

Title: Nitrogen Reduction by the Fe Sites of Synthetic [Mo₃S₄Fe] Cubes

Authors: Yasuhiro Ohki^{1,*}, Kenichiro Munakata², Yuto Matsuoka¹, Ryota Hara², Mami Kachi², Keisuke Uchida², Mizuki Tada², Roger E. Cramer³, W. M. C. Sameera^{4,5}, Tsutomu Takayama⁶, Yoichi Sakai⁶, Shogo Kuriyama⁷, Yoshiaki Nishibayashi⁷, and Kazuki Tanifuji¹

Affiliations: ¹ Institute for Chemical Research, Kyoto University, Gokasho, Uji 611-0011, Japan

² Department of Chemistry, Graduate School of Science, and Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

³ Department of Chemistry, University of Hawaii, Honolulu, HI 96822-2275, United States

⁴ Instituted of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan

⁵ Department of Chemistry, University of Colombo, 00300 Colombo, Sri Lanka

⁶ Department of Chemistry, Daido University, Takiharuru-cho, Minami-ku, Nagoya 457-8530, Japan

⁷ Department of Applied Chemistry, School of Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan

Corresponding author: Email: ohki@scl.kyoto-u.ac.jp

Summary paragraph: N₂ fixation by Nature, which is a crucial process to supply bio-available forms of nitrogen, is performed by nitrogenase. This enzyme employs a unique transition metal-sulfur-carbon cluster as its active-site cofactor ($[(R\text{-homocitrate})\text{MoFe}_7\text{S}_9\text{C}]$, FeMoco)^{1,2} and the sulfur-surrounded Fe atoms have been postulated to capture and reduce N₂.³⁻⁶ While there are a few examples of synthetic counterparts of the FeMoco, metal-sulfur cluster, which have displayed binding of N₂,⁷⁻⁹ the reduction of N₂ by any synthetic metal-sulfur cluster or even by the extracted form of FeMoco¹⁰ has remained elusive despite a near-50-year history of research. Here we show that the Fe atoms in our synthetic [Mo₃S₄Fe] cubes^{11,12} capture an N₂ molecule and catalyze N₂ silylation to form N(SiMe₃)₃ under treatment with excess Na and Me₃SiCl. These results exemplify the first catalytic silylation of N₂ by a synthetic metal-sulfur cluster and demonstrate the N₂-reducing capability of Fe atoms in a S-rich environment, which Nature has selected to accomplish a similar purpose.

Main Text

Nitrogen is an essential element to maintain every known form of life on Earth. Whereas the element is inexhaustible in the atmosphere as N_2 , only diazotrophs or lightning in thunderstorms can transform this stable molecule into bio-available forms (*e.g.* NH_3 and nitrogen oxides) in the natural world. Other organisms consequently rely on products of the fixation process and limited pre-existing sources to afford necessary nitrogen. In this sense, N_2 fixation is one of the most crucial bottlenecks in the Earth's ecosystem. Key players of N_2 fixation are nitrogenase enzymes that reduce N_2 into NH_3 . The most studied one of these, Mo-nitrogenase, employs a unique metal-sulfur-carbon cofactor described as [(*R*-homocitrate)MoFe₇S₉C] (FeMoco, Fig. 1)^{1,2} and performs the catalytic reduction at ambient temperature and pressure. Since FeMoco is found only in nitrogenase, its chemical and physical properties have attracted significant interest concerning the desirable N_2 -reducing activity. How FeMoco reduces N_2 has long been studied by biochemical analyses of the enzyme^{3,13} and by structural and functional modeling of FeMoco with small-molecule complexes^{14,15} and metal-sulfur (M-S) clusters^{16,17}.

While the detailed N_2 -reducing mechanism of FeMoco remains elusive, a growing number of results suggest that FeMoco eliminates one of the μ_2 -bridging S atoms and captures substrates at the produced vacant coordination sites on the Fe atoms⁴⁻⁶. Analogously, a common approach to generating small-molecule N_2 complexes has been removing of a metal-bound ligand under reducing conditions. However, applying this method to available synthetic counterparts of FeMoco, namely, M-S clusters, has been challenging. As these clusters contain coordinative S atoms in their inorganic cores, a vacant metal site often attracts core S atoms of M-S clusters rather than N_2 , which leads to aggregation¹⁷. Limiting the number of vacant metal atoms in the core is thus a plausible approach and led to the isolation of N_2 -bound clusters in several previous and recent examples, including ours⁷⁻⁹. Nevertheless, catalytic reduction of N_2 by these clusters remains unknown despite its relevance to the natural system.

