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Synthesis and Mechanism of Formation of Hydride-Sulfide Complexes of Iron

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Abstract

Iron-sulfide complexes with hydride ligands provide an experimental precedent for spectroscopically detected hydride species on the iron-sulfur FeMoco of nitrogenase. In this contribution, we expand upon our recent synthesis of the first iron sulfide hydride complex from an iron hydride and a sodium thiolate (Arnet, N. A.; Dugan, T. R.; Menges, F. S.; Mercado, B. Q.; Brennessel, W. W.; Bill, E.; Johnson, M. A.; Holland, P. L., *J. Am. Chem. Soc.* **2015**, *137*, 13220–13223). First, we describe the isolation of an analogous iron sulfide hydride with a smaller diketiminate supporting ligand, which benefits from easier preparation of the hydride precursor and easier isolation of the product. Second, we describe mechanistic studies on the C-S bond cleavage through which the iron sulfide hydride product is formed. In a key experiment, use of cyclopropylmethanethiolate as the sulfur precursor leads to products from cyclopropane ring opening, implicating an alkyl radical as an intermediate. Combined with the results of isotopic labeling studies, the data are consistent with a mechanism in which homolytic C-S bond cleavage is followed by rebound of the alkyl radical to abstract a hydrogen atom from the iron to give the observed alkane and iron-sulfide products.

Synopsis

The synthesis and mechanism of formation of diiron complexes with sulfide and hydride bridges demonstrates the access to this core, which has been proposed in nitrogenase

Introduction

Nitrogenases are the enzymes utilized by microorganisms to fix atmospheric N₂ into the more bioavailable ammonia (NH₃).^{1,2} The active site of the most studied nitrogenase

contains a $\text{MoFe}_7\text{S}_9\text{C}$ cofactor (FeMoco) that is bound to the protein only through a cysteine residue at the terminal iron and a histidine residue at the molybdenum (Figure 1), suggesting the potential for flexibility of the cofactor.^{3–5} Kinetic studies by Lowe and Thorneley provided evidence that the FeMoco undergoes three (E_3) or four (E_4) additions of proton/electron pairs before binding N_2 ,⁶ but the structural changes that arise from these reductions are unknown. It is also relevant that H_2 is a competitive inhibitor of N_2 reduction, and high-pressure experiments indicated that one equivalent of H_2 is released upon N_2 binding.¹ These early results led a number of scientists to suspect the presence of hydrides on FeMoco in the E-states that are accessed prior to N_2 binding.⁷

To further characterize the E_4 state, Dean, Seefeldt, and Hoffman have studied wild type and mutant nitrogenase enzymes using a combination of site-directed mutagenesis, activity assays, and spectroscopy.^{10, 11} An important breakthrough was the discovery that the $\alpha\text{-70}^{\text{Val}}$ residue acts as a gatekeeper, preventing molecules bigger or bulkier than N_2 from accessing the FeMoco active site.⁵ Site-directed mutagenesis to replace this valine residue with the bulkier isoleucine prevented N_2 from binding but still allowed reduction of protons.^{12, 13} With this mutant, an appreciable amount of a new species, assigned as the E_4 “Janus” intermediate, could be generated and subsequently studied by EPR and ENDOR spectroscopy.¹⁴ An analogous species is also observed in wild-type protein reduced under argon, in lower amounts.¹⁵ The aforementioned ENDOR analysis indicated that E_4 has two iron-bound hydride ligands that lie in a bridging binding mode. Photolysis of E_4 using 450 nm light caused elimination of H_2 , and the rate had a kinetic isotope effect when D_2O was used as the solvent, suggesting that there is a post-photolysis step with a barrier, such as hydride migration.¹⁶ Hydride migrations on the FeMoco have been studied in detail computationally by Dance.^{7e, 17–19} However, the way that bridging hydrides serve to help FeMoco bind and/or reduce N_2 is still a subject of debate.^{15, 20} It is possible that the hydrides directly hydrogenate N_2 to generate an N_2H_x intermediate shortly after N_2 binding. Alternatively, the hydrides could reductively couple to reversibly form a dihydrogen complex that reacts with N_2 to displace the H_2 . N_2 -for- H_2 displacement has precedents in the chemistry of phosphine-supported octahedral iron complexes,^{21–24} and Peters has developed a catalytic system in which H_2 loss brings the catalyst from the resting state into the catalytic cycle.²⁵ Another hypothesis is that hydrides lead to electronic structure changes that facilitate N_2 binding.²⁶

