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Unusual Thiolate-Bridged Diiron Clusters Bearing the *cis*-HN=NH Ligand and Their Reactivities with Terminal Alkynes

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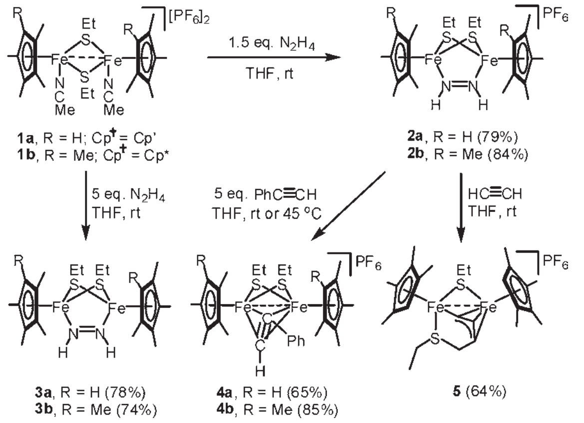
Supporting Information

ABSTRACT: A series of well-defined thiolate-bridged diiron clusters bearing the *cis*-HN=NH ligand, $[Cp^{\dagger}Fe(\mu\text{-}SEt)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}HN{=}NH)FeCp^{\dagger}][PF_6]$ ($Cp^{\dagger} = \eta^5\text{-}C_5Me_4H$ or $\eta^5\text{-}C_5Me_5$), are successfully prepared in high yields and fully characterized by spectroscopy and X-ray crystallography. Under moderate conditions, these new Fe/S clusters exhibit high activity, not only for the catalytic cleavage of the N−N bond of hydrazines but also for the activation and coupling of terminal alkynes.

The intensive research work on the mechanisms of nitrogen fixation in the MoFe-cofactor has led to the hypotheses of two models: One involves N_2 binding to the Mo atom, whereas the other suggests the participation of one or more Fe atoms located in the "belt" or "waist" region of the metallocluster.[1] Recent DFT calculations, spectroscopic (ENDOR and ESEEM) data, and the studies on the reduction rates of substrates in mutant enzymes are more suggestive of the latter.[1b,2,3] Because *sulfur* is one of the dominant elements in the natural nitrogenase core, sulfur atoms might play indispensable roles in nitrogen fixation. Noticeably, however, the majority of previous works were focused on models of sulfur-free iron complexes coordinated with N_2 or its reductive products (N_xH_y),[4−7] yet the model of Fe/S clusters received much less attention.[8] A rare example of the Fe/S cluster reported by Sellmann et al. is the $[\mu\text{-}N_2H_2\{Fe(\text{“}N_HS_4\text{”})\}_2]$ complex, in which the HN=NH subunit is coordinated in a *trans* mode,[8a] while the Fe/S clusters with *cis*-HN=NH attached to the two iron sites are still unknown. Regarding this aspect, preparation of well-defined Fe/S clusters bearing N_2 or N_xH_y intermediates and mimicking some nitrogenase functions remain challenges to understanding more deeply the role of the Fe/S cluster in the natural nitrogenase.

Recently, we investigated a class of thiolate-bridged diiron complexes and found that the structurally well characterized Fe_2/S_2 clusters were capable of cleaving the N−N bond of hydrazines catalytically with noticeable efficiency.[9] This discovery further supports the viewpoint that diiron centers may play a crucial role in biological N_2 reduction.[9] As an extension of work in this field, here we report our new findings: the isolation of the well-defined $Fe_2(\mu\text{-}SEt)_2$ clusters bearing the *cis*-HN=NH subunit, the complexes of $[Cp^{\dagger}Fe(\mu\text{-}SEt)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}HN{=}NH)FeCp^{\dagger}][PF_6]$ ($Cp^{\dagger}$: $Cp' = \eta^5\text{-}C_5Me_4H$, **2a**; $Cp^* = \eta^5\text{-}C_5Me_5$, **2b**), and their interactions with terminal alkynes.

Scheme 1



The reaction of $[Cp^{\dagger}Fe(\mu\text{-}SEt)MeCN]_2[PF_6]_2$ (**1a** or **1b**)[10] with 1.5 equiv of hydrazine in THF at ambient temperature results in the $\mu\text{-}\eta^1{:}\eta^1$-*cis*-diazene diiron thiolate-bridged cluster **2a** or **2b** as reddish brown microcrystalline solids in respective 79% and 84% yields, along with the formation of NH_4PF_6. When excessive amounts of hydrazine are used in the reaction medium, the neutral clusters **3a** and **3b** can be harvested in 78% and 74% yields, respectively (Scheme 1). Under similar conditions, the reaction of the fully deuterated hydrazine (N_2D_4, 1.5 equiv) with **1a** forms the deuterated version of **2a-N_2D_2** with a 59% yield (see the Supporting Information, SI).