Our framework to overcome these hurdles implements a triangular [Mo₃S₄] fragment bearing robust Mo-Cp^R bonds (Cp^R = C₅Me₅ (Cp*), C₅Me₄SiMe₃ (Cp^L) and C₅Me₄SiEt₃ (Cp^{XL}))^{11,12} as a platform to structurally encumber and protect a fourth metal incorporated into the vertex (Fig. 1). A Ti-derivative [Cp*₃Mo₃S₄Ti] captures and activates N_2 in the presence of KC₈, indicating that the [Mo₃S₄Ti] cube is robust under reducing conditions and avoids undesirable aggregation⁸. In contrast, catalytic reduction of the bound N_2 was not observed, probably due to the strong Ti-N bond that inhibits product release. We then hypothesized that a softer Fe atom as found in the biological systems might function more successfully to carry out N_2 reduction instead of the harder Ti atom. Results below demonstrate the capture and catalytic silylation of N_2 by the vertex Fe atoms of [Mo₃S₄Fe] cubes. While it is likely that there are mechanistic

differences between the silylation of N₂ and ammonia production by nitrogenase, our results demonstrate that an Fe center built into a M-S core and in a S-rich coordination environment can activate inert N₂ sufficiently for chemical conversion.

Treatment of our reported [Mo₃S₄Fe] clusters, [Cp^R₃Mo₃S₄FeCl] (Cp^R = Cp* (**1a**), Cp^L (**1b**), and Cp^{XL} (**1c**))^{11,12} with strong reductants (KC₈ for **1a** and Na(C₁₀H₈) for **1b** and **1c**) under N₂ in THF led to the formation of the corresponding N₂-clusters (Fig. 2a). The N₂ coordination mode varies depending on the bulkiness of the Cp^R ligands, so that a [Mo₃S₄Fe] dimer bridged by N₂, [{Cp*₃Mo₃S₄Fe}₂(μ-N₂)]²⁻ (**2a**), and monomers each bearing a terminal N₂ ligand, [Cp^R₃Mo₃S₄Fe(N₂)]⁻ (Cp^R = Cp^L (**2b**), and Cp^{XL} (**2c**)), were obtained. The N₂ binding modes of **2a-c** were assigned primarily from the ¹⁵N NMR spectra of ¹⁵N₂-labeled clusters (Supplementary Figs. 1-3). Cluster **2a** exhibited a single signal at δ -40.9 ppm as expected from the equivalent N atoms of the bridging ¹⁵N₂. Conversely, **2b** and **2c** gave two signals at δ 22.0 and -5.3 ppm for **2b** and δ 22.6 and -5.7 ppm for **2c**, corresponding to the inequivalent *proximal* and *distal* N atoms in these molecules. Terminal N₂ binding in **2b** and **2c** was further confirmed by IR-active N-N stretches observed at 1896 and 1902 cm⁻¹, respectively, both of which exhibited a bathochromic shift upon ¹⁵N₂ labeling (Supplementary Figs. 7 and 8). Despite our efforts, no meaningful N-N stretch for **2a** was detectable via resonance-Raman or IR measurements (Supplementary Fig. 6), perhaps due to slightly broken symmetry of the N₂ binding mode. X-ray crystallographic analyses revealed the molecular structures of **2a** and **2c** (Figs. 2b and 2c, Supplementary Figs. 11 and 12, and Supplementary Table 5). The structure of **2a** is an N₂-bridged [Mo₃S₄Fe] dimer with an inversion center at the middle of the two N atoms, while **2c** is a monomeric cluster bearing a terminally bound N₂. The N-N distances (1.151(4) Å for **2a** and 1.136(5) Å for **2c**) are in between those of *free* N₂ (1.098(1) Å) and N₂H₂ (1.252 Å), suggesting a weakened N-N bond. Likewise, the N-N stretching frequencies of **2b** and **2c** are close to the lower end of those reported for N₂ complexes of Fe^{II} or Fe^I,¹⁸ and the activation levels are even comparable to an Fe⁰-N₂ complex supported by S- and C-based ligands¹⁹.