This ongoing work on the nitrogenase enzyme, and comparisons between the sulfide-rich (weak-field) environment of the FeMoco and the CO-rich but thiolate-containing (strong-field) environment of the hydrogenase active sites,²⁷ motivate the study of well-characterized iron-sulfide species with hydrides. These studies aim to elucidate the fundamental structure, spectroscopy, electronic structure, and reactivity of hydrides in a sulfide-iron environment. However, despite the large variety of iron sulfur clusters that have been synthesized as structural models of enzymatic systems,^{28, 29} before 2015 none of the iron-sulfide systems had Fe-H bonds. Coucouvanis has reported a borohydride bound to the Mo site of a MoFe_3 cluster.³⁰

Recently, we reported the first synthetic iron sulfide species with a bridging hydride (**2** in Scheme 1).³¹ Interestingly, the precursor was not an iron-sulfur cluster; instead it came from

C-S bond cleavage of a sodium thiolate by the β -diketiminato-supported iron hydride dimer $[\text{L}^{\text{Me,iPr}}\text{FeH}]_2$ (**1**, Scheme 1). Deuterium labeling studies suggested that one of the two hydrides from **1** ends up on the alkyl group of the thiolate to generate the alkane. However, the mechanism of this transformation was unknown, and kinetic studies were not feasible because of concurrent production of a thiolate side product. Here, we report two new advances: first, we show the generality of the thiolate route to a related diketiminato-supported iron hydride sulfide complex; and secondly, we describe mechanistic studies that clarify the pathway from the hydride to the hydride-sulfide complex through C-S cleavage.

Results and Discussion

Synthesis of Sulfide-Hydride Complexes

We initially observed **2** as a result of the reaction between **1** and sodium *tert*-butylthiolate.³¹ However, the greater safety and ease of handling of sodium 1-dodecanethiolate led us to use the longer alkyl group on the thiolate. Crude samples generated through the process in Scheme 1 give **2** as well as an impurity. Quantitation using ¹H NMR and Mössbauer spectroscopies show that about 80% of the iron is present as **2**, while about 20% is present as the impurity, which has an isomer shift (δ) of 0.80 mm s⁻¹ and a quadrupole splitting ($|E_Q|$) of 2.38 mm s⁻¹.³¹ However, we were unable to crystallize samples of this impurity for structural identification. Based on the observation of dodecanethiol after addition of acids to the mixture, we considered an iron-thiolate complex to be the most likely identification.

In order to test the feasibility of different potential structures of iron-thiolate species, we used density-functional theory (DFT) studies on models with the dodecane groups truncated to methyl or ethyl groups. Using the protocol that we recently established for Mössbauer correlations,³² we optimized the geometries of several species (shown in Chart 1) at the BP86/def2-TZVP level. Using these optimized geometries, Mössbauer parameters were calculated at the B3LYP/def2-TZVP with or without the expanded CP(PPP) basis set on the iron atom. The results of these calculations as well as the experimentally observed values are given in Table 1. There is a large deviation in predicted isomer shift (off by 0.24–0.29 mm s⁻¹) and quadrupole splitting (off by 0.27–0.34 mm s⁻¹) between the calculated values for $[\text{L}^{\text{Me,iPr}}\text{Fe}(\text{SCH}_2\text{CH}_3)]^-$ and experiment, suggesting that the monothiolate structure is unlikely. On the other hand, both $[\text{L}^{\text{Me,iPr}}\text{Fe}(\text{SCH}_2\text{CH}_3)_2]^-$ and $[\text{L}^{\text{Me,iPr}}\text{Fe}(\text{SCH}_3)_2]^{2-}$ give predicted isomer shifts and quadrupole splittings that are close to the experimentally observed values. The similarity between the calculated Mössbauer parameters for these two models is not surprising, because the immediate coordination sphere around iron in the complexes is similar: each has a β -diketiminato and two alkylthiolates in a tetrahedral coordination geometry.

In order to distinguish between these models, we used electrospray mass spectrometry.³¹ In the negative ion spectrum, there was a prominent signal at 875.6 amu/e⁻, which is consistent with the mass of the bis(thiolate) iron(II) complex $\text{Na}[\text{L}^{\text{Me}}\text{Fe}(\text{SC}_{12}\text{H}_{25})_2]$. Note that the calculations predict Mössbauer parameters for this structure that are within 0.11 mm s⁻¹ in terms of both isomer shift and quadrupole splitting. Therefore, we conclude that the impurity derives from thiolate coordination with loss of hydrides and without C-S bond cleavage.

Since samples containing the impurity did not evolve further into **2**, this bis(thiolate) compound is not an intermediate but rather a side product.

