

## Recent Advances in Metal-Mediated Nitrogen Transfer

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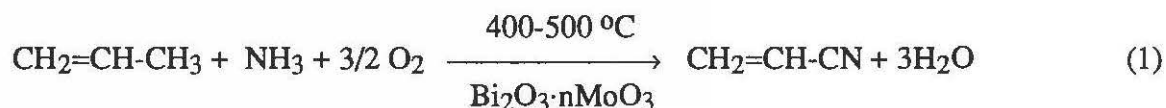
Literature Seminar

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Compared to metal-mediated oxygen transfer reactions, metal-mediated nitrogen transfer reactions are relatively rare. One of the goals in developing and understanding metal-mediated nitrogen transfer reactions is the possible utility of these reactions in improving existing preparations of various organic compounds. Some of these desired products include hydroxyamines, bisamines, imines, enamines aziridines, and nitriles.

Since the 1970's, Sharpless and coworkers have developed many different methods for the hydroxyamination and the diamination of olefins using osmium(VIII) reagents [1,2,3]. However, little is understood about the mechanism of these reactions. These nitrogen transfer reactions also suffer from other limitations. For example, in the earlier oxyamination reactions, a stoichiometric amount of the osmium reagent is required [1]. Metal-assisted aziridination reactions have also been developed in the last twenty years [4,5]. The mechanism of these reactions are also relatively unknown, however [4,5].

Acrylonitrile is used extensively in the polymer industry as a monomer for various fibers and plastics. Approximately eight billion pounds of acrylonitrile is produced annually world wide, almost all of which is produced catalytically by a process called ammoxidation [6]. In ammoxidation, propylene, ammonia, and air ( $O_2$  source) are passed over a bismuth molybdate heterogeneous catalyst and acrylonitrile is obtained in 65% yield (equation 1) [6].



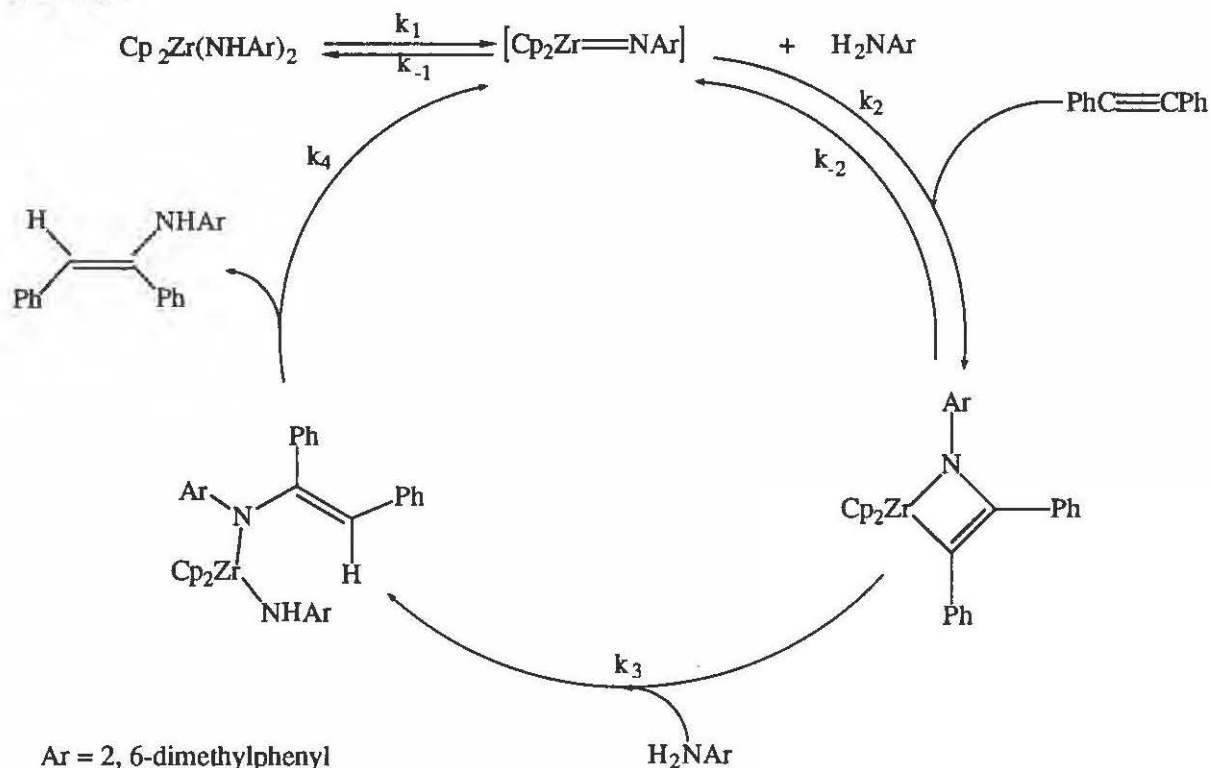
The relatively low yield of the ammoxidation process compared to the analogous oxo-transfer reaction in which acrolein is produced by the oxidation of propylene has stimulated intense effort to understand the mechanism of ammoxidation in the hopes of improving this procedure. However, due to the complex nature of the heterogeneous catalyst surface, researchers have resorted to synthesizing homogeneous models to elucidate the mechanism of ammoxidation [7,8,9].