Successful activation of N₂ at the Fe atoms of **2a-c** prompted us to pursue the catalytic reduction of N₂ using the [Mo₃S₄Fe] cubes. Reduction to NH₃ was observed but was not catalytic, giving at most 1.6 ± 0.1 equiv. NH₃ (per **2c**) under typical conditions^{14,15,20} (Supplementary Table 4). Protonation of S atoms possibly occurs in this reaction which weakens the Fe-S bonds and releases a vertex Fe atom from [Mo₃S₄Fe], in a relevant manner to degradation of the cubes under electrochemical oxidation^{11,12}. Nonetheless, more importantly, we discovered that the Cl-clusters **1a-c** and N₂-clusters **2b** and **2c** all catalytically reduce N₂ to N(SiMe₃)₃ in the presence of excess Na and ClSiMe₃. A minimum of 122.9 ± 3.0 (per **1c**) and up to 248.0 ± 15.6 (per **1b**) equiv. of N(SiMe₃)₃ were generated after 100 hours under an N₂

(1 atm) atmosphere at room temperature (Table 1 and Supplementary Tables 1 and 2). While the cause of the differences in the activity of these complexes has not been conclusively identified at this point, we assume that the steric, not electronic, effects of the Cp^R ligands play a major role (*vide infra*) because the Cp^R substituents did not notably affect the redox behaviors of **1a-c** ($E_{1/2}([\text{Mo}_3\text{S}_4\text{Fe}]^{5+/4+}) = -0.17$ (**1a**), -0.19 (**1b**), and -0.24 (**1c**) V vs. Ag/Ag⁺)¹² or redox features of **2b** and **2c** observed in cyclic voltammetry (Supplementary Fig. 14).

The N(SiMe₃)₃ yields, on a per-active-metal basis produced by **1b** and **2c**, are about 3 times higher than those of other Fe catalysts reported so far (Supplementary Table 3),²¹⁻²⁵ and are comparable to the highest yields by Mo²⁶ and Co^{27,28} catalysts. Similar to known systems, the catalytic reactions in THF concurrently formed Me₃SiSiMe₃, Me₃SiOC₄H₉, and Me₃SiOC₄H₈SiMe₃ as byproducts (Supplementary Figs. 15-17). These byproducts should originate from reactions of the trimethylsilyl radical ·SiMe₃ with itself or the THF solvent²⁸, as treatment of ClSiMe₃ with alkaline metals has been accepted to generate ·SiMe₃²⁶. Although the THF solvent is much more abundant than the N₂ reactant, the selectivity for N(SiMe₃)₃ was high in the case of **1b** and reached 37.2% (Table 1, entry 2). It is striking that any of the corresponding [Mo₃S₄] platforms, several relevant FeS clusters, or FeCl₂²⁰ did not provide N(SiMe₃)₃ at significant levels under the same conditions (Table 1 and Supplementary Table 3). After a catalytic run using **1a**, a mass spectrum of the reaction mixture revealed [Mo₃S₄Fe] cubes binding ring-opening products of THF (Supplementary Fig. 19), indicating sufficient stability of the cubic core during catalysis. Moreover, a CO-trapping experiment revealed the formation of a low yield (11%) of [(C₅Me₄SiEt₃)₃Mo₃S₄Fe(CO)] (**5**) from a catalytic reaction mixture with **1c**, Na and ClSiMe₃ (200 eq. each) under N₂ (Supplementary Figs. 24-27), implying the generation of [Mo₃S₄Fe] species with labile ligands (*e.g.* THF or N₂) on Fe. These results suggest that the Fe center of each [Mo₃S₄Fe] cube is the actual N₂-reducing site.