Since this impurity was a problem, and because the synthesis of precursor **1** is challenging (typical yields on scales above 100 mg were only around 40%), we also explored the use of another β -diketiminato supporting ligand. Specifically, we used the β -diketiminato in which the isopropyl groups of the aromatic rings are replaced with methyl groups, and there is an additional methyl group on the backbone ($L^{\text{Me}3}$). Though the difference in the supporting ligands seems minor, the behavior of complexes with the different ligands can vary substantially: for example, reduction of the iron(II) chloride complex of the isopropyl-substituted ligand gives only N_2 binding to give a bridging N_2 complex, while the analogous reduction with the smaller $L^{\text{Me}3}$ ligand gives N_2 splitting in a Fe_4 product.³³ The iron(II) hydride dimer of the $L^{\text{Me}3}$ ligand system also has a significant advantage in that it can be synthesized easily by treatment of the iron(II) chloride complex with cyclohexylmagnesium chloride.^{33, 34}

Thus, we treated the known hydride dimer $[\text{L}^{\text{Me}3}\text{Fe}(\mu\text{-H})]_2$ (**4**)^{33, 34} with sodium dodecanethiolate in THF, which gave a product **5** (Scheme 2) that was insoluble in alkane solvents. The solid could be purified easily by washing the dried reaction mixture with pentane, to give 66% isolated yield of analytically pure **5**. Its infrared spectrum is shown in Figure S1, and its electronic absorption spectrum is shown in Figure S2. This synthesis has a marked improvement over **2**, which was very soluble in non-polar solvents and was not isolated as a pure solid (it was only after chelation of the sodium with 2.2.2-cryptand to form **3** that it was isolated in pure form).¹³ However, the reaction that forms **5** also generates several byproducts that were observed by ^1H NMR spectroscopy. Because the populations of these species were low, we were not able to identify the byproducts using Mössbauer spectroscopy as done above. One of the byproducts (which forms in greater amounts when using 5 equiv of dodecanethiolate) is tentatively assigned as $\text{Na}[\text{L}^{\text{Me}3}\text{Fe}(\text{SC}_{12}\text{H}_{25})_2]$ on the basis of NMR and mass spectra (Figures S3 and S4) and by analogy to the behavior with the larger diketiminato ligand described above.

Despite the apparent similarity between **3** and **5**, there are differences in the optimum temperature and solvent used for the sulfide-hydride complexes of the two different β -diketiminato ligands. The reaction of **1** with $\text{NaSC}_{12}\text{H}_{25}$ required heating to 60 °C in benzene, and gave a substantially higher amount of impurities when the reaction was performed in THF.³¹ In contrast, THF was the better solvent for the reaction of **4** with $\text{NaSC}_{12}\text{H}_{25}$: this reaction gave no isolable amounts of **5** in benzene at 60 °C, and THF was effective at room temperature. Though we do not understand the reason for these differences, they are important for the successful syntheses of each.

The X-ray crystallographic structure of **5** shows that the diiron(II) sulfide hydride core has overall similarity to that in **2**. However, the lesser steric hindrance of the supporting ligand caused some differences. The most evident is that **5** dimerizes in the solid state, with two sodium atoms bridging the sulfides (Figure 2a). The red-brown color of a solution of **5** in benzene is visibly different from the crimson red color of a solution in THF, and the ^1H NMR spectra of **5** are also different between solutions in C_6D_6 vs. $\text{THF-}d_8$ (Figure 3).

Addition of different amounts of THF to a solution of **5** in C₆D₆ shifted the ¹H NMR spectrum toward that observed in THF-*d*₈, indicating fast exchange on the NMR time scale, and removal of the THF and redissolving gave a spectrum identical to the one originally observed in C₆D₆ (Figure S5). These changes lead us to conclude that the crystallographically observed dimeric structure in the structure of **5** is maintained in non-coordinating solvents such as benzene, but in THF it is reversibly broken up by coordination of THF to the sodium cations (Scheme 3).

The idea that **5** breaks up into monomers is supported by the X-ray diffraction analysis of a crystal grown from a mixture of THF and pentane, which shows a monomer with four coordinated THF molecules on each sodium. The Fe₂(μ-S)(μ-H) cores of the two forms of **5** are very similar between the dimeric and monomeric structures (Table 2). However, due to disorder in the structure of the THF adduct (Figure S6), we were unable to refine the location of the hydride in the Fourier map of **5**(THF)₄. For this reason, the hydride is missing in the thermal-ellipsoid plot in Figure 2b, but its presence is shown by the reversibility of the THF coordination process.

Table 2 also compares key metrical parameters between the two structures of **5** with the two structures previously reported for **2**, which differ by having an inner-sphere sodium cation (with a cation-π interaction with one ligand aromatic ring) or having the sodium cation pulled away by the chelator 2.2.2-cryptand.³¹ In the dimeric structure of **5**, the Fe-N distances are shorter than in the other three structures, presumably from the less bulky supporting ligand. The presence of the Na-S interaction in this structure lengthens the Fe-S bonds in each structure with S-Na interactions (all but **2**•cryptand), and the lengthening is more in **5**. Other metrical parameters are similar between the structures, and the hydride positions are not established with sufficient accuracy to draw any conclusions about the influence of cations and ligand size on the Fe-H interactions.

