

Elucidating Oxidation States of Metal Complexes with Redox Active Ligands

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The properties of metal complexes are the result of the interaction between metal centers and their surrounding ligands. In traditional systems, ligands usually play a spectator role, serving to influence the reactivity, selectivity, and electronic properties of the metal center but, ultimately, not directly participating in chemical reactions. However redox-active ligands, also called redox non-innocent ligands, can interact in a cooperative fashion with the metal center to facilitate chemical transformations. Due to the energies of their frontier orbitals, redox-active ligands can be easily oxidized or reduced.^{1, 2, 3}

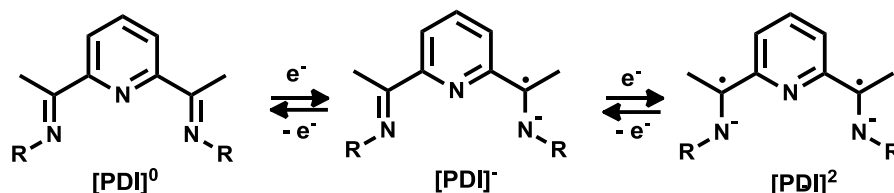


Figure 1. Chirik's redox-active ligand- bis(imino)pyridine

Redox active ligands are especially useful in tandem with first row transition metals. Whereas second and third-row transition metals readily undergo two-electron processes such as oxidative addition and reductive elimination, the first-row transition metals favor one-electron pathways. In catalytic cycles, such one-electron events can generate radical intermediates that often evolve non-selectively to products. The use of redox-active ligands serves as an effective way to circumvent this difficulty, providing the extra electrons necessary to influence two-electron transformations even with first-row transition metals.³

Chirik's bis(imino)pyridine (PDI) is an especially good example of a redox-active ligand (Figure 1). The singly and doubly reduced bis(imino)pyridine redox states are readily accessible, so that this ligand can serve as an electron sink (oxidant) or electron source (reductant) in chemical reactions.⁴ For example, when it is attached in its dianionic form to iron(II), two-electron oxidative addition of biphenylene results in oxidation to the radical ligand PDI^{•-} and Fe(III) (Figure 2). This example demonstrates the ability of redox active ligands to facilitate a two-electron process while preserving the formal one-electron events characteristic of iron.⁵

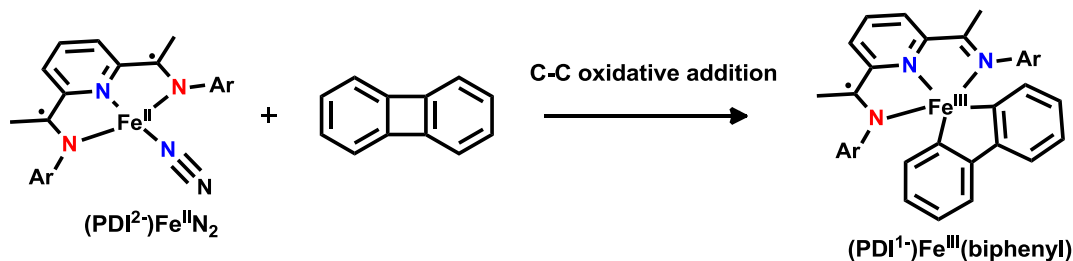


Figure 2. Oxidative addition of biphenylene with bis(imino)pyridine iron complex

Additional examples with the bis(imino)pyridine iron complex demonstrate the generality of this redox-active approach to achieve two-electron transformations with first-row metals. In the proposed mechanism shown below (Figure 3), the redox active ligand intermediate undergoes a one-electron reduction to become the radical anion while the iron center is oxidized from Fe(I) to Fe(III). This mechanism avoids Fe(0) intermediates, which potentially can decompose by chelate dissociation and formation of metallic iron. Moreover, Fe(III) favors sp^3 - sp^3 C–C reductive elimination over competing processes, such as β -hydrogen elimination, relative to the Fe(II) analogue.^{6,7,8}

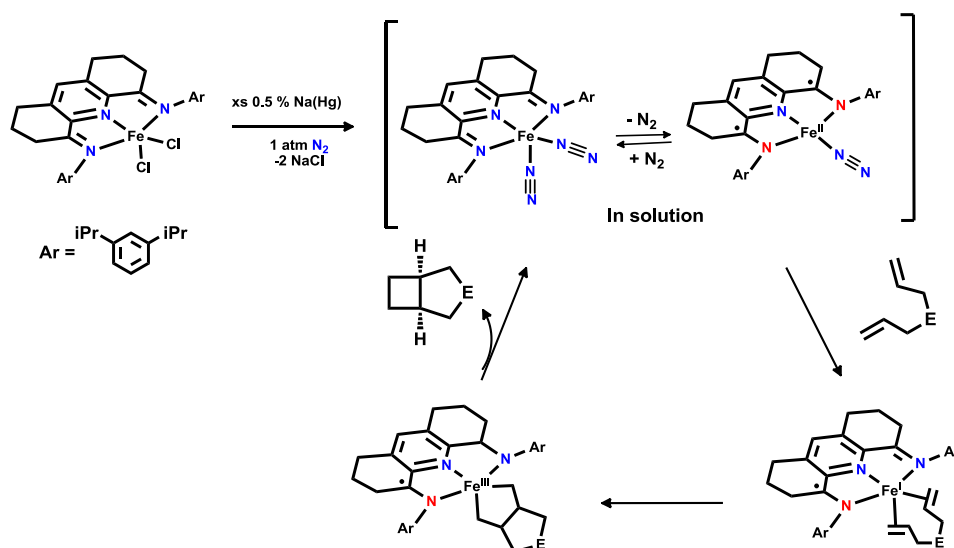


Figure 2. Cycloaddition with bis(imino)pyridine iron complex

These reports clearly establish the utility of redox-active ligands, particularly with first-row metals such as iron. Nevertheless, much remains to be explored. Future studies elucidating relevant mechanisms and oxidation states will undoubtedly improve our understanding of such systems, providing the insights needed to develop powerful and improved alternatives to noble metal catalysts.

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