# Dinitrogen Complexes of Sulfur-Ligated Iron

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S *Supporting Information*

ABSTRACT: We report a unique class of dinitrogen complexes of iron featuring sulfur donors in the ancillary ligand. The ligands utilized are related to the recently studied tris(phosphino)silyl ligands $(2\text{-}R_2PC_6H_4)_3Si$ (R = Ph, iPr) but have one or two phosphine arms replaced with thioether donors. Depending on the number of phosphine arms replaced, both mononuclear and dinuclear iron complexes with dinitrogen are accessible. These complexes contribute to a desirable class of model complexes that possess both dinitrogen and sulfur ligands in the immediate iron coordination sphere.
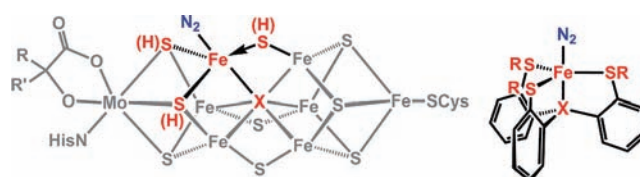
Figure 1. (left) Hypothetical binding mode of N_2 at the FeMoco and (right) a hypothetical model complex. Whether any of the S atoms shown in red for FeMoco (left) are protonated during catalysis is unknown.

Scheme 1

The intimate mechanism of nitrogen fixation by the nitrogenase enzymes remains a fascinating puzzle. Recent theoretical and experimental studies on the FeMo nitrogenase cofactor (FeMoco) have suggested N_2 binding at iron (Figure 1),[1] resulting in a growing interest in model complexes of iron with nitrogenous ligands (N_xH_y).[2] To date, such nitrogenase model chemistry has been dominated by complexes with phosphorus and nitrogen donors because of their propensity to afford N_2 complexes. This situation is striking given the sulfur-rich environment of the iron centers in the cofactor of FeMo nitrogenase.[3] Noteworthy in this context is the work by Sellmann[4] and more recently by Qu,[5] who have reported a number of iron complexes ligated by multiple sulfur donors and nitrogenous ligands.[6] Dinitrogen as a ligand remains a notable exception in these systems. In general, synthetic transition metal complexes with sulfur atom donors rarely afford N_2 adduct complexes; examples are known but remain comparatively uncommon.[7] With the exception of a single tetrahydrothiophene adduct of an Fe–N_2 complex,[8] the S–Fe–N_2 linkage is unknown, regardless of the number of S–Fe interactions.

Relative to phosphines and amines, π-donating sulfides and thiolates are weak-field ligands[9] that typically yield high-spin complexes with long Fe–L bonds.[10] Such a scenario is undesirable with respect to the favorable π back-bonding needed for a metal center to coordinate N_2. Accordingly, terminal N_2 adducts of transition metals do not populate high-spin states. In this regard, an electron-releasing and sulfur-containing ancillary ligand that yields low-spin metal centers may prove useful. Such scaffolds may help stabilize sulfur-ligated N_2 adducts of iron, especially in cases where N_2 is terminally bonded. Thioethers are particularly appealing since they are σ-donating and (weakly) π-accepting[11] and thus would favor states with lower spin relative to thiolates and sulfides. To test this idea, we targeted hybrid thioether/phosphine relatives of a tetradentate tris(phosphino)silyl
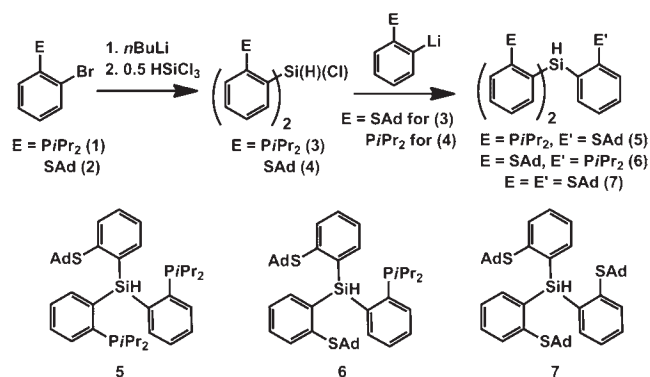
ligand, $(2\text{-}R_2PC_6H_4)_3Si$ ($[SiP^R_3]$; R = Ph, iPr), that has proven exceptionally successful in stabilizing terminal trigonal-bipyramidal $\{[SiP^R_3]Fe\text{–}N_2\}^n$ complexes ($n = -1, 0, +1$).[12] Herein we present a new class of iron complexes featuring the S–Fe–N_2 linkage supported by such hybrid ligands.