Considering previous proposals for analogous reactions^{26,28}, we propose a mechanism for N₂-silylation by our [Mo₃S₄Fe] cubes (Supplementary Fig. 18). In this pathway, we suppose that the Cl atom on Fe is removed by ·SiMe₃ to generate a vacant Fe site that binds N₂. In the resultant Fe-N₂ species, the more exposed *distal* N atom likely undergoes the first silylation to generate the Fe-NNSiMe₃ species. Further silylation and reduction would dissociate a hydrazido anion [Me₃SiN-N(SiMe₃)₂]⁻, as theoretically proposed for Mo- and Co-catalyzed reactions^{26,28}. Dissociation of the hydrazido anion can regenerate a vacant Fe site for the next catalytic cycle. Note that we cannot exclude the possibility that the catalysis is mediated by unidentified species generated in the solution. However, the isolation of the N₂-bound clusters establishes the substrate-binding by the [Mo₃S₄Fe] clusters. Below we additionally describe stoichiometric experiments that indicate the feasibility of the initial silylation of N₂.

The initial silylation of the N₂ ligand is arguably the most vital step in N₂ reduction. To validate it, the *in situ* generated **2c** (from **1c** and 2.3 equiv. K₂C₈) was treated with 1.1 equiv. ClSiPh₃ to furnish a mono-silylated N₂ species ([Cp^X₃Mo₃S₄Fe(N₂SiPh₃)], **3**) in 20% yield (Figs. 2a and 2d and Supplementary Figs. 4, 9, and 13). The same cluster **3** was alternatively generated from **2c** and ClSiPh₃ in C₆D₆ (Supplementary Fig. 5). The X-ray structure of **3** shows an elongated N-N distance (1.193(7) Å) from that found in the N₂-bound **2c** (1.136(5) Å), in accordance with a weakened N-N bond ($\nu_{\text{N-N}} = 1706 \text{ cm}^{-1}$). These values are close to those previously reported for Fe complexes bearing [N₂SiR₃] ligands (Supplementary Table 6)^{22,29,30}. While the phenyl substituents on the Si atom of **3** differ from the methyl groups employed in the catalytic process, the isolation of **3** supports the possible generation of an Fe-NNSiMe₃ analogue of **2c** in the catalytic cycle. This assumption was further reinforced when **3** was used as the precursor for the successful catalytic silylation of N₂, yielding 258.3 ± 4.9 equiv. of N(SiMe₃)₃ (Table 1, entry 6).

The irreversible chemical modification of the bound N₂ molecule highlights a reactivity difference between our system and a N₂-bridged [MoFe₃S₄] dimer reported recently.⁹ Treatment of [{Cp*MoFe₃S₄(IPr)₂}(μ-N₂)] (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) with [Cp^L₂Ti] was reported to give an equilibrium mixture of the [MoFe₃S₄]₂(μ-N₂) dimer and a heterometallic N₂-bridged complex [{Cp*MoFe₃S₄(IPr)₂}(μ-N₂)(Cp^L₂Ti)], but no further chemical conversions or catalytic reduction of the bound N₂ was reported. The difference in reactivity between this N₂ bridging system and the terminally bound N₂ system reported herein points to the importance of a terminal Fe-N₂ moiety for the successful reduction of N₂. Additionally, the isolation of a stable intermediate analog by our [Mo₃S₄Fe] platform indicates its potential utility as a synthetic toolkit to investigate catalytic as well as stoichiometric activation of other small molecules.

Structural models of the N₂-bound clusters reveal that the Cp^R ligands surround the N₂ ligand and the [Mo₃S₄Fe] cores (Fig. 3). The -SiMe₃ and -SiEt₃ groups of the Cp^R ligands are forced into the space around the Fe sites of the [Mo₃S₄Fe] cubes (Fig. 3b and 3c) to minimize steric repulsion between the Cp^R ligands. Thus, the -SiR₃ groups efficiently offer steric protection of the [Fe-N₂] moiety and prevent dimerization of cubes through either an Fe-N₂-Fe bridge or an inter-cube Fe-S interaction. On the other hand, the less bulky Cp* ligands lead to a more exposed Fe site (Fig. 3a) and allow the approach of the Fe site of another [Mo₃S₄Fe] cube to give an Fe-N₂-Fe dimer. The bulkiness of Cp^R ligands should affect the catalytic activities as well, since we suggest that the first N-Si bond formation occurs at the *distal* N atom. In an Fe-N₂-Fe dimer, both N atoms are protected until one of the Fe-N interactions breaks to generate monomers. In the catalytic reactions using Fe-Cl cubes, chloride abstraction (initiation) is expected to be slower with the bulkier Cp^R ligands.

