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Catalytic Reactivity of a Zirconium(IV) Redox-Active Ligand Complex with 1,2-Diphenylhydrazine

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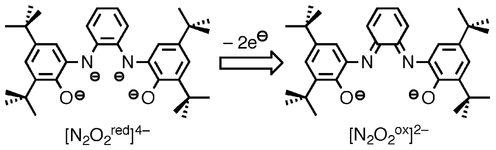
Hydrazine reactions with transition metals have implications for industrially important organic synthesis applications and can be informative substrates for modeling the metal-mediated reduction of nitrogen to ammonia.[1] Under oxidizing conditions, hydrazines can be converted into azo molecules with an N═N bond that is useful in electronic and materials applications.[2] Azobenzene formation via disproportionation of 1,2-diphenylhydrazine is favored thermodynamically (−14.6 kcal mol^{-1});[3] however, a metal catalyst with two-electron valence states is typically required to promote the reaction. Although this reaction can be viewed as a transfer hydrogenation, metal imides are often implied or even observed as intermediates in the catalytic cycle, which proceeds via a hydrogen-atom abstraction step.[4]

This Communication reports a new type of catalyst for the two-electron disproportionation of diphenylhydrazine to azobenzene and aniline. The results presented here are noteworthy because the metal catalyst relies on two-electron valence changes that occur at a redox-active ligand rather than at the metal center. It has been shown that redox-active amidophenolate ligands can provide the reducing equivalents for the two-electron oxidative addition of halogens to tetravalent zirconium centers with a formal d^0 electron count.[5] Similar zirconium complexes with redox-active diamide ligands participate in four-electron reactivity with oxygen.[6] Ligand-enabled, two-electron reductive elimination of C−C bonds has also been demonstrated for redox-active amidophenolate ligands;[7] however, further development of these reactions has been thwarted by complicated ligand exchange processes.[8] Herein, we report the zirconium chemistry of a tetradentate, tetraanionic, bis(amidophenolate) ligand, *N*,*N′*-bis(3,5-di-*tert*-butyl-2-phenoxy)-1,2-phenylenediamide, $[N_2O_2^{red}]^{4-}$.[9] Halogen oxidative-addition reactivity established the two-electron redox reactivity of $[N_2O_2^{red}]ZrL_3$ (**1a**, L = THF). Complex **1a** also was found to catalyze the disproportionation of 1,2-diphenylhydrazine to aniline and azobenzene. A two-electron oxidized $[N_2O_2^{ox}]$Zr-imido species is implicated as an intermediate in the disproportionation reaction.



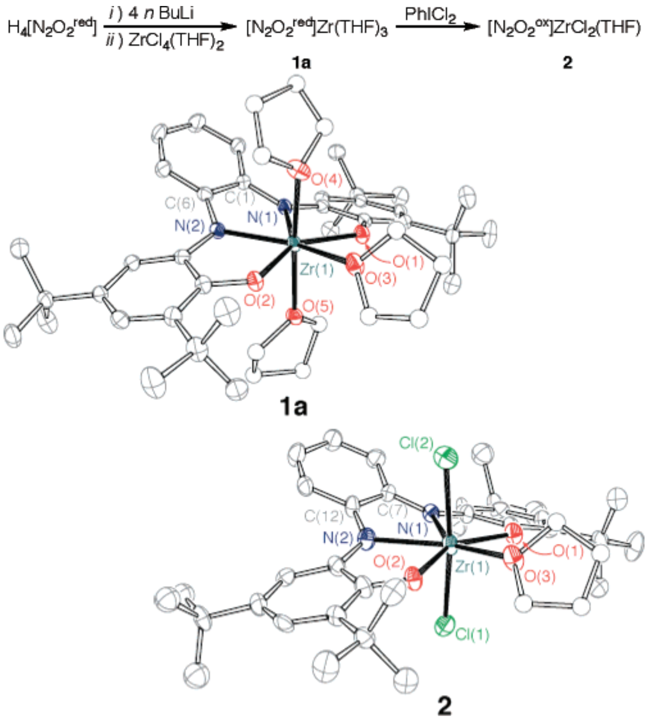


Figure 1. Synthesis and ORTEPs for $[N_2O_2^{red}]ZrL_3$ (**1a**, L = THF) and $[N_2O_2^{ox}]ZrCl_2(THF)$ (**2**). Thermal ellipsoids are shown at 50% probability. Solvent molecules and hydrogen atoms have been removed for clarity.

