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Reductive N−N Bond Cleavage of Diphenylhydrazine and Azobenzene Induced by Coordinatively Unsaturated $Cp^*Fe\{N(SiMe_3)_2\}$

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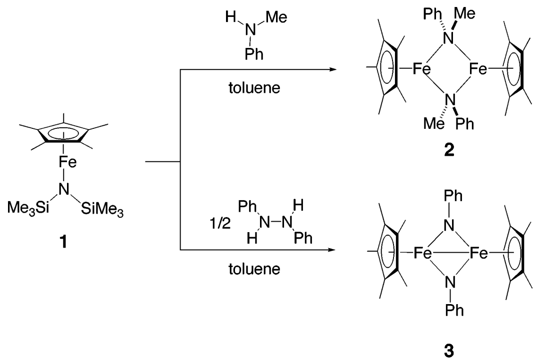
*Summary: The coordinatively unsaturated iron(II) amido complex $Cp^*Fe\{N(SiMe_3)_2\}$ (**1**) serves as an efficient precursor for the cleavage of the N−N bond of diphenylhydrazine. The N=N bond of azobenzene was also found to be activated by **1** in the presence of pinacolborane.*

The unique structures and function of nitrogenase active sites have inspired chemists to synthesize molecular models capable of cleaving N−N bonds.[1] Iron is a common transition element to the active sites of MoFe-, VFe-, and Fe-nitrogenases,[2] and thus reactions of iron toward nitrogenase-related substrates such as N_2, hydrazines, and azo compounds are of interest. Various dinitrogen complexes of iron have been synthesized,[3,4] and $Fe(DMeOPrPE)_2(N_2)$ (DMeOPrPE = 1,2-bis(bis(methoxypropyl)phosphino)ethane), which was spectroscopically characterized in solution, was recently demonstrated to promote the partial conversion of the iron-bound N_2 to $N_2H_5^+$ and ammonium cation.[4e] Whereas the N−N bond cleavage of hydrazines has been known to occur with early-transition-metal complexes and some ruthenium complexes,[5] there have only been a few examples of such reactions induced by iron.[6] We became interested in the activation of N−N and N=N bonds by organometallic iron complexes, in connection with our studies on modeling the active sites of nitrogenase.[7] We herein report that a coordinatively unsaturated monomeric iron(II) amido complex reported by Siemeling et al, $Cp^*Fe\{N(SiMe_3)_2\}$ (**1**),[8] serves as an efficient precursor for the cleavage of N−N bond of diphenylhydrazine. The N=N bond of azobenzene was also found to be activated by **1** in the presence of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane).

Scheme 1



Bis(trimethylsilyl)amide on transition metals is known to serve as a base. Indeed, treatment of $Cp^*Fe\{N(SiMe_3)_2\}$ (**1**) with 1 equiv of *N*-methylaniline gave rise to a dimeric methylphenylamido complex, $Cp^*_2Fe_2(\mu\text{-}NMePh)_2$ (**2**), in 79% yield via deprotonation of methylaniline (Scheme 1). Complex **2** is paramagnetic at ambient temperature, and the ^1H NMR spectrum features by broad signals at δ 91.7 (Cp*), at δ 72.1 (N−Me), and at δ 84.6, −28.8, and −33.7 (N−Ph). The X-ray diffraction study confirmed the formulation of **2** as shown in Figure 1 (left).[9] Complex **2** has an inversion center at the midpoint between the two iron atoms, and the amide nitrogens and irons are crystallographically coplanar. The Fe−Fe distance is 2.7925(8) Å, and the Fe−N distances (2.063(4) and 2.087(4)

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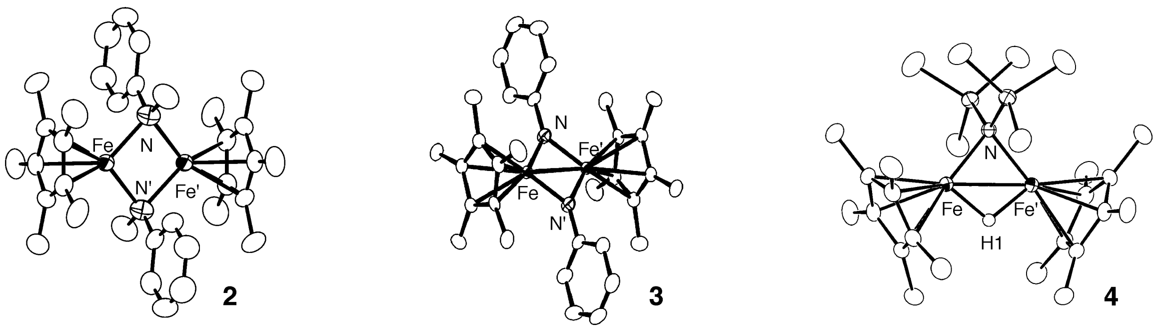
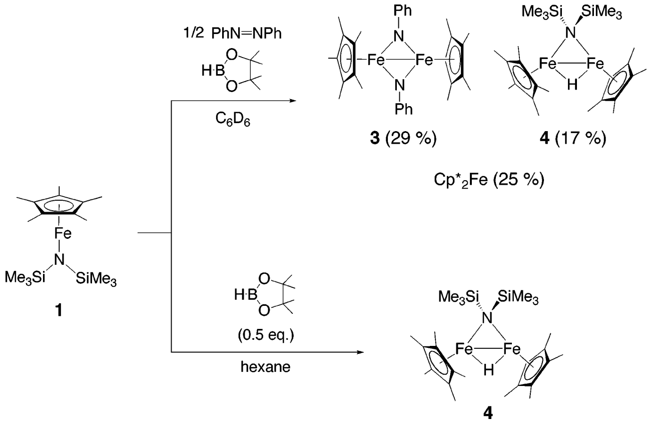


