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Synthesis of Sulfur- and Nitrogen-Bridged Diiron Complexes and Catalytic Behavior toward Hydrazines

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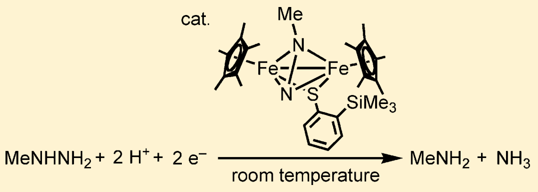
S Supporting Information

ABSTRACT: Novel thiolate-bridged diiron complexes bearing diazenido and diazene ligands in a side-on manner have been prepared and characterized by X-ray analysis. These sulfur-bridged diiron complexes work as effective catalysts toward the reduction of hydrazines into amines and ammonia via a sequential process of protonation and reduction on the sulfur-bridged diiron skeleton, as is likely observed at the active site of nitrogenase.



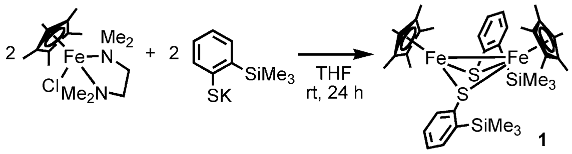
The development of nitrogen fixation under mild reaction conditions is one of the most important subjects in chemistry. Industrially, ammonia is produced from molecular dinitrogen and dihydrogen by the use of iron-based heterogeneous catalysts. In this reaction system, extreme reaction conditions such as high reaction temperatures and high pressures are required in order to activate molecular dinitrogen. In sharp contrast to the Haber−Bosch process, biological nitrogen fixation by the nitrogenase enzyme is well-known to occur at ambient temperature and pressure. A recent X-ray structural study has revealed that the active site of nitrogenase contains an Fe_7MoS_9C cluster core.[1] Although a detailed reaction mechanism of the conversion of molecular dinitrogen into ammonia by the nitrogenase enzyme has not yet been disclosed, recent theoretical studies have proposed reactive intermediates that contain nitrogenous species bound to two iron centers in the cluster.[2] Therefore, sulfur-bridged transition-metal cluster complexes have received much attention as being possibly relevant to the active site of nitrogenase.[3] Especially, studies on the function of the reduction of nitrogenous species by diiron complexes bearing sulfur ligands are limited to only a few cases.[4]

Toward the goal of achievement of a novel nitrogen fixation system under mild reaction conditions, we have quite recently found the molybdenum-catalyzed reduction of molecular dinitrogen into ammonia under mild reaction conditions by using a dinitrogen-bridged dimolybdenum complex bearing a tridentate PNP-type pincer ligand as a catalyst.[5] In this reaction system, molecular dinitrogen under atmospheric pressure was catalytically converted into ammonia in the presence of both electron source and proton source, and up to 23 equiv of ammonia was produced on the basis of the catalyst (12 equiv of ammonia was produced on the basis of the molybdenum atom of the catalyst). This is another successful example of the catalytic and direct conversion of molecular dinitrogen into ammonia under ambient conditions.[6]

As an extension of our study on the development of a novel nitrogen fixation system under mild reaction conditions,[7] we have synthesized the thiolate-bridged diiron complex $[(Cp^*Fe)_2(\mu\text{-SAr})]$ (Ar = 2-(trimethylsilyl)phenyl).[8] During this study, diazenido- and diazene-bridged diiron complexes were isolated as reactive intermediates from the reaction of the thiolate-bridged diiron complex with methylhydrazine and further protonation. Interestingly, the diiron complexes work as effective catalysts toward the catalytic reduction of hydrazines into ammonia via nitrogen−nitrogen bond cleavage of hydrazines. We believe that the properties of these complexes give useful information to elucidate the function of the nitrogenase enzyme. Herein, we describe the preparation and reactivity of the thiolate-bridged diiron complexes.

The reaction of $[Cp^*FeCl(tmeda)]$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) with 1 equiv of KSAr in THF at room temperature for 24 h gave the doubly thiolate bridged diiron complex $[Cp^*Fe(\mu\text{-SAr})]_2$ (**1**) in 77% yield (Scheme 1).