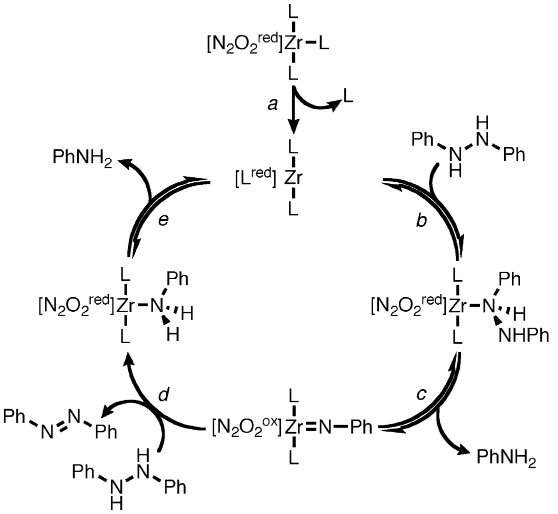
Metalation of $[N_2O_2^{red}]^{4-}$ with $ZrCl_4(THF)_2$ proceeded smoothly to form **1a** according to the strategy summarized in Figure 1. Zirconium complex **1a** was obtained as a bright-yellow, microcrystalline solid. X-ray quality single crystals were obtained from diethylether solutions chilled to −35 °C and yielded the seven-coordinate structure shown as an ORTEP in Figure 1. The tetradentate ligand occupies four equatorial positions of a pentagonal bipyramid. The bite angles within the ligand are small (∼72°), leaving the oxygen−zirconium−oxygen angle large at 143.28(14)°. This open angle provides room for the coordination of one THF molecule in the equatorial plane in addition to the two axial THF molecules. NMR spectroscopy indicates that the solid-state structure is largely preserved in solution. Sharp ligand resonances, consistent with C_{2v} symmetry, were observed in the ^{1}H NMR spectrum along with broad resonances for the coordinated THF molecules.

Oxidation of **1a** with $PhICl_2$ occurred rapidly at −35 °C, resulting in an immediate color change from pale yellow to intense forest green. Crystals of $[N_2O_2^{ox}]ZrCl_2(THF)$, **2**, suitable for X-ray crystallography were grown from ether/pentane solutions of the complex. As shown in Figure 1, the two axial positions are occupied by chloride ligands introduced upon oxidation. The tetradentate ligand and one THF molecule comprise the equatorial plane of the zirconium. The ligand oxidation state can be determined from metrical parameters.[9] Notably, a long C(7)−C(12) distance of 1.455(9) Å and short C−N distances of 1.347(11) and 1.333(12) Å are indicative of the cyclohexadiene-diimine oxidation state depicted for $[N_2O_2^{ox}]^{2-}$. The ligand backbone ^{1}H NMR resonances for **2** in C_6D_6 shifted upfield by 0.5 ppm to 7.52 and 6.35 ppm, consistent with a cyclohexadiene-diimine oxidation state. A broad and intense absorbance at λ_{max} = 945 nm (ϵ = 20,800 M^{-1} cm^{-1}) in the UV−vis spectrum of **2** is responsible for the dark-green color observed for the complex.[9]

Complex **1a** reacted with 1,2-diphenylhydrazine at room temperature to afford azobenzene and aniline.[10] Addition of 2 equiv