When we prepared **5** using a mixture of **4** and the deuteride analogue of **4** (**4-D**),³⁵ the resonances in the ¹H NMR spectrum of the product in benzene-*d*₆ were doubled, featuring a greater difference between the resonances the further they are shifted from the diamagnetic region. Figure 4 shows a spectrum of a mixture of **5** and **5-D**, which were mixed to demonstrate the shift. This paramagnetic isotope effect on chemical shift (PIECS) has been observed for the deuterium isotopologues of other bridging hydride complexes.^{36, 37} Compound **3** also displayed PIECS, but it could only be observed when the sample was cooled to -80 °C.³¹

The solid state Mössbauer spectrum of **5** shows a quadrupole doublet with an isomer shift of 0.70 mm s⁻¹ and quadrupole splitting of 1.20 mm s⁻¹ (Figure 5). These parameters are very similar to those reported for **2**, which featured an isomer shift of 0.72 mm s⁻¹ and quadrupole splitting of 1.17 mm s⁻¹.³¹

GCMS analysis of the product mixture generated from **4** and sodium dodecanethiolate indicated the presence of dodecane in 70(7)% yield, and when **4-D** was used as starting material, the produced dodecane was exclusively mono-deuterated. This is similar to what

we previously observed during the formation of **2** from **1**,³¹ and suggests a similarity in the mechanism of the reaction (notwithstanding the solvent dependence described above).

Mechanistic studies on the formation of the sulfide-hydride complex **2**

Above, the formation of dodecane and an iron-sulfide complex from dodecanethiolate demonstrated that the insertion of S to give the iron-sulfide-hydride complexes comes from the cleavage of C-S bonds. Cleaving the C-S bond of a thiolate is an unusual pathway to generate an iron sulfide complex. Tritylthiol has been used by the Liaw group in 2009 to generate iron sulfide complexes from reaction with an iron ethylthiolate species.³⁸ More recently, Kim reported the formation of an [2Fe-2S] cluster through C-S bond cleavage with a cysteine analogue,³⁹ and Murray reported the formation of a novel planar [3Fe-3S] cluster using tritylthiolate C-S cleavage.⁴⁰

We also note other selected examples where the cleavage of a C-S bond was used to form metal sulfides. In 1994, Kitajima reported the synthesis of a disulfide-bridged copper(II) complex from a monomeric copper(II) tritylthiolate complex.⁴¹ Riordan has reported the formation of a dinuclear S₂²⁻-bridged complex from a nickel(II) thiolate, which may go through a sulfide intermediate.⁴² Hayton made use of a thiolate as a S^{•-} transfer agent to form novel uranium and nickel sulfide species.^{43, 44} In each of these cases tritylthiolate was used, and the byproduct in these reactions was Gomberg's dimer, the coupled product of two CPh₃ radicals. The observation of Gomberg's dimer strongly suggests that these literature reactions proceeded through homolytic C-S bond cleavage, although detailed mechanistic studies were not performed.

It was of particular interest to provide experimental evidence relating to the mechanism of the unusual hydride-sulfide exchange. Mechanistic studies are challenging in this system because in neither case (**1** to **2** or **4** to **5**) was the product formed without byproducts, and in addition the starting thiolate salts are poorly soluble. No intermediates were observed by ¹H NMR spectroscopy during either reaction. Given these difficulties, we did not use kinetic studies. However, other pieces of mechanistic information are relevant. For example, the conversion of **1** to **2** requires a lithium or sodium thiolate.³¹ When potassium dodecanethiolate was used instead, GCMS of the product mixture showed no dodecane, and only dodecanethiol. This suggests that the C-S bond is not broken during the reaction with the potassium salt. The alkali metal dependence suggests that coordination of the alkali metal cation likely plays a role in the mechanism, with the most likely possibility being association with the thiolate as shown in Scheme 4.

To distinguish a potential radical pathway, we took advantage of the ability to bring about the conversion of **1** to **2** with a variety of alkylthiolates. The use of a cyclopropylmethyl group is advantageous because the cyclopropylmethyl radical is well known to undergo a ring-opening transformation at a rate of $1.3 \times 10^8 \text{ s}^{-1}$ to form the 1-butenyl radical (a "radical clock").⁴⁵ Evidence of 1-butene as a product would be indicative of the C-S bond being cleaved homolytically, and exclusive formation of methylcyclopropane would point towards concerted sulfur transfer (Scheme 5). Thus, we prepared sodium cyclopropylmethylthiolate (see Experimental Section) and verified that it was able to bring about the conversion of **1** to **2** in 88% spectroscopic yield.

