Communication

Nitrogenase Model Complexes [Cp*Fe(μ-SR)(μ-#-RN#NH)FeCp*] (R = Me, Et; R = Me, Ph; Cp* = #-CMe): Synthesis, Structure, and Catalytic N#N Bond Cleavage of Hydrazines on Diiron Centers

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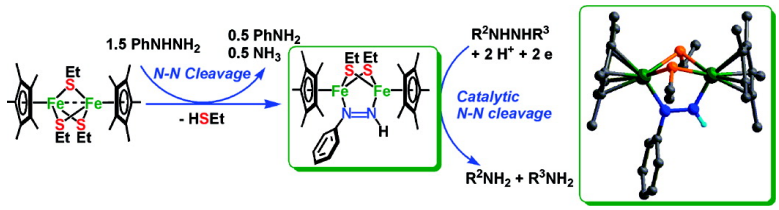

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Nitrogenase Model Complexes [Cp*Fe(μ-SR^1)$_2$(μ-η^2-R^{2}N=NH)FeCp*] (R^1 = Me, Et; R^2 = Me, Ph; Cp* = η^5-C$_5$Me$_5$): Synthesis, Structure, and Catalytic N−N Bond Cleavage of Hydrazines on Diiron Centers

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The research on the structure and function of nitrogenases constitutes a major task in chemistry and biochemistry, because of their remarkable roles on biological transformation of N_2 to NH_3 under ambient conditions.[1] Although the structure of FeMoco has been elucidated by single-crystal X-ray diffraction analysis in recent years,[2] precisely where and how the N_2 interacts with the FeMoco is still unclear. Two essentially different assumptions on the active site for N_2 conversion have been proposed: one is at single molybdenum or iron center,[3] and the other is at di(multi)-iron centers. However, compared with the enormous studies on N_2, diazenes and hydrazines at the single atom center,[4] those at the di(multi)-iron centers, especially iron sulfur clusters, are relatively rare, mainly because of the difficulties in obtaining stable intermediate model complexes bearing N_2, diazenes, and hydrazines.[5] Thus, the reactions of N_2, diazenes, and hydrazines mediated by the di(multi)-iron centers bearing sulfur ligands are of particular interest.

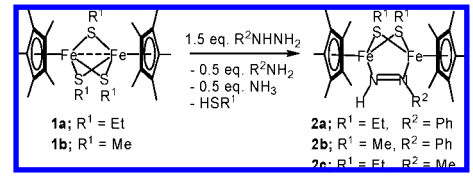
Recently, Holland et al. reported a sulfide-bridged diiron complex with a bridging phenylhydrazido ligand, and found the cleavage of N−N single bond of phenylhydrazine.[6] Sellmann et al. previously reported some diazene diiron sulfur complexes in which the HN=NH ligand bridges the two isolate monoiron sulfur units.[7] However, the diiron sulfur (thiolate)-bridged complex with diazenes ligand and its roles in catalytic cleaving N−N bond of nitrogenase substrates, such as diazenes and hydrazines, have never been explored. Here, we report the synthesis and characterization of a class of new nitrogenases model complexes [Cp*Fe(μ-SR^1)$_2$(μ-η^2-R^{2}N=NH)FeCp*] (Cp* = η^5-C$_5$Me$_5$; **2a**, R^1 = Et, R^2 = Ph; **2b**, R^1 = Me, R^2 = Ph; **2c**, R^1 = Et, R^2 = Me), together with their excellent catalytic N−N bond cleavage of hydrazines on diiron centers under ambient conditions.

The reaction of complex [Cp*Fe(μ-SEt)$_3$FeCp*] (**1a**)[8] with 1.5 equiv $PhNHNH_2$ in THF at 60 °C for 36 h gives a μ-η^2-phenyldiazene diiron thiolate-bridged **2a**, along with the formation of $PhNH_2$ and NH_3. Complex **2a** is isolated as brown microcrystalline solid in 86% yield. Analogous complexes, **2b** and **2c**, are obtained similarly (Scheme 1). These complexes have been characterized by ^{1}H NMR[9] and IR spectroscopy, element analysis, and single-crystal X-ray diffraction.

The ^{1}H NMR spectrum of **2a** exhibits a singlet with the intensity of 1 H in low field (δ = 13.19), which is the characteristic of proton attached to the η^1-N atom in phenyldiazene ligand.[10] The IR spectrum of **2a** (KBr) shows the ν(N−H) band at 3216 cm^{-1}.[10a] ^{1}H NMR spectra of complexes of **2b** and **2c** (Supporting Information, Figures S3 and S4) are also consistent with their structures. The solid-state structure of **2a** is shown in Figure 1.