Scheme 1. Preparation of the Doubly Thiolate Bridged Diiron Complex $[Cp^*Fe(\mu\text{-SAr})]_2$ (1)



The molecular structure of **1** was confirmed by X-ray analysis. An ORTEP drawing of **1** is shown in Figure S1 (Supporting Information). The bond distance between the two iron atoms is revealed to be 2.7429(4) Å. This result indicates the presence of a direct interaction between the two iron atoms in **1**. Although the preparation and reactions of the doubly thiolate bridged diruthenium complexes $[Cp^*Ru^{II}(\mu\text{-SR})]_2$ have been reported for the last two decades,[9] this is the first example of the preparation of the analogous iron complex $[Cp^*Fe^{II}(\mu\text{-SR})]_2$.

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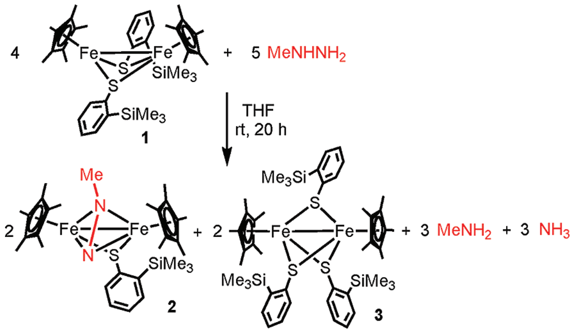
The reaction of **1** with 1.25 equiv of methylhydrazine in THF at room temperature for 20 h gave the methyldiazenido-bridged diiron complex [(Cp*Fe)$_2$(μ-SAr)(μ-η^2:η^2-NNMe)] (**2**) in 64% yield and triply thiolate bridged diiron complex [Cp*Fe(μ-SAr)$_3$FeCp*] (**3**) in 36% yield together with the formation of methylamine in 57% yield and ammonia in 57% yield (Scheme 2). In this reaction, all yields of the complexes and products are estimated on the basis of **1**. The molecular structures of **2** and **3** were confirmed by X-ray analysis. ORTEP drawings of **2** and **3** are shown in Figure 1a and Figure S3 (Supporting Information). The X-ray analysis of **2** reveals that two iron atoms in **2** are bridged by thiolate and methyldiazenido ligands, respectively. The bond distance between two nitrogen atoms in the methyldiazenido ligand with side-on coordination is 1.331(3) Å. This bond distance is similar to that of the diazenido ligand in the dicobalt complex [Co$_2$(CO)$_4$(μ-dppm)(μ-η^2:η^2-NNTol)]SbF$_6$ (dppm = bis(diphenylphosphino)methane; Tol = p-CH$_3$C$_6$H$_4$).[10] Complex **2** is the first example of a diiron complex bearing a methyldiazenido ligand with side-on coordination.[11] The core skeleton, including the bond distance between the two iron atoms and the bond angles between iron and sulfur atoms in **2**, is similar to that of the Fe$_7$MoS$_9$C cluster core in nitrogenase. On the other hand, the molecular structure of **3** is almost the same as that of the reported triply thiolate bridged diiron complexes [Cp*Fe(μ-SR)$_3$FeCp*] (R = Me, Et, Ph).[12]

Scheme 2. Reaction of [Cp*Fe(μ-SAr)]$_2$ (1) with 1.25 equiv of Methylhydrazine



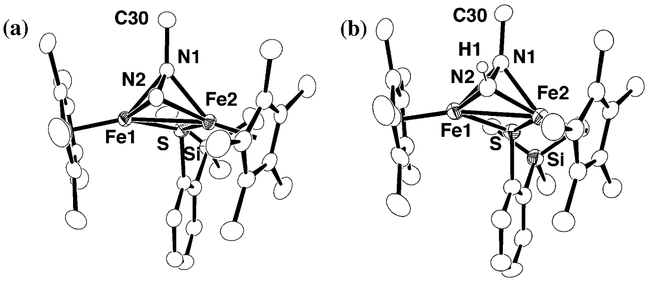
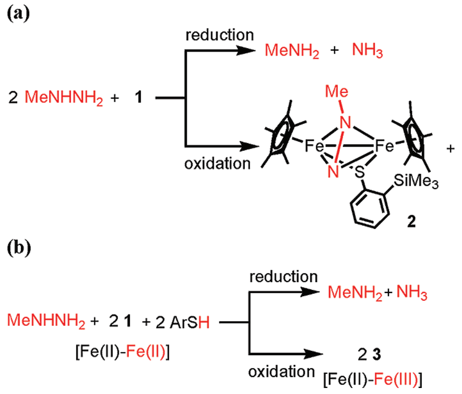
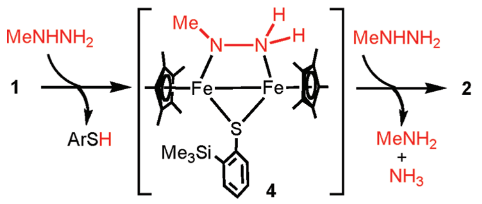


