

## 2019 Narrative Progress Report

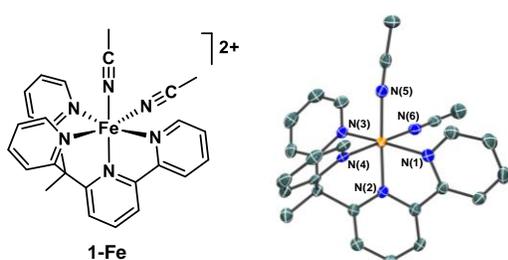
PRF# 58707-DNI3

**Project Title:** Developing Durable and Highly Reactive Iron-Oxo Catalysts for Hydrocarbon Functionalization

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The ACS Petroleum Research Fund has supported our work to develop more robust molecular iron complexes for catalytic hydrocarbon C-H bond functionalization. Petroleum is an important source of inexpensive hydrocarbons for accessing both commodity and fine chemicals by the chemical and pharmaceutical industries. However, it is challenging to convert the strong C-H bonds of this abundant feedstock into new functional groups to prepare synthetically versatile organic building blocks. In this context, the production of high-volume as well as specialty chemicals can be improved with access to more efficient and durable catalysts for hydrocarbon oxidation.

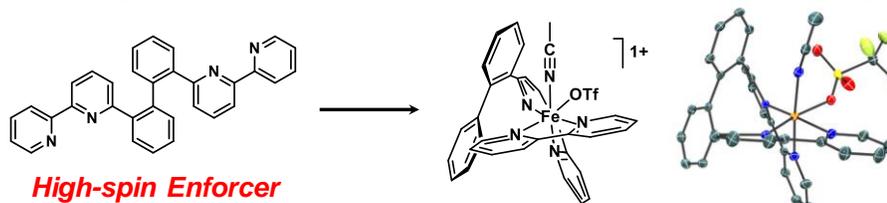
Synthetic iron-oxo complexes are known to be capable oxidants for functionalizing unactivated C-H bonds. These intermediates are generally formed by adding sacrificial oxidants such as peracids, iodosobenzene, Ce(IV), and H<sub>2</sub>O<sub>2</sub> to an Fe(II) precursor. Previous studies have advanced our mechanistic understanding of these reactive species and



**Figure 1.** Crystal structure of the cation of **[1-Fe](OTf)<sub>2</sub>** with thermal ellipsoids shown at the 70% probability level. Hydrogen atoms omitted for clarity.

OTf is triflate), as shown in **Figure 1**, in which nearly all of the ligand C-H bonds are aromatic and not likely to be oxidized. From the crystal structure, the average Fe-N bond distance is 1.95 Å, indicative of a low-spin iron complex and consistent with its diamagnetic <sup>1</sup>H NMR spectrum. Addition of terminal oxidant *meta*-chloroperbenzoic acid to a solution of **1-Fe** leads to formation of a new absorption feature with  $\lambda_{\text{max}} = 739 \text{ nm}$  ( $\epsilon = 100 \text{ M}^{-1}\text{cm}^{-1}$ ) that is characteristic of known Fe(IV)-oxo complexes. The presence of this intermediate was confirmed by electrospray ionization-mass spectrometry and its activity was investigated for catalyzing the oxidation of unactivated alkane C-H bonds. Catalysis was observed using model hydrocarbon substrates of cyclohexane, *cis*-1,2-dimethylcyclohexane, and adamantane with C-H bond dissociation energies as high as 100 kcal/mol. Turnover numbers were dependent on the catalyst:oxidant:substrate ratio where higher relative amounts of substrate improved stability. Importantly, the selectivity observed in the oxidation of cyclohexane and adamantane suggest that a metal-centered oxidant is involved in the catalytic process rather than hydroxyl radicals. High selectivities with this catalyst were observed in cyclohexane oxidation resulting in alcohol-to-ketone ratios as high as 7.5, in the stereospecific hydroxylation of *cis*-1,2-dimethylcyclohexane with up to 100% retention of configuration, and in adamantane oxidation where the tertiary C-H bonds were strongly preferred. Indeed, catalyst **1-Fe** has one of the highest reported selectivities for adamantane oxidation among known molecular iron-oxo catalysts with a tertiary-to-secondary C-H bond selectivity ratio of 45. The improved stability of **1-Fe** in hydrocarbon oxygenation is demonstrated by the high conversion yields obtained with respect to added oxidant. These results have been published in the journal *Organometallics*.<sup>1</sup>

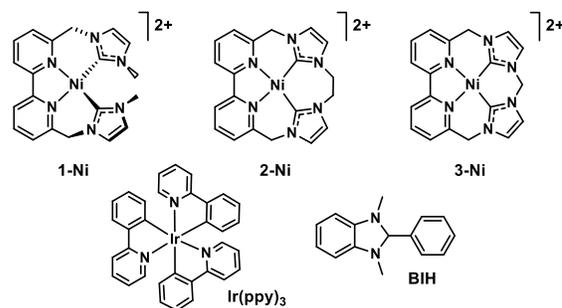
In a second project, a significantly improved synthesis was developed for a novel tetradentate polypyridyl ligand 2,2'-di([2,2'-bipyridin]-6-yl)-1,1'-biphenyl. The ligand is comprised entirely of aromatic rings and features bipyridine donors linked by a rigid 1,1'-biphenyl backbone (**Figure 2**). Our goal was to apply this polyaromatic ligand to iron-catalyzed C-H bond oxidation. We note that