The volatile materials from the reaction were transferred under vacuum to a separate NMR tube and methylcyclopropane was detected in 1.7% yield with no indication of 1-butene. However, the reaction of cyclopropylmethanethiolate with **1** generated **2** along with the *n*-butyl complex, $L^{\text{Me,iPr}}\text{Fe}^n\text{Bu}$ (**6**, Scheme 6), which was reported previously.⁴⁶ Compound **1** has been established to react with the terminal alkene 1-hexene to give the corresponding insertion product $L^{\text{Me,iPr}}\text{Fe-hexyl}$.⁴⁷ Thus, we suspected that **6** arose from the reaction between remaining **1** and 1-butene formed during the reaction, and tested this in a control experiment. Treating cyclopropylmethanethiolate with 3.0 equivalents of **1**, so that cyclopropylmethanethiolate was the limiting reagent, led to a 77(11)% yield of **6** as judged by ¹H NMR spectroscopy (Figure S7), which is within error of the 88(5)% yield of **2** in the same reaction. These data are most consistent with the conclusion that C-S homolytic cleavage gives a cyclopropylmethyl radical, which ring opens to form the 1-butenyl radical, then abstracts a hydride as an H• to form 1-butene, and finally reacts quickly with **1** to form **6** (Scheme 6).

As noted in the introduction, there are a number of other literature reports, mostly of triphenylmethylthiolate complexes, in which homolytic C-S bond cleavage gives a sulfide. Because the loss of a triphenylmethyl group gives a stable radical, it has often been possible to detect it (as Gomberg's dimer) directly. In the case studied here, the alkyl radical (before or after ring-opening in the case of the cyclopropylmethyl radical) is much less stable, and presumably would undergo bimolecular decomposition⁴⁸ if it were not trapped by the iron-hydride. We note that when the reaction between **1** and $\text{NaSC}_{12}\text{H}_{25}$ was performed in THF-*d*₈, GCMS analysis of the product mixture indicated only natural abundance deuteration of dodecane. This suggests that the radical extracts the hydride H-atom before it has an opportunity to escape the solvent cage to abstract an H-atom from the solvent.

Overall, the sequence of reactions along the left of Scheme 4 is reasonable given the following qualitative considerations. Coordination of the thiolate is expected to weaken the C-S bond, by analogy to the considerable weakening of the homolytic bond strength of S-H bonds that has been measured in hydrosulfide complexes.⁴⁹ As noted above, the presence of Li^+ or Na^+ is important for the reaction, and this could come from either a kinetic effect from pre-organization through cation- π interactions with the aryl rings of the ligand, or a thermodynamic effect from stabilization of the incipient sulfide after C-S cleavage (or both). At this point, the C-S bond is cleaved, and the stepwise nature of the reaction is strongly supported by the radical clock experiment. The alkyl radical is formed in proximity to an Fe-H bond on a high-spin iron center, and this type of hydride is highly activated toward cleavage (implying a weak Fe-H bond dissociation energy) in related bimetallic hydride complexes.⁴⁷ Then, the closing of the Fe-S-Fe unit may be facilitated by the pre-existing Fe-H-Fe bridge. The remaining hydride at the end of the reaction is more sterically masked than in the starting material, explaining why a second S substitution does not take place.

Conclusions

Here we have taken advantage of the flexibility of choices of ligand and alkyl group for thiolate C-S cleavage. These have enabled us to discover an easier method for preparing dinuclear sulfide-hydride complexes, and also to provide new data regarding the mechanism

of iron-sulfide formation from an iron hydride complex and a sodium thiolate. Specifically, a radical clock substrate shows that a short-lived radical intermediate is likely produced from homolytic C-S bond cleavage, which suggests a reasonable mechanism for sulfur abstraction and subsequent hydride loss.

Experimental Section

General Considerations

Unless otherwise noted, all reactions were performed under an argon atmosphere in an M. Braun glovebox maintained at or below 1 ppm of O₂ and H₂O. Glassware was dried at 160 °C and Celite was dried at 200 °C under vacuum. Solvents were dried by passage through activated alumina and Q5 columns from Glass Contour Co., with the exception of THF, which was distilled under Ar from a potassium benzophenone ketyl solution. All solvents were stored over activated 4 Å molecular sieves. Benzene-*d*₆ was dried and stored over activated alumina and filtered before use. THF-*d*₈, pyridine-*d*₅, and cyclohexane-*d*₁₂ were dried in a potassium benzophenone ketyl solution and distilled before used. The hydride complexes [L^{Me,iPr}FeH]₂ (**1**) and [L^{Me3}FeH]₂ (**4**) were prepared according to published procedures.^{33, 34, 50} The deuteride analogue [L^{Me3}FeD]₂ (**4-D**) was prepared by exposing **4** to 1 atm of D₂ for 2 minutes, removing the headspace, and repeating this sequence three times.