Figure 1. ORTEP drawings of (a) [(Cp*Fe)$_2$(μ-SAr)(μ-η^2:η^2-NNMe)] (**2**) and (b) [(Cp*Fe)$_2$(μ-SAr)(μ-η^2:η^2-NHNMe)]OTf (**6**).

Scheme 3. (a) Disproportionation of Methylhydrazine and (b) Reduction of Methylhydrazine with [Fe(II)−Fe(II)] (1)



The result of the formation of **2** and **3** in Scheme 2 suggests the existence of the two competitive reactions shown in Scheme 3. With regard to the formation of **2** from the reaction of **1** with 2 equiv of methylhydrazine, 2 equiv of methylhydrazine disproportionates into methylamine and ammonia as reduced products and a bridging methyldiazenido ligand as an oxidized product together with free thiol (ArSH) (Scheme 3a). Although a detailed reaction mechanism of the oxidation of **1** with methylhydrazine has not yet been determined, the hydrazido complex [(Cp*Fe)$_2$(μ-SAr)(μ-NHNHMe)] (**4**) may be formed by ligand exchange of the coordinated thiolate with 1 equiv of methylhydrazine as the first step (eq 1). A similar hydrazido complex was previously isolated and proposed as a reactive intermediate in the reductive process of molecular dinitrogen at the active site of nitrogenase.[13] Then, the produced hydrazido complex **4** is oxidized with another 1 equiv of methylhydrazine to afford **2** together with methylamine and ammonia (eq 1). On the other hand, **3** is formed by the reaction of **1** with 0.5 equiv of methylhydrazine and ArSH, where methylhydrazine oxidizes one of the two iron atoms Fe(II)−Fe(II) in **1** to Fe(II)−Fe(III) in **3** together with methylamine and ammonia (Scheme 3b). It is noteworthy that methylhydrazine works as both a reducing and an oxidizing reagent.



(1)

Next, we examined the catalytic activity of the diiron complexes toward reduction of hydrazines into amines and ammonia via nitrogen−nitrogen bond cleavage of hydrazines. Typical results are shown in Table 1. The reaction of methylhydrazine with 2 equiv of lutidinum tetraphenylborate ([LutH]BPh$_4$) as a proton source and cobaltocene as a reductant in the presence of 5 mol % of **2** in THF at room temperature for 1 h under an atmospheric pressure of argon gave methylamine and ammonia in 93% and 80% yields, respectively, without the formation of molecular dihydrogen and dinitrogen (Table 1, run 1). Although only small amounts of methylamine and ammonia were observed even in the absence of catalyst (Table 1, run 3), the reduction of methylhydrazine proceeded smoothly in the presence of only 0.5 mol % of **2** to produce lower amounts of methylamine and ammonia (Table 1, run 2). No reaction occurred at all in the absence of [LutH]BPh$_4$ and cobaltocene (Table 1, run 4). This result indicates that no disproportionation of methylhydrazine takes place under the same reaction conditions. Separately, we confirmed that no reaction occurred at all when the catalytic reduction was carried out under an atmospheric pressure of

Table 1. Iron-Catalyzed Reduction of Hydrazines[a]

$$\mathrm{MeNHNH_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \xrightarrow[\text{THF, room temp, 1 h}]{\text{5 mol \% catalyst}} \mathrm{MeNH_2} + \mathrm{NH_3}$$

run	cat.	yield (%) MeNH$_2$	NH$_3$	H$_2$
1	**2**	93	80	0
2	**2**[b]	32	26	0
3	*c*	10	7	58
4[d]	**2**	0	2	0
5[d,e]	**2**	0	0	
6	**1**	72	70	6
7	**3**	53	55	20
8	**5**	32	26	44
9	**6**	76	68	0
10[f]	**2**		>99	0
11[g]	**2**	56[h]	59	5
12[i]	**2**	54[j]	51	15