Complex **2a** consists of a di(μ-thiolate)diiron unit Cp*Fe(μ-SEt)$_2$FeCp* bridged by a bidentate HN=NPh group, which is σ-bonded to the Fe$_2$ through two nitrogen atoms (Fe1−N1 = 1.89 Å, Fe2−N2 = 1.83 Å). The N−N and Fe−Fe bonds are essentially coplanar, with N1−Fe1−Fe2−N2 torsion angle of 1.78°. The N1−N2 bond length of 1.33 Å is in the range of the N=N double bond.[10b,11] The solid-state structure of **2c** shows an analogous structure of **2a** except a symmetrical mirror plane through S1, S2 atom, and the center of N1 and N2 atoms causing a disorder in crystallography (Figure S20). Such a coordination geometry with the bidentate N=N group bonding to two iron atoms in iron sulfur cluster suggests a new nitrogenase model. In the FeMoco, the six "belt" iron atoms appear to be distorted from tetrahedral toward a trigonal pyramidal geometry with the average pyramidalization parameter τ = 0.46 ± 0.03,[6a] the iron atoms in **1a**, **2a**, **2b**, and **2c** are also pyramidalized with the approximative τ values in the range from 0.57 to 0.66 (Table S4).

Scheme 1



The formation of $PhNH_2$ and NH_3 is the clear evidence of cleaving N−N bond of $PhNHNH_2$ by the thiolate-bridged diiron complexes. Such a cleavage is well-known for metals in groups 4−6, but the reactivity of multinuclear complexes, especially iron sulfur clusters, is relatively unexplored.[6a,12]

These nitrogenase model complexes promote us to investigate catalytic cleaving N−N bond of hydrazines (eq 1). Treatment of **2a** with excess $PhNHNH_2$ can not produce $PhNH_2$, NH_3, and N_2 under the ambient conditions, even at 60 °C, while the catalytic reaction proceeds smoothly in the presence of appropriate reductive and protonic acid. The catalytic reactions of N−N cleavages of hydrazines with **2a** are investigated (Table 1). The results show that **2a** exhibits an excellent catalytic activity. In the entries 3 and 4, the yields of $PhNH_2$ are up to 93% and 94%, while in the

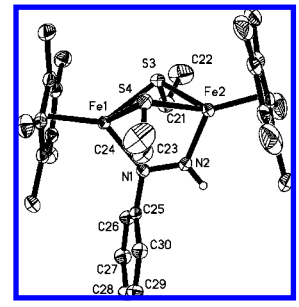


Figure 1. ORTEP (ellipsoids at 30% probability) diagram of **2a**.

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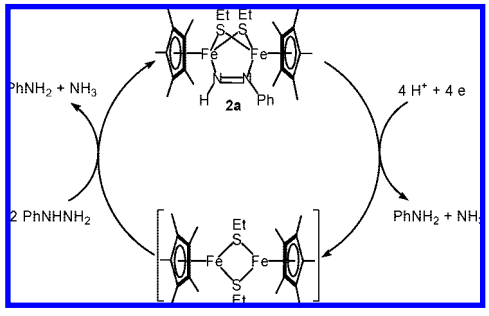
Table 1. Catalytic Cleaving N−N Bonds of Hydrazines on Diiron−Sulfur Cluster **2a**[a]

$$R^2NHNHR^3 + 2H^+ + \mathbf{2e} \xrightarrow[\text{THF, rt, 12 h}]{\text{cat } \mathbf{2a}} R^2NH_2 + R^3NH_2 \quad (1)$$

entry	substrate	proton source	reducing agent	yield (%) NH_3	yield (%) $PhNH_2$
1	$PhNHNH_2$	none	none	trace	trace
2[b]	$PhNHNH_2$	Lut · $HBPh_4$	Cp_2Cr	trace	trace
3	$PhNHNH_2$	Lut · $HBPh_4$	Cp_2Cr	19	93
4	$PhNHNH_2$	Lut · HBF_4	Cp_2Cr	23	94
5[c]	$PhNHNH_2$	Lut · HBF_4	Cp_2Cr	28	89
6[d]	$PhNHNH_2$	Lut · HBF_4	Cp_2Cr	10	63
7	$PhNHNH_2$	Lut · TsOH	Cp_2Cr	trace	8
8	$PhNHNH_2$	Lut · HCl	Cp_2Cr	trace	trace
9	$PhNHNH_2$	Lut · HBF_4	Cp_2Co	trace	22
10[e]	$MeNHNH_2$	Lut · $HBPh_4$	Cp_2Co	93	71 ($MeNH_2$)
11[e]	NH_2NH_2	Lut · $HBPh_4$	Cp_2Co	73	none
12	PhNHNHPh	Lut · $HBPh_4$	Cp_2Cr	none	45
13	PhN=NPh	Lut · $HBPh_4$	Cp_2Cr	none	36