10.1021/ja710611v CCC: $40.75

Scheme 1



of 1,2-diphenylhydrazine to a yellow solution of **1a** resulted in an immediate color change to dark green. Upon completion of the reaction the color change lightened to orange. The ^{1}H NMR spectrum of the final mixture revealed 1 equiv of azobenzene, 2 equiv of aniline, and $[N_2O_2^{red}]ZrL_3$ (**1b**, L = NH_2Ph). GC−MS confirmed the identity and quantities of the organic products. Increased equivalents of 1,2-diphenylhydrazine led to longer reaction times but yielded the same product ratios. Thus, 10 equiv of hydrazine yielded 5 equiv of azobenzene and 10 equiv of aniline after 1 day. Reactions with 100 equiv of 1,2-diphenylhydrazine were completed in 6 days.

$$2\text{PhHN}-\text{NHPh} \xrightarrow{\mathbf{1}} \text{PhN}{=}\text{NPh} + 2\text{NH}_2\text{Ph}$$

Preliminary experiments to elucidate the mechanism of the 1,2-diphenylhydrazine reaction have been conducted. Concentration-dependence studies suggest that the reaction rate is first order in **1** and first order in 1,2-diphenylhydrazine. Reactions carried out at 0.04 M **1** gave a pseudo-first-order k_{obs} of $4.5(7) \times 10^{-5}$ s^{-1}. Whereas reactions carried out under an H_2 atmosphere did not change the ratio of azobenzene to aniline products, reactions carried out in the presence of excess 9,10-dihydroanthracene afforded aniline and anthracene with minimal azobenzene. These results suggest that azobenzene is formed by H-atom abstraction rather than by H_2 elimination; however, reactions carried out with 1,2-diphenylhydrazine-d_2 yielded only a small kinetic isotope effect of 1.25. Finally, the addition of excess aniline did not measurably inhibit the disproportionation reaction, but no reaction occurred if THF was used as the reaction solvent or in the presence of pyridine.

On the basis of the mechanistic studies above and the well-established H-atom abstraction chemistry of metal imidos and metal oxos,[11] we propose the catalytic cycle shown in Scheme 1, the key species being a $[N_2O_2^{ox}]Zr({=}NPh)L_2$ oxidant formed in step c.[12] This proposal is supported by the development of a dark-green solution and a UV−vis absorbance at $\lambda_{max} = 739$ nm during the reaction. Furthermore, **1a** reacted rapidly with the nitrene transfer reagent (p-tolyl)N_3 to release N_2 and give a similar green solution. Though the putative zirconium-imido complex could not be isolated from this reaction, in the presence of 1,2-diphenylhydrazine it reacted further to release (p-tolyl)NH_2 and azobenzene.

A Zr═NPh intermediate could be formed in two ways (step c). After coordination of 1,2-diphenylhydrazine to **1**, an α,β-NH elimination of aniline could form the imide directly. This path is analogous to the heterolytic activation of a peroxide O−O bond by a transition metal.[13] Alternatively, the imide could be formed by N−N oxidative addition[14] followed by 1,2-NH elimination from the resulting zirconium bis(amide) complex.[15] We do not favor this path because we have seen no evidence for N−N oxidative addition reactivity with hydrazines such as Me_2N-NMe_2 and 1-dimethylaminopyrrole; however, we cannot rule out a reversible oxidative addition followed by fast 1,2-NH elimination to generate the zirconium imido species.

Complex **1** is the first example of a d^0 metal complex that catalyzes a multielectron reaction through the use of ligand-based valence changes. While the disproportionation of 1,2-diphenylhydrazine is thermodynamically favorable, there are few examples of catalysts for this reaction.[16] In the case of **1**, the electrophilic properties of the zirconium center coupled with the redox properties of the ligand enable catalytic turnover in the system. Further studies are required to determine if auxiliary reagents can be used to realize selective N−N oxidations or reductions.

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Supporting Information Available: Detailed experimental procedures, characterization data for **1a** and **2**, X-ray diffraction data, and further discussion of reactive oxidizing species. This material is available free of charge via the Internet at http://pubs.acs.org.

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