[a] All reactions of methylhydrazine (0.60 mmol) with 2 equiv of [LuH]BPh$_4$ (1.20 mmol) and Cp$_2$Co (1.20 mmol) in the presence of 5 mol % of catalyst (0.03 mmol) were carried out in THF (10 mL) at room temperature for 1 h under an atmospheric pressure of argon. [b] **2** (0.5 mol %) was used. [c] In the absence of catalyst. [d] In the absence of both [LuH]BPh$_4$ and Cp$_2$Co. [e] Under an atmospheric pressure of H$_2$. [f] Hydrazine was used in place of methylhydrazine. [g] Phenylhydrazine was used in place of methylhydrazine. [h] Phenylamine was formed. [i] 1,1-Dimethylhydrazine was used in place of methylhydrazine. [j] Dimethylamine was formed.

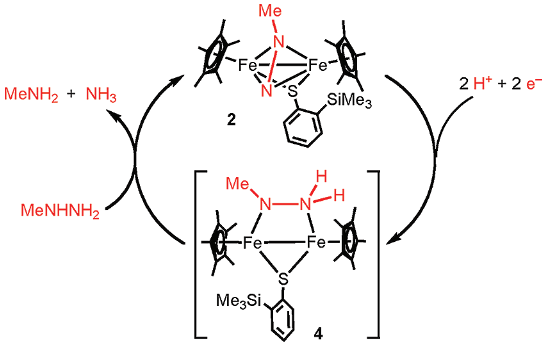
dihydrogen in the absence of [LutH]BPh$_4$ and cobaltocene (Table 1, run 5). These results indicate that molecular dihydrogen did not work as a proton or electron source. At present, we consider that the reduction of methylhydrazine proceeds via a sequential process of protonation and reduction on the sulfur-bridged diiron skeleton of **2**.

When **1** was used in place of **2** as a catalyst, both methylamine and ammonia were obtained in 72% and 70% yields, respectively, together with a small amount of dihydrogen (Table 1, run 6). When either **3** or the thiolate-bridged diruthenium complex [Cp*Ru(μ-SAr)]$_2$ (**5**)[15] was used as a catalyst, the selectivity for methylamine and ammonia was low and a larger amount of dihydrogen was produced (Table 1, runs 7 and 8). These results indicate that **2** works as the most effective catalyst in the reduction of methylhydrazine.

Interestingly, **2** works as an effective catalyst toward the catalytic reduction of hydrazine, where ammonia was formed quantitatively (Table 1, run 10). Other hydrazine derivatives such as phenylhydrazine and 1,1-dimethylhydrazine can be reduced into the corresponding amines and ammonia under the same reaction conditions (Table 1, runs 11 and 12). Results of the stoichiometric and catalytic reactions indicate that **2** works as a key reactive intermediate in the catalytic reduction of hydrazines.

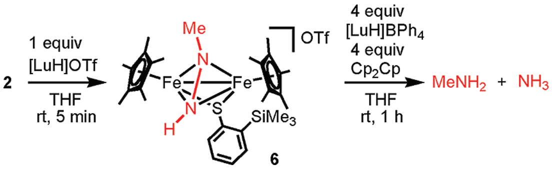
On the basis of experimental results of the stoichiometric and catalytic reactions, a proposed reaction pathway for the catalytic reduction using **2** as a catalyst is shown in Scheme 4. The initial step is the formation of the hydrazido complex **4** by the protonation and reduction of **2**. Then, **4** is oxidized with 1 equiv of methylhydrazine to give the starting complex **2** together with methylamine and ammonia as reduced products. This step is quite similar to the reaction of **1** with methylhydrazine, as shown in Scheme 3a. Thus, methylhydrazine is reduced into methylamine and ammonia and the bridging hydrazido ligand in **4** is oxidized into the bridging methyldiazenido ligand in **2**. It is noteworthy that the disproportionation of hydrazines is considered to be involved in the catalytic reduction of hydrazines. However, we have not yet excluded other reaction pathways involving key reactive intermediates such as **2**.