Various high oxidation state molybdenum and tungsten imido complexes have been synthesized and studied to learn more about the ammoxidation mechanism [7,8,9,10,11]. The imido groups on Mo(VI) have been found to transfer to aldehydes as nucleophiles in Wittig-like reactions to form imines [10].

While Mo(VI) and W(VI) imido complexes are relatively abundant, they usually exhibit little reactivity at the imido functional group. On the other hand, before 1988 there were no known monomeric metallocene imido complexes of the group IV metals [13]. Several researchers reasoned that if these group IV metallocene imido complexes could be synthesized, they might exhibit some unique reactivity. Doxsee and coworkers have synthesized a titanocene vinylimido complex which react with nitriles and ketones to form nitrogen-metal heterocycles, which can then be hydrolyzed to produce hydroxyketones and ketoenamines [12].

More recently, Bergman and coworkers have observed a transient zirconocene imido complex,  $[\text{Cp}_2\text{Zr}=\text{NAr}]$ , (Ar = 2, 6 dimethylphenyl), which they speculate is involved in the catalytic cycle of the hydroamination of diphenylacetylene to the corresponding enamine (Scheme I) [14]. This imido complex is generated by  $\alpha$ -elimination from the bisamide complex,  $\text{Cp}_2\text{Zr}(\text{NHAr})_2$ , and can be trapped as the THF-adduct,  $\text{Cp}_2\text{Zr}=\text{NAr}(\text{THF})$ . This zirconocene imido is unreactive towards olefins but reacts with alkynes to form the corresponding azametallacyclobutane.

Scheme I



McElwee-White and coworkers have reported a tungsten nitrene complex that is reactive towards both nucleophiles and electrophiles [20]. Electrophiles such as carbonyl compounds react with  $(\text{CO})_5\text{W}=\text{NPh}$  in a  $[2 + 2]$  fashion to form  $(\text{CO})_5\text{W}=\text{O}$  and the corresponding methyl imine. Nucleophiles, such as triphenylphosphine, react at nitrogen to form the zwitterionic complex  $(\text{CO})_5\text{W}^--\text{N}(\text{Ph})(^+\text{PPh}_3)$  [20]. The ambiphilic properties of this transient nitrene complex not only make it a novel compound but also more versatile in its nitrogen transfer reactions.

Metal-mediated nitrogen transfer is not only of interest from a pure science perspective, but a better understanding of these phenomena could lead to improved synthetic procedures for many commonly used organic substrates. Much progress has been made in the past decade to widen the scope of metal-mediated nitrogen transfer research and to gain a better understanding of the mechanisms involved.

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