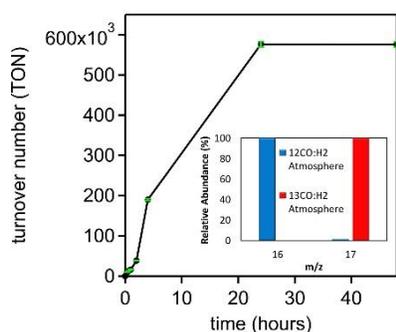
**Figure 2.** Polyaromatic ligand, 2,2'-di([2,2'-bipyridin]-6-yl)-1,1'-biphenyl, and its corresponding iron(II) complex. Crystal structure of the cation shown with thermal ellipsoids rendered at 50% probability level. Hydrogen atoms have been omitted for clarity.

this design strategy is a significant departure from the majority of iron-oxo complexes reported in the literature. However, sluggish reactivity of the resulting iron complex was observed. In order to understand the coordination chemistry of this ligand, a series of complexes were prepared with first-row metals Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II). The structural, electrochemical, spectroscopic, and magnetic properties of the series was investigated and compared to known metal bis(bipyridine) complexes to assess how the limited flexibility of the biphenyl-based ligand affects these properties. The copper and zinc complexes possess five-coordinate geometries while the remaining complexes were octahedral with their coordination spheres completed by acetonitrile and an anion. Interestingly, high-spin electronic states were observed for the Mn(II), Fe(II), and Co(II) complexes despite the typically strong-field bipyridine donors. For comparison to **1-Fe**, the average metal-ligand bond distance in this Fe(II) complex (**Figure 2**) is 2.17 Å. Variable-temperature solid-state SQUID magnetometry was performed on this iron complex as well as a bis(isothiocyanato) derivative where it was found that the compounds remain high-spin over the entire temperature range. These results suggest that, in addition to weakening the ligand field around the metal ion, the ligand may be less accommodating to the shorter metal-ligand bond distances that would be expected of a low-spin electronic state. These results have been reported in *New Journal of Chemistry*.<sup>2</sup>

In a third project, a series of nickel bipyridyl-*N*-heterocyclic carbene (NHC) complexes was evaluated under various conditions for photocatalytic CO<sub>2</sub> reduction (**Figure 3**). The relationship between structure and activity was probed as **1-Ni** has a non-macrocyclic supporting ligand and **2-Ni** and **3-Ni** are supported by tunable macrocycles in which the alkyl-bridge between NHC donors is varied from ethyl (**2-Ni**) to methyl (**3-Ni**). Using water as a co-solvent, we found that **2-Ni** is the most selective catalyst from the series for photocatalytic CO<sub>2</sub> reduction. CO, H<sub>2</sub>, and CH<sub>4</sub> are observed as products. The formation of CH<sub>4</sub>, an 8e<sup>-</sup>/8H<sup>+</sup> reduction product, is remarkable. Initially methane is not evolved. At early times, CO and H<sub>2</sub> are produced as detected intermediate products which are consumed later as CH<sub>4</sub> is generated. Both CO and H<sub>2</sub> were found to be critical for significant methane production as revealed by carbon-13 and deuterium labeling studies using <sup>13</sup>CO (**Figure 4**) and D<sub>2</sub> gas (not shown), and in experiments varying the atmospheric components in the headspace of photocatalytic reactions. In reactions with a 1:1 CO:H<sub>2</sub> atmosphere, over half a million (570,000) turnovers for CH<sub>4</sub> production were achieved with **2-Ni** at low catalyst concentrations. CO<sub>2</sub> reduction to CH<sub>4</sub> thus proceeds by a photodriven formal hydrogenation of CO. The mechanism of C-H bond formation in this system is the subject of ongoing mechanistic studies. High selectivity for carbon-based reduction was also observed under a CO<sub>2</sub> atmosphere in anhydrous conditions with 310,000 turnovers for evolved CO. These are extraordinary values for a molecular catalyst, and this work was recently reported in *Journal of the American Chemical Society*.<sup>3</sup>



**Figure 3.** Studied catalysts **1-Ni**, **2-Ni**, and **3-Ni** with photosensitizer Ir(ppy)<sub>3</sub> and sacrificial electron donor BIH.



**Figure 4.** CH<sub>4</sub> production over time with **2-Ni** at 2 nM concentration under a 1:1 CO:H<sub>2</sub> atmosphere. The bar graph inset depicts the mass spectrometry results of a pair of photoreactions with <sup>13</sup>CO and <sup>12</sup>CO.

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