To better understand the properties of **2a-c** and **3**, Zero-field ^{57}Fe Mössbauer spectra were measured at 78 K using powdered crystals (Supplementary Fig. 10). The spectra were fitted as single quadrupole doublets with the following values of the isomer shift (δ) and the quadrupole splitting ($|\Delta E_Q|$): $\delta = 0.479(4)$ (**2a**), $0.410(2)$ (**2b**), $0.401(3)$ (**2c**), and $0.263(3)$ (**3**) mm/s; $|\Delta E_Q| = 1.258(8)$ (**2a**), $1.422(5)$ (**2b**), $1.466(5)$ (**2c**), and $0.906(5)$ (**3**) mm/s, respectively. The δ values of **2a-c** are lower than those of the precursors **1a-c** featuring Fe^{II} centers ($\delta = 0.555(2)$ – $0.563(3)$ mm/s), even though **2a-c** are supposedly more reduced. A reduced Fe center typically displays a higher δ than an oxidized Fe in similar coordination environments, due to shielding of electrons in *s* orbitals by the increased *3d* electron densities. This has also been verified for $[\text{Fe}_4\text{S}_4]$ and $[\text{Fe}_3\text{S}_4]$ clusters bearing thiolate ligands³¹. The opposite trend observed here could be ascribed to π back-donation from Fe to the N_2 ligand. As suggested from theoretical calculations, such increased covalency of the Fe-ligand bond leads to high electron density at the Fe nucleus and consequently, a low δ value³². Thus, while determination of the Fe oxidation state is not straightforward, we tentatively assign the Fe centers in **2a-c** as close to Fe^{II} but only slightly reduced. Kohn-Sham frontier orbitals of optimized **2a** and **2c** reveal major contributions of Mo atoms in the occupied orbitals to store reducing equivalents (Supplementary Figs. 21-23). The DFT-calculated δ values of **2a**, **2c**, and **3** based on the crystal and optimized structures are qualitatively in agreement with the experimental data (Supplementary Tables 7-10), supporting the utility of orbital analysis.

The covalent nature of Fe-N interaction can also rationalize the δ value of **3**. As illustrated by the N–N bond distance and N–N stretching frequency of the cluster, silylation of the N_2 ligand has led to stronger back-donation from Fe and a shorter Fe–N distance ($1.687(5)$ Å) than those of **2a** and **2c**. This is consistent with a highly covalent Fe–N interaction and does not contradict the decrease of the δ value in **3** compared to **2a-c**, implying a major contribution of a resonance structure of $\text{Fe}=\text{N}=\text{N}-\text{SiPh}_3$. A notably bent N–N–Si angle of **3** ($133.4(5)^\circ$), a linear Fe-N-N alignment ($171.6(6)^\circ$), and computed Mayer bond orders (Fe–N, 1.49 (**3**) vs. 0.89 (**2a**) and 1.12 (**2c**); N–N, 1.68 (**3**) vs. 2.00 (**2a**) and 2.31 (**2c**); Supplementary Tables 11-13) are in good agreement with a diazenido assignment. The effect of the Fe–N interaction on the δ variation of a series of clusters can be illustrated by a plot of their Fe–N bond distances versus δ values. The plot using data points of **2a**, **2c**, and **3** exhibits a pseudo-linear relationship as shown in Supplementary Fig. 20. Interestingly, similar relationships were also seen in $[(\text{Si}^{\text{Pr}_3})\text{Fe}(\text{N}_2)]^{0/-}$ and $[(\text{Si}^{\text{Pr}_3})\text{Fe}(\text{N}_2\text{SiMe}_3)]$ ($\text{Si}^{\text{Pr}_3} = \text{Si}(\sigma\text{-C}_6\text{H}_4\text{P}^{\text{Pr}_2})_3$)³⁰, and $[\text{LSnFe}(\text{N}_2)]^{0/-}$ and $[\text{LSnFe}(\text{N}_2\text{SiMe}_3)]$ ($\text{L} = [\text{N}(\sigma\text{-}(\text{NCH}_2\text{P}^{\text{Pr}_2})(\text{C}_6\text{H}_4)_3]^{3-}$)³³, and regression lines from each series have nearly the same slope.