Scheme 4. Proposed Reaction Pathway for Reduction of Methylhydrazine



Unfortunately, we have not yet been successful in isolating the proposed hydrazido complex **4**, although a similar hydrazido complex was isolated by another research group.[13] However, we could isolate the methyldiazene-bridged diiron complex [(Cp*Fe)$_2$(μ-SAr)(μ–η^2:η^2-NHNMe)]OTf (**6**) from the reaction of **2** with 1 equiv of [LutH]OTf (Scheme 5). The molecular structure of **6** was confirmed by X-ray analysis. An ORTEP drawing of **6** is shown in Figure 1b. The bond distance between two nitrogen atoms in the methyldiazene ligand with side-on coordination is 1.373(4) Å, which is slightly longer than that in the methyldiazenido ligand in **2**. The reaction of **6** with 4 equiv of [LutH]BPh$_4$ and 4 equiv of cobaltocene in THF at room temperature for 1 h gave methylamine and ammonia in 51% and 67% yields, respectively. In addition, we confirmed that **6** has a similar catalytic activity toward the reduction of methylhydrazine (Table 1, run 9). These results indicate that **6** can be considered one of the reactive intermediates in the catalytic reduction of hydrazines.

Scheme 5. Preparation and Reactivity of 6



Qu and co-workers have prepared related doubly thiolate bridged diiron complexes bearing a bridging diazene ligand with end-on coordination and investigated their catalytic activity toward the reduction of hydrazines, where the diiron complexes worked as effective catalysts.[4b] In sharp contrast to the end-on mode of the diazene ligand for the diiron complexes,[4b] the side-on modes of the diazenido ligand for **2** and diazene ligand for **6** were observed in our case due to the presence of only one sterically demanding substituent such as the 2-trimethylsilylbenzenthiolate group. Unfortunately, the use of a more sterically demanding substituent such as 2,6-bis(trimethylsilyl)-benzenthiolate group did not afford the corresponding thiolate-bridged diiron complexes but rather a mononuclear iron complex bearing a π-arenethiolate ligand, $[\mathrm{Cp^*Fe}(\eta^5\text{-}\mathrm{SAr'})]$ (Ar′ = 2,6-bis(trimethyl)phenyl) (7).[16] As described in Scheme 4, the reaction pathway for the reduction of hydrazines using **2** as a catalyst is considered to be quite different from that proposed by Qu and co-workers.[4b] The results described in this paper provide another successful example of the catalytic reduction of hydrazines by using sulfur-bridged diiron complexes as catalysts, although other transition-metal complexes bearing bridging sulfur ligands were previously reported to work as catalysts.[17]

In summary, we have newly prepared thiolate-bridged diiron complexes bearing diazenido and diazene ligands with side-on coordination. These sulfur-bridged diiron complexes have been revealed to work as effective catalysts toward the reduction of hydrazines into amines and ammonia. The reduction of hydrazine is considered to proceed via a sequential process of protonation and reduction on the sulfur-bridged diiron skeleton. On the basis of experimental results, a novel reaction pathway for the reduction of hydrazines has been proposed, where the disproportionation of hydrazines is considered to be one of the key steps. We believe that the result described in this paper provides the ability of two iron atoms to cooperatively bind and transform a nitrogenous substrate, which is a capability that may be shared by the $\mathrm{Fe_7MoS_9C}$ cluster core in nitrogenase.[18] Further work is currently in progress to develop the iron-catalyzed reduction of dinitrogen into ammonia under mild reaction conditions.[19]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, text, and CIF files giving experimental procedures, spectroscopic data, and X-ray data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) See the Supporting Information for experimental details.

(15) The complex **5** was prepared and characterized by X-ray crystallography. See the Supporting Information for experimental details.

(16) (a) See the Supporting Information for experimental details. (b) A similar mononuclear ruthenium complex bearing a π-arenethiolate ligand, $[\mathrm{Cp^*Ru}(\eta^5\text{-}\mathrm{SAr'})]$, has already been reported: Yuki, M.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2010**, *29*, 4148.

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