Precursors of the desired ligands were conveniently synthesized by lithiation of the aryl bromides $2\text{-}i\text{Pr}_2P(C_6H_4Br)$ (**1**) and $2\text{-}AdS(C_6H_4Br)$ (**2**) with n-BuLi followed by quenching with 0.5 equiv of $HSiCl_3$, which yielded the chlorosilanes $(2\text{-}i\text{Pr}_2PC_6H_4)_2\text{-}Si(H)(Cl)$ (**3**) and $(AdSC_6H_4)_2Si(H)(Cl)$ (**4**) in quantitative yield (Scheme 1). Addition of another equivalent of the lithiation product of **2** and **1** to **3** and **4**, respectively, afforded the hybrid ligands $(2\text{-}i\text{Pr}_2PC_6H_4)_2(2\text{-}AdSC_6H_4)SiH$ ($[SiP^{iPr}_2S^{Ad}]H$, **5**) and $(2\text{-}i\text{Pr}_2PC_6H_4)(2\text{-}AdSC_6H_4)_2SiH$ ($[SiP^{iPr}S^{Ad}_2]H$, **6**) in high yield. The tris(thioether)silane ligand $(2\text{-}AdSC_6H_4)_3SiH$, ($[SiS^{Ad}_3]H$, **7**) was also synthesized by addition of 0.33 equiv of $HSiCl_3$ to the lithiation product of **2**.[13]

Scheme 2

Scheme 3

Scheme 4
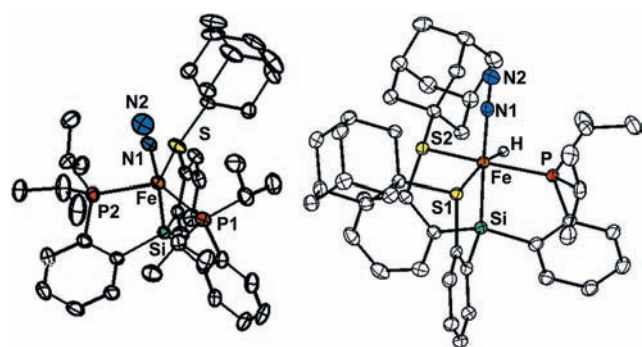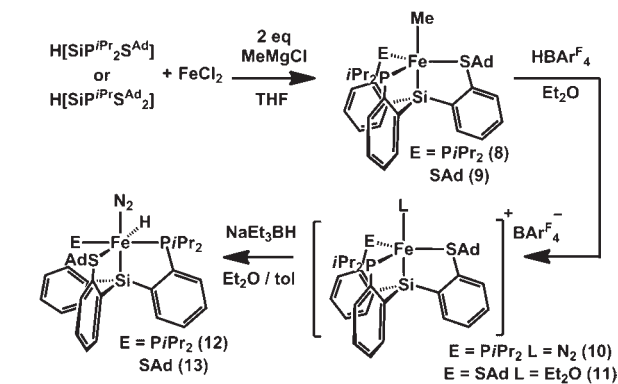
**Figure 2.** Solid-state structures of (left) **10** and (right) **13** (50% probability; H atoms and solvent for **10** and **13** and BAr$^F_4{}^-$ for **10** have been removed). Selected bond lengths (Å) and angles (deg) for **10**: Fe–N1, 1.954(3); Fe–Si, 2.3106(9); Fe–P1, 2.353(1); Fe–P2, 2.3542(9); Fe–S, 2.2941(9); Si–Fe–N1, 173.66(9); S–Fe–P1, 119.42(4); S–Fe–P2, 104.80, P1–Fe–P2, 129.76(4). For **13**: Fe–N1, 1.828(2); Fe–Si, 2.2157(8); Fe–P, 2.185(7); Fe–S1, 2.3002(7); Fe–S2, 2.2887(7); N1–N2, 1.116(3); Si–Fe–N1, 177.79(7).