Overall, the above results represent the first catalytic silylation of N_2 by a synthetic M-S cluster and suggest some key features for successful N_2 reduction. Sufficient stability of the M-S core under

reducing conditions can make an Fe center sufficiently electron-rich to activate N₂. These results imply that suppression of inter-molecular aggregation of M-S cores is a key to stabilizing a terminal N₂-bound species and maintaining the reactivity at the *distal* N atom of the bound N₂ molecule. In this sense, the steric protection given by the Cp^R ligands loosely mirrors the role of a protein matrix isolating metal centers to control reactivity and avoid undesirable decomposition. While N₂ reduction to NH₃ or to N(SiMe₃)₃ should have substantial mechanistic differences, our results provided the first compelling clues that the N₂ molecule can become susceptible to reduction by Fe centers in S-rich environments, as is the case with FeMoco.

Data availability: X-ray data are available free of charge from the Cambridge Crystallographic Data Centre under reference numbers CCDC 2079174-2079176 and 2141451. All other experimental, spectroscopic, crystallographic, and computational data are included in the supplementary information.

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Additional information

Supplementary information is available for this paper

Correspondence and requests for materials should be addressed to Y.O.

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Main Figure Titles and Legends

Fig. 1.

Title: A proposed N₂-binding state of FeMoco and an N₂-bound Mo-Fe-S cluster in this work.

Legend: n/a

Fig. 2.

Title: (a) Synthetic schemes of N₂-bound [Mo₃S₄Fe] clusters **2a-2c** and subsequent silylation of the bound N₂ to give **3**. (b-d) Structure of **2a**, **2c**, and **3**.

Legend: The equivalence of **2a** (1/2 eq.) is omitted for readability. Carbon and oxygen atoms are drawn as capped sticks for clarity.

Fig. 3.

Title: Structural models of N₂-bound [Mo₃S₄Fe] clusters.

Legend: Space-filling model is applied to two Cp^R ligands, while the other Cp^R is omitted to show the [Mo₃S₄Fe]-N₂ moiety. (a) and (c) were prepared from the crystal structures of **2a** and **2c**, while (b) was prepared via software using the Cl-bound cluster **1b**.

Main Table

Table 1. Catalytic reduction of N₂ into N(SiMe₃)₃ promoted by [Mo₃S₄Fe] clusters.^a

$$\text{N}_2 + 6 \text{ Na} + 6 \text{ Me}_3\text{SiCl} \xrightarrow[\text{THF, r.t.}]{\text{Precatalyst}} \text{N(SiMe}_3)_3$$

(1 atm) 100 h

Entry	Precatalysts	N(SiMe ₃) ₃ yield (equiv/catalyst) ^b
1	1a	127.0 ± 34.6
2	1b	248.0 ± 15.6
3	1c	122.9 ± 3.0
4	2b	142.5 ± 16.0
5	2c	227.1 ± 40.8
6	3	258.3 ± 6.1
7	Cp* ₃ Mo ₃ S ₄	6.5 ± 1.5
8	Cp ^L ₃ Mo ₃ S ₄	9.6 ± 2.7
9	Cp ^{XL} ₃ Mo ₃ S ₄	12.9 ± 8.7

^a 2000 equiv. each of Na and ClSiMe₃ were added to the catalyst in THF at room temperature and stirred for 100 h under 1 atm N₂. Reactions by **2a** were not examined due to the low isolated yield and the lower performance of the Cp* (C₅Me₅) system. Yields represent the average of three runs. ^b Yields were obtained from three independent experiments (*n* = 3) and are shown as mean ± s.d.