Potassium graphite (KC₈) was prepared by heating stoichiometric amounts of potassium and graphite to 160 °C under an argon atmosphere. Sodium bis(trimethylsilyl)amide was purchased from Acros Organics. Hydrogen gas (research grade) and methane gas (tech grade) were purchased from TechAir. Gaseous D₂ (99.8%) was purchased from Cambridge Isotope Laboratories.

¹H NMR data were recorded on a Bruker Avance 500 spectrometer (500 MHz) or a Bruker Avance 400 spectrometer (400 MHz). All resonances in the ¹H NMR spectra are referenced to the residual solvent peaks (δ 7.16 ppm for benzene, δ 3.58 ppm for THF, δ 1.38 ppm for cyclohexane, δ 8.74 for pyridine). Resonances were singlets unless otherwise noted. ¹H NMR spectroscopic quantifications were measured using a nickelocene or ferrocene capillary internal standard. IR data were recorded on a Bruker ALPHA spectrometer equipped with a Platinum-ATR attachment. UV-vis spectra were recorded on a Cary 60 spectrophotometer using Schlenk-adapted quartz cuvettes with a 1 mm optical path length. Solution magnetic susceptibilities were determined by adding an internal capillary standard of the appropriate deuterated solvent to 14–23 mM ¹H NMR samples of metal complex. The difference between the capillary and solvent peaks in Hz was used to determine μ_{eff} via the Evans method,⁵¹ using at least three different concentrations for verification. Mössbauer data were recorded on a SEECo spectrometer with alternating constant acceleration; isomer shifts are relative to iron metal at 298 K. The sample temperature was maintained at 80 K in a Janis Research Company Inc. cryostat. The zero-field spectra were simulated using Lorentzian doublets using WMoss (SeeCo). GC/MS analyses were performed on a Agilent GC 6890N and MS 5973 equipped with an RTX-1 column (15.0 m × 250 μm × 0.25 μm) using helium as the carrier gas. The analysis method used in all cases was 1.0 μL injection of sample, injection temperature of 250 °C, 100:1 split ratio, initial inlet pressure of 1.10 psi

(but varied as the column flow was held constant at 1.0 mL/min for the duration of the run), the interface temperature was held at 280 °C, and the ion source (EI, 70 eV) was held at 230 °C. The initial oven temperature was held at 50 °C for 3 min followed by a temperature ramp to 300 °C at 20 °C/min, and finally the temperature was held at 300 °C for 2 min. Elemental analyses were obtained from the CENTC Elemental Analysis Facility at the University of Rochester. Microanalysis samples were weighed with a PerkinElmer Model 2400 Series II Analyzer, and handled in a VAC Atmospheres glovebox under argon.

Sodium Thiolate Salts

Sodium dodecanethiolate ($\text{NaSC}_{12}\text{H}_{25}$) was synthesized by adding sodium hydride (109.3 mg, 4.554 mmol), purchased from Acros Organics, to a solution of 1-dodecanethiol, purchased from Sigma-Aldrich Corporation (10 mL of a 0.5 M solution in THF, 5 mmol) and stirring in a loosely capped vial for 24 h. The white solid was washed with THF and dried under vacuum, and used as a powder. Cyclopropylmethanethiol (HSC_4H_7) was prepared according to published procedures,⁵² then deprotonated with sodium bis(trimethylsilyl)amide in toluene to give sodium cyclopropylmethanethiolate as a white solid. The solid was washed thoroughly with THF and dried under vacuum. The ^1H NMR spectrum of the powder dissolved in D_2O matches the published spectrum for cyclopropylmethanethiol,^{52, 53} except that the SH proton is absent (Figure S8).

Synthesis of $\text{Na}[\text{L}^{\text{Me}_3}\text{Fe}(\mu\text{-H})(\mu\text{-S})\text{FeL}^{\text{Me}_3}]$ (**5**)