Metalation with iron was found to be facile for **5** and **6**. Addition of 2 equiv of MeMgCl to a solution of FeCl$_2$ and **5** or **6** at −78 °C yielded the paramagnetic ($S = 1$) iron(II) methyl complex [SiP$^{iPr}_2$S^{Ad}]FeMe (**8**) or [SiP^{iPr}S$^{Ad}_2$]FeMe (**9**), respectively (Scheme 2). The tris(thioether)silane **7** was not metalated under similar conditions, perhaps underscoring the need of a phosphine donor to aid the chelate-assisted Si–H bond activation.[12b]

Complexes **8** and **9** served as convenient entry points into the Fe–N$_2$ chemistry of interest. Protonation of the methyl ligand in **8** and **9** with HBAr$^F_4$ [BAr$^F_4$ = tetrakis(3,5-trifluoromethyl-phenyl)borate] in Et$_2$O resulted in loss of methane. For complex **8**, loss of methane was followed by binding of N$_2$ to yield the cationic, paramagnetic ($S = 1$) dinitrogen complex {[SiP$^{iPr}_2$S^{Ad}]Fe(N$_2$)}BAr$^F_4$ (**10**), as evident from the N$_2$ stretch in its IR spectrum at $\nu_{N_2} = 2156$ cm^{-1}. Consistent with the high IR frequency, the N$_2$ ligand was appreciably labile, and a rapid color change from green to orange occurred under reduced pressure.

The solid-state structure of **10** (Figure 2 left) reveals a distorted trigonal-bipyramidal (TBP) geometry ($\tau = 0.73$[14]) with a terminal N$_2$ ligand.[15] The distorted structure is in contrast to that of the corresponding {[SiP$^{iPr}_3$]Fe(N$_2$)}[BAr$^F_4$] complex,
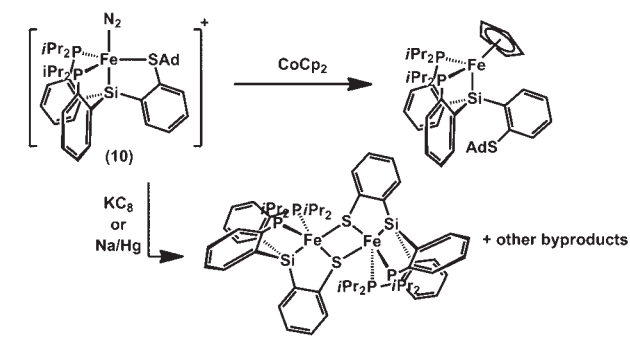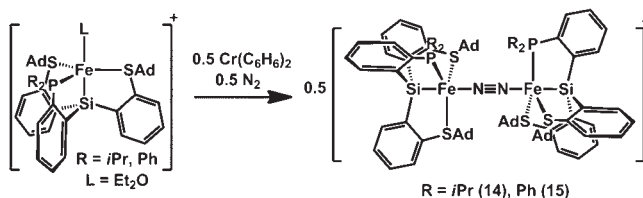
which exhibits a more rigorous TBP geometry.[12d] This difference likely reflects the smaller steric influence of a thioether relative to a phosphine donor, resulting in expansion of the P–Fe–P angle in **10** relative to {[SiP$^{iPr}_3$]Fe(N$_2$)}[BAr$^F_4$].

For the bis(thioether) complex **9**, protonation in Et$_2$O led instead to the solvent adduct {[SiP^{iPr}S$^{Ad}_2$]Fe(Et$_2$O)}BAr$^F_4$ (**11**). The lack of N$_2$ binding is likely dictated by the slightly reduced electron density at the iron center chelated by **6** relative to that by **5** due to the smaller number of phosphine donors. To increase the electron-richness of the iron center, the addition of a hydride donor was explored.

Accordingly, addition of NaEt$_3$BH to **10** and **11** resulted in clean conversion to the corresponding neutral and diamagnetic hydride–N$_2$ complexes [SiP$^{iPr}_2$S^{Ad}]Fe(H)(N$_2$) (**12**) and [SiP^{iPr}S$^{Ad}_2$]Fe(H)(N$_2$) (**13**), which exhibited ν_{N_2} values of 2055 and 2060 cm^{-1}, respectively. While isomers in which the hydride ligand is trans to either a thioether or a phosphine are conceivable, only one hydride signal (triplet for **12** and doublet for **13**) was observable in their respective ^{1}H NMR spectra at ca. −19 ppm. The solid-state structure of **13** featuring two thioether donors (Figure 2 right) exhibits a hydride ligand trans to one of the thioether ligands, as would be expected on the basis of the greater trans influence of a phosphine.[16] Density functional theory calculations indicated an energy difference of 17.5 kcal/mol in favor of the observed isomer [see the Supporting Information (SI) for details]. The structure of **12** is presumed to be similar in light of the equivalence of the P atoms in the ^{31}P{^{1}H} spectrum.