Complexes **2a** and **2b** are paramagnetic at ambient temperatures. Cluster **2a** is in an $S = 1/2$ spin state, displayed by a characteristic EPR spectrum ($g = 2.07$) (see Figure S22). The $S = 1/2$ spin state is also favorably suggested by the DFT calculation results (see the SI).

The electrospray ionization high resolution mass spectrometry (ESI-HRMS) shows the molecular ion peak $[\mathbf{2a}{-}PF_6]^+$ with an m/z of 506.1179 (calcd 506.1176) and its ^{15}N-labeled congener's molecular ion $[\mathbf{2a}\text{-}^{15}\mathbf{N_2H_2}{-}PF_6]^+$ with an m/z of 508.1117 (calcd 508.1116). Further examination of the molecular ion peak of $[\mathbf{2a}\text{-}\mathbf{N_2D_2}{-}PF_6]^+$ with ESI-HRMS gives an m/z of 508.1300 (calcd 508.1301). The molecular masses of **2a**, **2a-^{15}N$_2$H$_2$**, and **2a-N_2D_2** have unambiguously established the existence of the diazene subunit in these molecules.

The ^{1}H NMR spectrum of **2a** in acetone-d_6 exhibits two resonances for Cp′ methyl protons: at −4.39 and −14.18 ppm,

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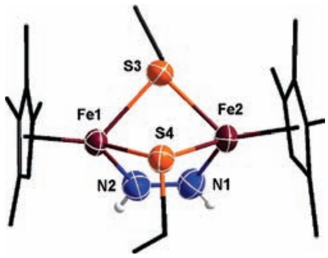

Figure 1. ORTEP (ellipsoids at 50% probability) diagram of **2a** cation.

while **2b** shows an intense broad signal at −10.21 ppm assigned to two equivalent Cp* protons, based on their peak integrations. The ^{1}H NMR spectra of neutral **3a** and **3b** feature an intense signal of two protons attached to the η^1-N atom of the HN=NH ligand in very low fields (15.19 ppm, **3a**; 13.01 ppm, **3b**).[9,11] The quantified NMR signals of the N−H protons (see the SI) explicitly indicate the identity of the diazene subunit in both **3a** and **3b** molecules. The IR spectra (with KBr) of these clusters show the ν(N−H) band at about 3253 cm^{-1}, while the N−D band shifts to 2425 cm^{-1} for **2a-N$_2$D$_2$**. DFT calculations also suggested that the N−D stretch of **2a-N$_2$D$_2$** is located at 2406 cm^{-1} (see the SI). The above spectral characterizations are all consistent with their solid-state structures.

The cationic **2a** consists of a di(μ-thiolate)diiron unit {Cp′Fe(μ-SEt)}$_2$ bridged with a bidentate HN=NH ligand in *cis*-fashion (Figure 1). The long Fe···Fe distance of 3.1441(2) Å is indicative of the absence of bonding interaction between the two iron centers. The N1, N2, Fe1, and Fe2 atoms are essentially coplanar, with the deviation being only 0.001°. Both the Fe−N bond distances (Fe1−N2 1.844(2) Å, Fe2−N1 1.824(2) Å) and the N1−N2 bond distance of 1.317(3) Å are comparable to the previously reported complexes of {[PhBP$^{\mathrm{CH_2Cy}}{}_3$]Fe}$_2$(μ-η^1:η^1-N$_2$H$_2$)(μ-NH$_2$)$_2$ and {[PhBP$^{\mathrm{Ph}}{}_3$]Fe}$_2$(μ-η^1:η^1-N$_2$H$_2$)(μ-η^1:η^1-N$_2$H$_2$).[7c] The shortened Fe−N bond is likely due to the combination of the smaller covalent radii of the *sp*^{2}-hybridized relative to the *sp*^{3}-hybridized N-atom, and the modest back-bonding, which is also found in other structurally characterized diazene complexes.[7c,8a,12] To the best of our knowledge, **2a** represents the first example of a well-defined thiolate-bridged diiron cluster bearing the *cis*-HN=NH ligand, distinctly different from another Fe/S complex: [μ-N$_2$H$_2${Fe("N$_\mathrm{H}$S$_4$")}$_2$]. In the latter example, the *trans*-HN=NH ligand bridges the two isolated monoiron sulfur units.[8a] The structure of **2b** is analogous to that of **2a**.

In the course of N$_2$ reduction on the nitrogenase, it is believed that HN=NH is the product of the first step 2e/2H$^+$ reduction of dinitrogen. Recent DFT studies indicate that the freshly generated diazene HN=NH on the FeMoco is attached to two irons in a *cis* manner.[2g] Hence, **2a** and **2b** are considered to be the new nitrogenase mimics. Further experiments on the catalytic cleavage of N−N bond of hydrazines by **2a** provide convincing evidence, showing that **2a** is comparable to monosubstituted diazenes catalysts[9] in its catalytic performances.