A sample of $[\text{LFe}^{\text{Me}_3}\text{H}]_2$ (**6**, 160.6 mg, 0.2134 mmol) was dissolved in THF (8 mL) to give a brown solution. The solution was transferred onto sodium dodecanethiolate (47.4 mg, 0.211 mmol) and stirred for 5 hours, turning dark crimson. The solution was filtered, and volatile materials were removed under vacuum. The solid was washed with pentane (10 mL) and dried under vacuum, giving a red-brown solid (86.9 mg, 51.1%). The pentane wash was stored at room temperature for 16 hours, precipitating further product (25.1 mg, 14.7%). ^1H NMR (25 °C, benzene- d_6): δ 21.5 (12H, $\gamma\text{-CH}_3$), 6.1 (16H, $m\text{-H}$), 0.1 (8H, $p\text{-H}$), -0.7 (24H, $\beta\text{-CH}_3$), -4.9 (48H, $\alpha\text{-CH}_3$) ppm. ^1H NMR (25 °C, THF- d_8): δ 20.6 (6H, $\gamma\text{-CH}_3$), 5.8 (8H, $m\text{-H}$), -0.9 (4H, $p\text{-H}$), -1.2 (24H, $\alpha\text{-CH}_3$), -3.2 (12H, $\beta\text{-CH}_3$) ppm. See Figure S5 for ^1H NMR spectra. μ_{eff} (benzene- d_6 , 25 °C) = 4.1(1) μ_{B} . IR (cm^{-1}): 3064 (w), 2955 (m), 2914 (m), 2854 (m), 1520 (m), 1460 (m), 1406 (m), 1336 (s), 1292 (m), 1253 (w), 1194 (s), 1132 (w), 1088 (m), 1032 (s), 989 (w), 917 (w), 888 (m), 854 (m), 760 (s), 638 (m), 618 (w), 572 (w), 495 (m), 430 (m). UV-vis (benzene; λ_{max} , nm (e, $\text{mM}^{-1}\text{cm}^{-1}$)) 344 (15.0 ± 0.2), 490 (2.20 ± 0.02). UV-vis (THF; λ_{max} , nm (e, $\text{mM}^{-1}\text{cm}^{-1}$), Figure S2) 346 (23.8 ± 0.4), 520 (3.72 ± 0.01). Anal. Calcd for $\text{NaC}_{44}\text{H}_{55}\text{N}_4\text{Fe}_2\text{S}$: C, 65.51; H, 6.87; N, 6.95. Found: C, 65.12; H, 7.13; N, 6.66. $\text{Na}[\text{L}^{\text{Me}_3}\text{Fe}(\mu\text{-D})(\mu\text{-S})\text{FeL}^{\text{Me}_3}]$ (**5-D**) was synthesized analogously using **4-D** as starting material. ^1H NMR (25 °C, benzene- d_6): δ 21.2 (12H, $\gamma\text{-CH}_3$), 6.1 (16H, $m\text{-H}$), 0.2 (8H, $p\text{-H}$), -0.6 (24H, $\beta\text{-CH}_3$), -4.6 (48H, $\alpha\text{-CH}_3$) ppm. The infrared spectra of **5** and **5-D** are compared in Figure S1.

Spectroscopic Observation of $\text{Na}[\text{L}^{\text{Me}_3}\text{Fe}(\text{SC}_{12}\text{H}_{25})_2]$

Compound **4** (2.1 mg, 0.0026 mmol) was dissolved in THF- d_8 and transferred to a J. Young NMR tube with a nickelocene capillary internal standard. $\text{NaSC}_{12}\text{H}_{25}$ (3.1 mg, 0.0138

mmol) was added and the tube was shaken at room temperature for 3 h. Integrations indicated 82(5)% yield of $\text{Na}[\text{L}^{\text{Me},\text{iPr}}\text{Fe}(\text{SC}_{12}\text{H}_{25})_2]$. ^1H NMR (25 °C, $\text{THF}-d_8$, Figure S3): δ 214.4, 160.1, 151.0 (3H, $\gamma\text{-CH}_3$), 144.0, 39.2, 29.9, 20.6 (12H, $\alpha\text{-CH}_3$), -0.88, -1.18 (4H, $m\text{-H}$), -3.16, -4.07, -49.1, -51.9 (2H, $p\text{-H}$), -61.5, -73.1, -75.1 (6H, $\beta\text{-CH}_3$), 91.9 ppm. The electrospray mass spectrum is shown in Figure S4.

Synthesis of $\text{Na}[\text{L}^{\text{Me},\text{iPr}}\text{Fe}(\mu\text{-H})_2\text{FeL}^{\text{Me},\text{iPr}}]$ (**1**) with Sodium Cyclopropylmethanethiolate

A sample of $[\text{L}^{\text{Me},\text{iPr}}\text{FeH}]_2$ (**1**, 14.0 mg, 0.0148 mmol) was dissolved in benzene- d_6 (0.5 mL) and transferred to a J. Young NMR tube with a nickelocene capillary internal standard. Sodium cyclopropylmethanethiolate (0.5 mg, 0.005 mmol) was added to the tube. The tube was sonicated for 4 minutes, then placed in a 60 °C oil bath for 15 h. Integration of the ^1H NMR spectrum indicated an 88(5)% yield of $\text{Na}[\text{L}^{\text{Me},\text{iPr}}\text{Fe}(\mu\text{-H})(\mu\text{-S})\text{FeL}^{\text{Me},\text{iPr}}]$ (**2**) and a 77(11)% yield of $\text{L}^{\text{Me},\text{iPr}}\text{Fe}(^n\text{Bu})$ (**6**). Volatile materials were vacuum transferred to a J. Young NMR tube with a ferrocene capillary internal standard. Integration of the ^1H NMR spectrum indicated a 1.7% yield of methylcyclopropane.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

The resting state structure of the nitrogenase active site cofactor, FeMoco.⁵ Likely oxidation states from recent X-ray studies are indicated.^{8, 9}

Figure 2.

