

Introduction

The goal of this work is to develop a class of coordination complexes with guanidine ligands that can serve as catalysts for carrying out oxidative transformations (*e.g.*, aziridination, epoxidation, and nitrene/O-atom insertion into C–H bonds) of organic substrates. We are interested in guanidine based ligands because of their good donor properties for stabilizing high-oxidation state intermediates and have focused on ligand designs that discourage intramolecular C–H activation pathways that lead to catalysts deactivation.

The specific objectives of this work are: (1) To synthesize a family of chelating guanidine ligands where chelation is achieved through linkages that attach at non-donor nitrogen atoms; (2) To synthesize coordination complexes of these ligands, focusing on Fe, Co, and Cu complexes, and to quantify the ligand field strength of the guanidine donors; and (3) To achieve imido- and oxo-group transfer from high oxidation state complexes to organic substrates and understand the mechanism of these reactions. Over this reporting period we have made progress on all three objectives.

Progress on Objectives

Objective 1: The first objective of our work was to synthesize a family of chelating guanidine ligands linked through the non-donor (3-coordinate) nitrogen atoms. In this area we expanded on our preliminary findings and optimized the synthesis of tbo_2Pyr , which has become the workhorse ligand on this project. We also introduced the previously known tbd_2Pyr ligand to our lab and have begun to explore its chemistry.[1,2] Unfortunately, our efforts toward chelating unsaturated guanidine rings was met with synthetic difficulties at the penultimate step. We have thus directed our efforts at exploring the chemistry of tbo_2Pyr and tbd_2Pyr in the context of Objectives 2 and 3, Figure 1.

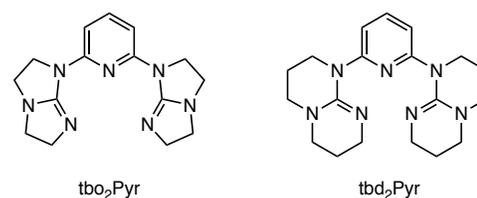


Figure 1. Structures of tbo_2Pyr and tbd_2Pyr .

Objective 2: We have successfully synthesized and published the 1:1 coordination complexes formed between tbo_2Pyr and the triflate salts of iron(II), cobalt(II), nickel(II), copper(II), copper(I), and zinc(II).[2] These complexes adopt a variety of geometries around the metal center, ranging from T-shaped to octahedral, Figure 2. The shape adopted by the tbo_2Pyr ligand (planar and pincer-like, or puckered and face-capping) depends on metal ion size, with smaller ions fitting in the pocket of the planar ligand, and larger ions resulting in a twisted ligand and a more open binding site.

All of our complexes isolated thus far are high-spin, revealing that the tbo_2Pyr ligand imparts a relatively weak ligand field on the 3d metals, in contrast to some other guanidine ligands.[3] We attribute this partially to the weak and distant coordination of the pyridine ligand and effective low coordination numbers. The octahedral nickel(II) complex allows for a relatively straightforward comparison of ligand-field strength by UV-visible spectroscopy, and by this measure the ligand-field is comparable or weaker than that achieved in $[\text{Ni}(\text{MeCN})_6]^{2+}$.