Figure 1. Molecular structures of **2**−**4**, with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): **2**, Fe−Fe′ = 2.7925(8), Fe−N = 2.063(4), Fe−N′ = 2.087(4), Fe−N−Fe′ = 84.58(19); **3**, Fe−Fe′ = 2.4389(5), Fe−N = 1.804(1), Fe−N′ = 1.807(1), Fe−N−Fe′ = 84.99(5); **4**, Fe−Fe′ = 2.5353(6), Fe−N = 1.979(2), Fe−N−Fe′ = 79.69(9).

Scheme 2



Å) are similar to those in the related amido-bridged complexes of iron(II).[10]

Interestingly, when **1** was reacted with 1,2-diphenylhydrazine, not only deprotonation of hydrazine but also N−N bond cleavage took place. Addition of 1,2-diphenylhydrazine into a toluene solution of **1** led to a dark brown solution, from which the dinuclear ferric imido complex Cp*$_2$Fe$_2$(μ-NPh)$_2$ (**3**) was obtained in 59% yield as a brown solid (Scheme 2). The X-ray-derived molecular structure is given at the center of Figure 1. Complex **3** is diamagnetic according to the ^{1}H NMR spectrum, and the two iron(III) centers are magnetically coupled through the short Fe−Fe (2.4389(5) Å) bond. The bridging imido nitrogens donate π-electrons into the vacant Fe dπ orbitals perpendicular to the Fe$_2$N$_2$ plane, and the consequence is the very short Fe−N distance (1.804(1), 1.807(1) Å). The reaction to give **3** was presumably initiated by a deprotonation step of diphenylhydrazine with 2 equiv of **1**, and the N−N bond cleavage could have proceeded via the resulting azobenzene-bridged dinuclear intermediate Cp*$_2$Fe$_2$(μ-N$_2$Ph$_2$) (**A** in Scheme 3). The related dinuclear iron fragments have been reported to bind hydrazines, azobenzene, and molecular nitrogen.[4,11] The cooperation of two iron centers must be important for both substrate binding and successive N−N bond cleavage, because two electrons are needed for the reductive cleavage of hydrazine. The requirement of multiple iron centers is of possible relevance to the proposal that multiple iron centers could be the site of N$_2$ activation,[12] whereas the possibility of molybdenum-coordinated N$_2$ is also described.[13]

The isolation of **3** prompted us to examine activation of the N═N bond of azobenzene by **1**. It was anticipated that azobenzene would not be activated by **1** alone, because unlike the case for diphenylhydrazine there are no protons in azobenzene to react with the amide of **1**. In fact, treatment of **1** with azobenzene ended up with mere recovery of the reactants. We sensed that azobenzene might be activated if external proton or Lewis acid generates "Cp*Fe" or "Cp*$_2$Fe$_2$" from **1** as a reactive moiety, in light of the possible intermediate **A** for the reaction between **1** and diphenylhydrazine to give **3**. Thus, we carried out an NMR-tube experiment in benzene-d_6 for the reaction of **1** with azobenzene in the presence of 1 equiv of pinacolborane (HBpin), to find that **3** was generated in 29% yield. Unfortunately, this reaction is not very clean, and Cp*$_2$Fe$_2$(μ-H){μ-N(SiMe$_3$)$_2$} (**4**) and Cp*$_2$Fe were also detected in 17% and 25% yields, respectively. Since the solubility of **3** in common organic solvents is similar to that of **4** and Cp*$_2$Fe, isolation of **3** from the reaction mixture has not been successful. Nonetheless, it is interesting to find that **1** can act as a precursor of active species for the N═N bond cleavage of azobenzene.