Natural nitrogenase can catalyze the biological reduction of CH≡CH to CH$_2$=CH$_2$, as well as the reduction of N$_2$ to NH$_3$, but the exact binding sites on the FeMoco core remain unclear.[13] This fact prompted us to investigate the interactions of the new nitrogenase mimics with alkynes.

Treatment of **2a** with 5 equiv of PhC≡CH at room temperature for 12 h affords [Cp′Fe(μ-SEt)$_2$(μ-η^2:η^2-PhC≡CH)Cp′Fe][PF$_6$] (**4a**) in 65% yield (**4b**, 85% yield at 45 °C) (Scheme 1).

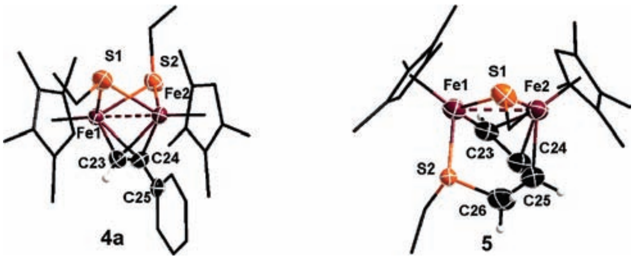

Figure 2. ORTEP (ellipsoids at 50% probability) diagram of **4a** and **5** cations.

In sharp contrast, the monosubstituted diazene HN=NR coordinated (R = Me, or Ph) thiolate-bridged diiron clusters[9] are inactive to PhC≡CH under similar conditions. The ^{1}H NMR spectra of **4a** and **4b** show paramagneticly shifted and extremely broadened resonances, which cannot be unambiguously assigned. However, ESI-MS gives the expected molecular ion masses of [**4a**−PF$_6$]$^+$ and [**4b**−PF$_6$]$^+$ with an m/z of 578 and 606, respectively. This indicates clearly that the PhC≡CH fragment is firmly embedded into the thiolate-bridged diiron clusters.

The cationic **4a** consists of a well-defined {Cp′Fe(μ-SEt)}$_2$ core bridged by a PhC≡CH group *via* the π-electrons of the triple bonds in a *side-on* pattern (Figure 2). The Fe−C bond lengths (1.995(1)−2.043(8) Å) are in the normal range,[14] and the Fe−Fe metal bond vector (2.5123(17) Å) is nearly orthogonal to the C≡C bond of the alkyne ligand. The π back-bonding from the Fe to the neutral PhC≡CH exerts considerable variations on the structural feature of the coordinated alkyne subunit in **4a**, such as the elongation of the C≡C bond (1.319(13) Å), the significant bending of the C≡C−C unit (143.1(9)°), and the highly reduced C≡C stretching frequency (IR spectrum shows the disappearance of the C≡C stretching band in the range 1595−2100 cm^{-1}). A DFT study of the cation of **4a** shows that the Mulliken charge population on the PhC≡CH moiety is −0.68 and the C≡C stretching frequency of the PhC≡CH ligand is decreased to 1594 cm^{-1}, implying that the C≡C bond of alkyne in **4a** has been significantly weakened (see the SI). The attempted catalytic reduction of PhC≡CH to PhCH=CH$_2$ by **4a** does not occur however, when the e/H$^+$ pair of e (Cp$_2$Cr) and H$^+$ (Lut·HBPh$_4$) are introduced into the reaction system.

Stirring the solution of **2a** in the acetylene atmosphere at room temperature produces a new cluster: [Cp′Fe(μ-SEt)(μ-η^1:η^3-CH−CH=CH−CH$_2$SEt)FeCp′][PF$_6$] (**5**) (Scheme 1). The ORTEP diagram of **5** is shown in Figure 2. Two Cp′Fe motifs are bridged with a rare eight-electron-donor allylidene anion [:CH−CH=CH−CH$_2$SEt]$^{2-}$, which is proved by the ^{1}H NMR and ESI-MS spectra (see the SI). The C23−C24 and C24−C25 bond lengths (1.403(7) and 1.403(8) Å) and the C23−C24−C25 angle (119.1(5)°) are in the typical ranges for η^3-allyl ligands.[15] The mechanism for the formation of the allylidene anion is unclear at the moment, but it is certain that N−H bond activation of the coordinated diazene and carbon−carbon coupling of two CH≡CH molecules must have been promoted by the Fe$_2$(μ-SEt)$_2$ core.[16]

In summary, we have presented the synthesis of nitrogenase model compounds of thiolate-bridged diiron clusters bearing the *cis*-HN=NH subunit and their high performances toward alkynes for the first time. These results are potentially important for understanding the nature of binding N$_2$ or alternative substrates to the active sites of the nitrogenase. Further studies on the coordinate activation of N_2 and activation of the sp^3-hydridized N−H bond on the thiolate-bridged diiron clusters are now in progress.

■ ASSOCIATED CONTENT

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

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