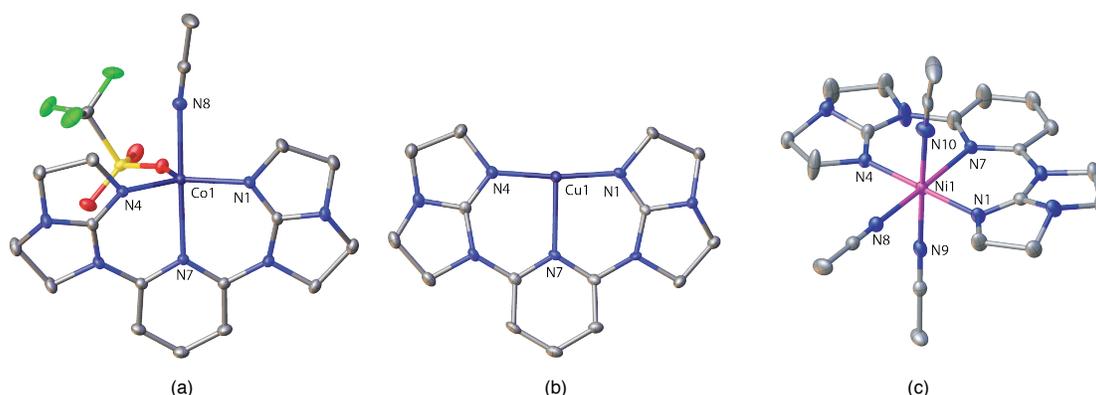


Figure 2. X-ray crystal structures of late first-row metal complexes with tbo_2Pyr . Thermal ellipsoids are at the 50% probability with hydrogen atoms omitted for clarity. (a) The cation in $[\text{Co}(\text{tbo}_2\text{Pyr})(\text{OTf})(\text{MeCN})]\text{OTf}$; (b) the cation in $[\text{Cu}(\text{tbo}_2\text{Pyr})]\text{OTf}$; (c) the dication in $[\text{Ni}(\text{tbo}_2\text{Pyr})(\text{MeCN})_3](\text{OTf})_2$.

Objective 3: The third objective of this work is to use our coordination complexes with chelating guanidine ligands as catalysts for organic transformations and to probe the mechanism of these transformations. These efforts have so far been focused on the copper(I) complexes as catalysts for nitrene transfer reactions. While this work has not yet been published, we have presented on it at the two 2018 National ACS Meetings (New Orleans and Boston). Our results show that these complexes are capable of facilitating the aziridination of styrene and the C–H bond oxidation of tetrahydrofuran to a tosylamine; we are currently exploring an expanded substrate scope. These reactions use PhINTs or Ph*INTs (Ts=tosyl, Ph*I = 2-tert-butylsulfonyliodobenzene) as a nitrene source and are postulated to proceed through a copper nitrene intermediate. We have identified this intermediate spectroscopically by UV-vis absorption spectroscopy at -70°C in isobutyronitrile solvent, Figure 3a, and assigned it by comparison to recent results from the Herres-Pawlis Group.[4] When the reaction between $[\text{Cu}(\text{tbo}_2\text{Pyr})]\text{OTf}$ and PhINTs is carried out on synthetic scales, we isolate the tosylamidocopper(II) triflate complex, Figure 3b and 3c, and see no evidence for intramolecular C–H bond activation, an important distinction from previously reported work that validates our ligand design.

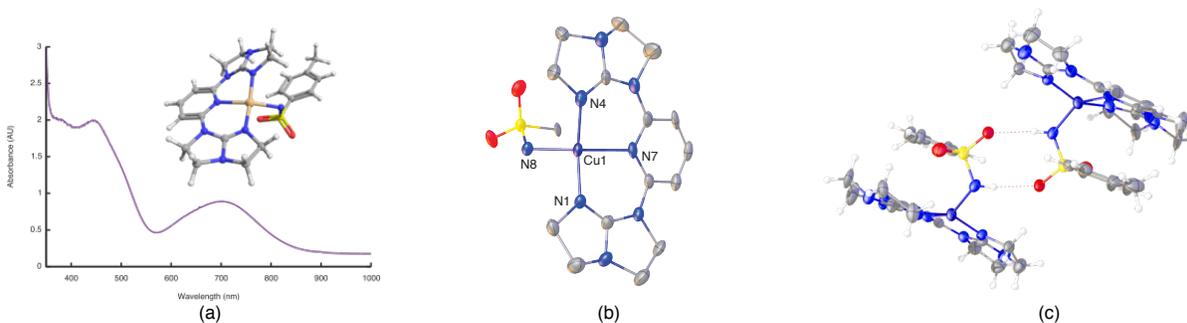


Figure 3. (a) Visible absorption spectrum and calculated structure of the assigned nitrene intermediate obtained from the reaction of Ph*INTs with $[\text{Cu}(\text{tbo}_2\text{Pyr})]\text{OTf}$ in isobutyronitrile at -70°C ; (b) The crystal structure of the cation in $[\text{Cu}(\text{tbo}_2\text{Pyr})(\text{HNTs})]\text{ClO}_4$ with hydrogen atoms omitted for clarity; (c) the dimeric unit showing a pair of N–H...O hydrogen bonds between two $[\text{Cu}(\text{tbo}_2\text{Pyr})(\text{HNTs})]^+$ cations.

Impact on Personnel

In this reporting period, this grant has provided support for Summer and Interim (January) research experiences for two undergraduates and allowed each of them to attend a National ACS Meeting to present on different aspects of the work described here. The support has also allowed Dr. Piro to attend the Summer 2018 ACS National Meeting with his student, and to focus his summer research program on this project. One student trained on this grant is now in the Chemistry PhD program at Temple University. We are looking forward to recruiting new Albright students to this project in the coming academic year.

References

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