Abstract
Several new Co(II) complexes supported by NNN pincer ligands in various ligand-to-metal ratios are reported. The synthesis and characterization of CzBu(PyrPr)2Co (1) completes a series of analogous compounds (CzBu(PyrPr)2M, M = Fe(II), Co(II), Ni(II)), offering insights into chemical trends across late first-row transition metal complexes. Additionally, chemical oxidation of (CzBu(PyrPr)2)2Co (2) gave complex 5, in which unprecedented, cobalt-facilitated C-C coupling of pyrazole moieties has occurred.

Ligand Synthesis

Metal Complex Syntheses

Electrochemical Studies

Proposed Scheme of 5 Formation

We propose that the C-C coupling in 5 occurs via a Co(III) intermediate because only one equivalent of AgOTf was used and pyrazole-containing compounds only exhibit C-C coupling with a catalyst.

Ligand Substitution Reactivity of 1

Conclusions
With the successful synthesis and characterization of 1, we have completed a series of CzBu(PyrPr)2-supported M(II) (M = Fe, Co, Ni) complexes. Different from our observations of Fe(II) and Ni(II), numerous other Co(II) complexes could be obtained in addition to 1 depending on the synthetic approach. Interestingly, the chemical oxidation of 2 resulted in an unprecedented product, 5, in which C-C coupling has occurred at the C5 position of two uncoordinated pyrazole arms. This is proposed to have occurred via a Co(III) intermediate and encourages further research into pyrazole coupling chemistry using cobalt complexes. Future work by this group will include investigating the mechanism by which the pyrazole moieties couple. Additionally, isolation of the fluoro- and tert-butoxy-substituted complexes will be pursued, and additional functionalization will be explored. Given the interesting properties of the ever elusive 3, we will also continue to target this compound using various synthetic means. Finally, the synthetic techniques we employed to target these desired products may be of use to the practicing synthetic inorganic chemist and display the importance of solvent selection, concentration, and control of redox activity when synthesizing new inorganic complexes.

References