University and UC-Irvine) and one in medical school. Within my larger research scope, this project has provided opportunities to understand interactions of metals and silicon when they are not directly connected and provided insights as to how metal/silicon cooperation can be exploited in catalysis.

Figure 3. Oxidation of (dtbpe)Ni–N(TMS)(DIPP) and proposed deprotection

Figure 5. Synthetic routes to (dtbpe)Co imido complexes explored and targeted