To verify the formation of the dinuclear hydride/amide **4**, the amide complex **1** was treated with 1/2 equiv of HBpin. From this reaction, **4** was isolated as dark brown crystals in 24% yield, and its crystal structure was determined. As shown in Figure 1 (right), two iron atoms of **4** are bridged by one amide and one hydride with an Fe−Fe distance of 2.5353(6) Å, where the Fe−N distance (1.979(2) Å) is between those of **2** and **3**. The formation of **4** indicates that HBpin served as a hydride source to replace the amide of **1**,[14] generating the aminoborane (Me$_3$Si)$_2$N−Bpin and the putative hydride compound "Cp*FeH",

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(9) Crystal data for **2**: triclinic, $P\bar{1}$, $a = 10.349(8)$ Å, $b = 12.101(4)$ Å, $c = 12.420(3)$ Å, $\alpha = 91.378(10)°$, $\beta = 90.12(6)°$, $\gamma = 99.34(4)°$, $V = 1534.3(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.287$ g cm^{-3}, 6745 reflections ($2\theta \leq 55°$), 5290 observed with $F > 2\sigma(F)$, 333 parameters, $R = 0.083$, $R_w = 0.110$, GOF = 1.47. Crystal data for **3**: monoclinic, $C2/c$, $a = 17.794(3)$ Å, $b = 11.639(2)$ Å, $c = 13.517(2)$ Å, $\beta = 93.709(2)$, $V = 2793.6(7)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.330$ g cm^{-3}, 3184 reflections ($2\theta \leq 55°$), 3151 observed with $F > 0\sigma(F)$, 163 parameters, $R = 0.030$, $R_w = 0.036$, GOF = 1.31. Crystal data for **4**: orthorhombic, $Fddd$, $a = 20.681(3)$ Å, $b = 22.191(3)$ Å, $c = 25.607(3)$ Å, $V = 11751.4(2)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.229$ g cm^{-3}, 3377 reflections ($2\theta \leq 55°$), 3361 observed with $F > 0\sigma(F)$, 142 parameters, $R = 0.046$, $R_w = 0.047$, GOF = 0.90.

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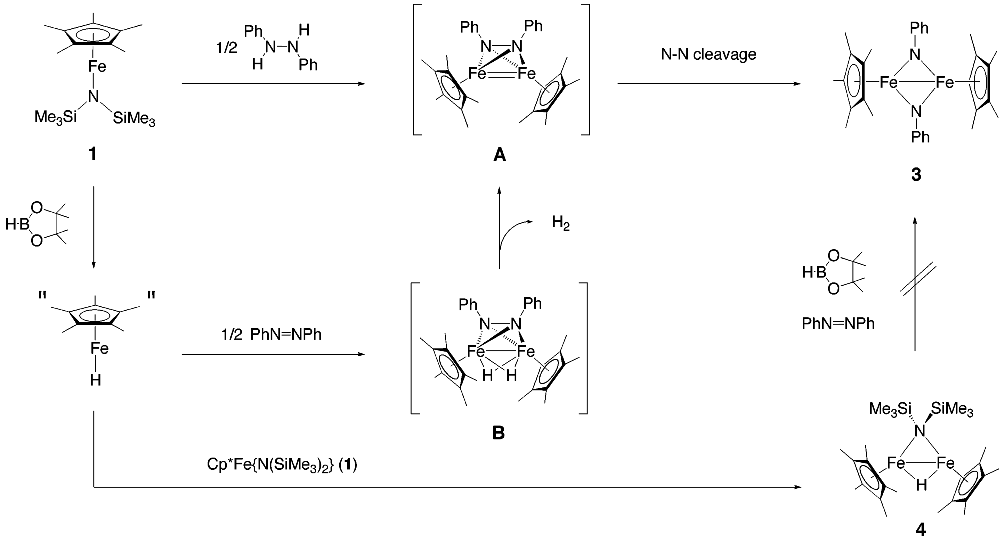
Scheme 3



which then reacted with the remaining **1** to give the dinuclear complex **4**. The formation of $(Me_3Si)_2N-Bpin$ was confirmed by a ^1H NMR spectrum in benzene-d_6, where the methyl signals of aminoborane appeared at δ 1.03 and 0.32. Complex **4** was found not to react with azobenzene.

Taking the above results into consideration, we propose a possible mechanism for the N═N bond cleavage of azobenzene promoted by **1** and HBpin. As is the case of the reaction between **1** and 1/2 equiv of HBpin to give **4**, the N═N activation reaction probably proceeds by way of the hydride species "Cp*FeH" or its dimerized form "$Cp^*{}_2Fe_2(\mu\text{-}H)_2$", which may be stabilized with azobenzene, solvent, or aminoborane. The hydride complex, in either a monomeric or a dimeric form, would take up azobenzene, leading probably to the azobenzene/hydride-bridged dinuclear intermediate $Cp^*{}_2Fe_2(\mu\text{-}H)_2(\mu\text{-}N_2Ph_2)$ (**B**). Reductive elimination of H_2 from **B** supplies two electrons to the dinuclear iron center, giving rise to $Cp^*{}_2Fe_2(\mu\text{-}N_2Ph_2)$ (**A**), which may in turn facilitate the reductive cleavage of the N═N bond. The observation of a singlet signal at δ 4.45 in the NMR experiment indicates the formation of H_2, whereas a quantitative analysis was not available. As mentioned earlier in this paper, **A** is also a possible intermediate in the reaction of **1** with diphenylhydrazine.

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Supporting Information Available: Text, a table, and CIF files giving details of the synthesis and characterization and crystallographic data for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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