The utilization of small molecules (such as CO2, CO, CNR, CH4, N2, NH3, etc.) for chemical synthesis is attractive because these coupling partners are abundant and benign. The ability to access value-added products, such as alkanes for fuels or complex organic targets of biological importance, from these starting materials requires the ability to activate these inert substrates while controlling multiple proton and electron transfer steps that occur alongside bond-forming and -breaking steps. For these reasons, we have been interested in exploring the fundamental reactivity of CNR and CO with first row transition metals such as Fe, and now also Co, under reductive and oxidative bond-forming conditions.

Prior Work. We previously synthesized a series of iron isocyanide complexes, [TmFe(CNR)2](OTf) (R = Me, Ph, Mes; R’ = tBu, Bn, Cy). The reaction of [TmFe(CNtBu)3](OTf) with KC8 as the reductant and H2O as a proton source generates 1,3-di-tert-buty1 urea, a new isocyanide derived coupling product (Scheme 1). A series of mechanistic experiments suggested a pathway involving initial reduction of CNtBu to tBuNH2 and air as the source of the urea oxygen. During our first award period, we studied the influence of the ligand structure R and the isonitrile substitution (R’ ) on the efficiency of reduction and the product distribution obtained. We are now probing the spectroscopic features of the reduced iron intermediate.

Spectroscopic Characterization of the Reduction Event. Spectroelectrochemical studies have revealed that the electrochemical reduction of 1a generates a species distinct from that formed from KC8 reduction. Reduction experiments conducted in the presence of 18-crown-6 and monitored by UV-Visible spectroscopy show no incorporation of the K+ ion and we have focused our subsequent efforts on the characterization of the species resulting from KC8 reduction. Mössbauer and magnetic susceptibility measurements of 1a have confirmed the expected low-spin (S=0) iron(II) configuration (Figure 1, left). Upon reduction of 1a with KC8, three new species are formed with quadrupole splitting values of ΔE0 = 0.49, 1.18, and 1.77 mm s−1, in an approximate ratio of 64:25:11 (Figure 1, right). Subsequent treatment with water results in the formation of a single Fe-containing species. This species is NMR active and shows a 13C NMR resonance at 200 ppm, characteristic of a diaminocarbene carbon. These data support our current
mechanistic postulate, that the formation of di-tert-butylurea proceeds an iron-diaminocarbene intermediate. Additional Mössbauer experiments are underway to confirm that the same species arises from the addition of tBuNH₂ to 1a following reduction.

**Steric Characterization of the Complexes.** We have also probed the importance of R and R’ on the structural features of the complexes. The steric accessibility of the metal center in a small series of complexes was evaluated from the single crystal X-ray structures. The C≡N bond length changes very little when the Tm²⁺ substituent is changed (R’ = Me, Ph, Bn). However, these ligands do influence the structure of the complexes, as can be seen by the change in their cone angles (θ_Tm, Figure 2) with variation of the Tm ligand. In contrast, the steric nature of the isocyanides has little influence on the geometries of the complexes. For all isocyanides explored, the Fe-C-N angle remains fairly linear (173.9 – 177.0°) and the cone angle defined by the three isocyanide ligands (θ_CNR Figure 2) decreases only slightly with increasing R’ bulk. The structural data suggest that the space occupied by each Tm²⁺ ligand is dependent on the size of the isocyanide ligands, as smaller Tm³⁺ cone angles are seen with larger CNR’ substituents. The cone angle defined by the isonitriles, however, changes very little as the steric nature of the Tm²⁺ ligand is increased. The majority of the spectroscopic and structural characterization work was done by a postdoctoral research, Oliver Mitevski.

**TmFe(CO)₅[(OTf)].** The reduction of CNR to RNH₂ suggests that these TmFe complexes may also facilitate the challenging cleavage of the C≡O bond of CO. We have now begun to explore the possible reductive coupling of the related carbonyl complex [TmFe(CO)₅](OTf). Treatment of [TmFe(CO)₅](OTf) with K₃[C₆H₇] and H₂O results in the formation of formate in low yields. We have also begun to explore the reactivity of this species under thermal conditions and UV irradiation as well as in reactions with common ligands and substrates (PPh₃, PhCCPh, PhCH₂OH). In all cases, we observe dissociation of the carbonyl ligands to generate a paramagnetic species that we have tentatively assigned as Tm₃Fe. Further exploration of this system will probe the possibility of using [TmFe(CO)₅](OTf) as a precursor to access catalytically active bare ‘TmFe’. This work work being conducted by a new graduate student, Rebecca Krupa.

**Co-Catalyzed Aerobic Oxidation Reactions of CNR.** During our reduction reactions employing Cp₂Co, we observed the formation of minor amounts of CNR coupling products. We identified this reaction to be Cp₂Co-promoted and we have since extended this finding into a new synthetic reaction: the cobalt-catalyzed oxidative coupling of aminophenols and isonitriles (Scheme 2, X=O). This reaction operates under ligand- and additive-free conditions while utilizing simple Co³⁺ salt precatalysts and employing air as the terminal oxidant. A current 4th year graduate student, Jiaqi Liu, has developed this methodology and has synthesized a large scope of 2-aminobenzoxazoles using this methodology and are currently exploring the nature of the cobalt intermediates that are responsible for the efficient utilization of O₂. Preliminary experiments suggest a key role of aminophenol as a non-innocent ligand in facilitating the oxidation step. We have also begun to expand the scope of this synthetic transformation to the formation of 2-aminobenzimidazoles (Scheme 2, X = N). An undergraduate student in the group, Sarah Morgan, is now working on this project.

**Figure 2.** X-ray crystal structure of 1a and graphical depictions of the Tm cone angle (θ_Tm) and the CNR ligand cone (θ_CNR).

**Scheme 2.** Co-catalyzed oxidative cyclization reactions of CNR.