[a] Reaction conditions: substrate (0.2 mmol), **2a** (10 μmol, 5.0 mol%), proton source (0.4 mmol), reducing agent (0.4 mmol), THF (10 mL), 12 h at room temp, Lut = 2,6-Lutidine. $PhNH_2$ is analyzed by HPLC, and the yield was obtained by integration against an integral standard of *m*-toluidine according to a calibration curve. The yields of NH_3 and $MeNH_2$ are obtained by ^{1}H NMR analysis.[4b,13] [b] The blank experiment. [c] **2a** (4.0 μmol, 2.0 mol%). [d] **2a** (2.0 μmol, 1.0 mol%). [e] Substrate (1.0 mmol).

Scheme 2



comparative blank experiment, only trace $PhNH_2$ is detected. Further experiments revealed a significant dependence of catalytic reaction about N−N bond cleavage on the nature of the acid. The acidity of protonic acid is not the decisive effects on the reaction, but the affinity of coordination is the governing factor. At the same time, the redox potential of reductant also plays an important role in catalytic N−N bond cleavage. To evaluate the scope of this system, the reactions of N−N cleavage of various hydrazines are undertaken. The NH_2NH_2 and $MeNHNH_2$ give good response to the catalytic reaction, while the bulkier substituted 1,2-diphenylhydrazine does not.

A possible reaction pathway for catalytic cleaving N−N single bond of $PhNHNH_2$ is shown in Scheme 2. First, the cleavage of N=N double bond leads to the formation of intermediate [Cp*Fe(μ-SEt)]$_2$, $PhNH_2$, and NH_3 from catalyst **2a** through a four-electron/four-proton redox. Second, the intermediate comes back to original catalyst by the reaction with $PhNHNH_2$, along with the N−N single bond cleavage and the formation of $PhNH_2$ and NH_3. Both stages have been explained by reactions of dimolybdenum and diruthenium sulfur clusters, respectively.[10a,14]

To verify the formation of intermediate, the CO-inhibition experiments are investigated (see Supporting Information). The results show that CO ligand rapidly restrains the N−N bond cleavage of $PhNHNH_2$, with the formation of CO complex [Cp*Fe(μ-SEt)CO]$_2$, which implies that the catalyst transform to the intermediate [Cp*Fe(μ-SEt)]$_2$ by the cleavage of N=N double bond of phenyldiazene on the diiron centers.

In summary, the new nitrogenase model complexes as well as their excellent catalytic properties of cleaving N−N bond of hydrazines on diiron centers under ambient conditions are demonstrated. These results suggest that some steps of the biological N_2 reduction could take place at diiron sites. Further studies are under way to clarify the catalytic reactivity of the diazene complexes reported herein.

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Supporting Information Available: Synthesis, characterization, structure, catalytic experiment, and the spectroscopic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) **2a**, ^{1}H NMR (THF-d_8): δ 13.19 (br, 1H, N*H*, disappeared upon treatment with D_2O), 7.39 (m, 2H, Ph), 7.29 (m, 3H, Ph), 1.56−1.62 (m, 4H, CH_2CH_3), 1.52 (s, 15H, Cp*-CH_3), 1.26 (s, 15H, Cp*-CH_3), 0.98−1.02 (m, 6H, CH_2CH_3). **2b**, ^{1}H NMR (C_6D_6-d_6): δ 13.11 (br, 1H, N*H*, disappeared upon treatment with D_2O), 7.16 (br, 5H, Ph), 1.43 (br, 30H, Cp*-CH_3), 1.16 (br, 6H, CH_3). **2c**, ^{1}H NMR (C_6D_6-d_6): δ 12.65 (br, 1H, N*H*, disappeared upon treatment with D_2O), 3.83 (s, 3H, CH_3), 1.60 (br, 34H, CH_2CH_3, Cp*-CH_3), 1.03 (br, 6H, CH_2CH_3).

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