(top) Thermal-ellipsoid plot of the X-ray crystal structure of **5**. (bottom) Thermal-ellipsoid plot of the X-ray crystal structure of **5**(THF)₄ showing the major disorder component. In the structure of **5**(THF)₄, the disorder prevented us from locating the peak for the hydride.

However, its presence is supported by the observation of reversible formation from **5**, by the similarity of Mössbauer spectra to compound **2**, and by PIECS in the NMR spectrum (see text). In both pictures, the methyl groups of the aryl rings are omitted for clarity, and 50% probability ellipsoids are used.

Figure 3.
¹H NMR spectra of **5** in benzene-*d*₆ (top) and THF-*d*₈ (bottom).

Figure 4.

^1H NMR spectrum of a mixture of 57% **5-D** and 43% **5** in benzene- d_6 .

Figure 5.

The solid state Mössbauer spectrum of **5** at 80 K. The black circles are the data, the red line is a simulation with $\delta = 0.70 \text{ mm s}^{-1}$ and $|E_Q| = 1.20 \text{ mm s}^{-1}$, and the gray line is the residual.

Scheme 1. Formation of the previously characterized iron hydride sulfide species.³¹

Scheme 2.

Preparation of **5** through a C-S bond cleaving reaction.

Scheme 3.

Proposed dissociation of the THF ligands of **5** in benzene to give the dimeric form.

Scheme 4.

Two possible mechanisms for iron hydride sulfide formation: a radical pathway (left) and a concerted pathway (right). The ligand framework has been abbreviated for simplicity.

Scheme 5.

The reaction between **1** and sodium cyclopropylmethanethiolate could lead to different products. The methylcyclopropane product would support the concerted pathway and the 1-butene product would suggest the radical pathway.

Scheme 6.

The proposed reaction pathway to form **2** and **6** from the reaction between **1** and cyclopropylmethanethiolate.

Chart 1.

Possible structures of the impurity that were considered: $[L^{\text{Me,iPr}}\text{Fe}(\text{SC}_{12}\text{H}_{25})_2]^-$, $[L^{\text{Me,iPr}}\text{Fe}(\text{SC}_{12}\text{H}_{25})]^-$, and $[L^{\text{Me,iPr}}\text{Fe}(\text{SC}_{12}\text{H}_{25})]_2^{2-}$.

Table 1

Comparison of Experimental and Calculated Mössbauer Parameters for Prospective Structures of the Impurity Observed During Synthesis of 2

Structure	δ (mm s ⁻¹) def2-TZVP	δ (mm s ⁻¹) CP(PPP)	$ E_Q $ (mm s ⁻¹) def2-TZVP	$ E_Q $ (mm s ⁻¹) CP(PPP)
Experimental	0.80		2.38	
[L ^{Me,iPr} Fe(SCH ₂ CH ₃)] ⁻	0.51	0.56	2.04	2.11
[L ^{Me,iPr} Fe(SCH ₂ CH ₃) ₂] ⁻	0.68	0.69	2.28	2.43
[L ^{Me,iPr} Fe(SCH ₃) ₂] ²⁻	0.84	0.83	2.27	2.29

Table 2

Metrical parameters in iron sulfide hydride complexes.

	2	2(cryptand)	Dimer of 5	major component of 5(THF)₄
Fe-S (Å)	2.2394(6), 2.2553(7)	2.215(1), 2.220(1)	2.269(1), 2.269(1), 2.273(1), 2.273(1)	2.267(3), 2.305(3)
Fe-Fe (Å)	2.7735(5)	2.741(1)	2.738(1), 2.747(1)	2.777(2)
Fe-S-Fe (°)	76.20(2)	76.34(4)	74.14(4), 74.36(4)	74.80(9)
Fe-H (Å)	1.66(3), 1.68(3)	1.66(4), 1.68(4)	1.72(5), 1.72(5), 1.85(5), 1.85(5)	
Fe-N (Å)	2.045(2), 2.046(2)	2.062(4), 2.065(4)	1.998(4), 1.999(4), 2.004(4), 2.006(4), 2.006(4), 2.009(4), 2.016(4), 2.020(4)	2.030(8), 2.042(8), 2.050(8), 2.054(7)
Na-S (Å)	2.671(1)	N/A	2.719(2), 2.722(3), 2.736(2), 2.736(2)	2.801(4)