Despite the stability of [SiP$^{iPr}_3$]Fe^I(N$_2$),[12a,b,d] the corresponding iron(I) complexes using ligands **5** and **6** did not prove to be accessible. For **10**, strong reductants such as KC$_8$ and Na/Hg resulted in a mixture of products. One of these products was determined by X-ray diffraction to be a dimeric complex formed by cleavage of the S–C(alkyl) bond of the thioether arm to yield a thiolate ligand that bridges two iron centers (Scheme 3).
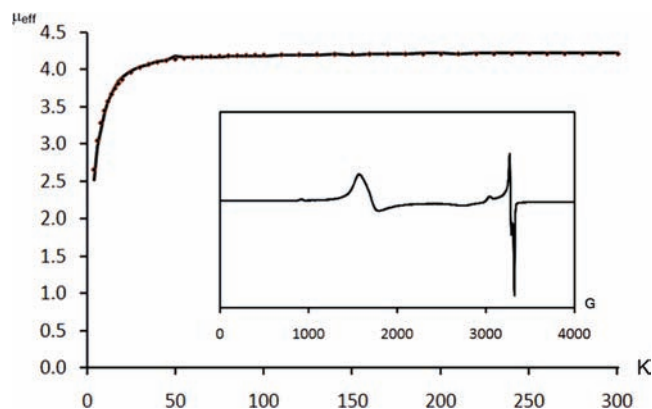
Figure 3. Variable-temperature SQUID data (fit in black) and (inset) EPR data (20 K in 2-Me-THF) for **14**.

Related dimeric iron cores with bridging thiolates that are chelated by tripodal tris(thiolate) ligands have been reported elsewhere.[17] In contrast, addition of $CoCp_2$ to **10** unexpectedly led to transmetalation of one Cp ligand with concomitant displacement of a thioether arm (see the SI). These observations underscore some of the problems associated with stabilizing dinitrogen complexes using thiolates/thioethers, as thiolates tend to bridge metal centers and occupy sites that may otherwise be available for N_2 binding while thioethers can be labile in comparison with phosphines or undergo reductive S−C cleavage.

Reduction of the solvent adduct **11** using $CoCp_2$ or Cr-$(C_6H_6)_2$ proved to be more interesting and led to a mixed-valent Fe(II)/Fe(I) complex with a bridging dinitrogen ligand, $[\{[SiP^{iPr}S^{Ad}_2]Fe\}_2(N_2)]BAr^F_4$ (**14**) (Scheme 4).[18] The combustion analysis data and stoichiometry of the reaction were consistent with our formulation of **14**, the latter requiring 0.5 equiv each of reductant and N_2 (Toepler pump analysis) per Fe center. While crystals suitable for X-ray diffraction invariably led to disorder/twinning problems arising from crystallization in a cubic space group, insights into the precise coordination environment of **14** were gained through its spectroscopic properties. Complex **14** exhibited a weak IR stretch at 1881 cm^{-1} that shifted to 1819 cm^{-1} when the reaction was performed under $^{15}N_2$ (calcd harmonic oscillator model: 1818 cm^{-1}). This ν_{N_2} stretch was much lower in energy and significantly weaker in intensity than that for the terminal Fe(I) dinitrogen complex $[SiP^{iPr}_3]Fe(N_2)$ (2008 cm^{-1}); the frequency was closer to the value for the corresponding Fe(0) complex $[(SiP^{iPr}_3)Fe^0(N_2)]^-$ (1891 cm^{-1}), highlighting the influence of a second metal center.[12d] Since a molecule with an inversion center cannot yield an IR-active N_2 stretch, complex **14** must be asymmetric on the IR time scale, presumably via an asymmetric orientation of the phosphine/thioether arms (Scheme 4). Additionally, an inter-valence charge-transfer band, characteristic of a mixed-valent species, was observed at 1360 nm in the NIR spectrum of **14** in Et_2O, and its assignment was supported by the observation of a solvent-dependent λ_{max}. The 20 K EPR spectrum of **14** exhibited features at g = 4.23, 3.98, and 2.02 due to the Kramer's doublet transition in an $S > 1/2$ spin system (Figure 3). Indeed, the solution and solid-state magnetic moments were consistent with the EPR spectrum, supporting an $S = 3/2$ spin state arising from ferromagnetic coupling between the S = 1 Fe(II) and $S = 1/2$ Fe(I) centers [or two Fe(1.5) centers].[19] The temperature

independence of the solid-state data suggests an $S = 3/2$ state that is largely separated from the other spins states. The N_2-bridged diiron complex $\{[SiP^{Ph}S^{Ad}_2]Fe\}_2(N_2)\}[BAr^F_4]$ (**15**) ($[SiP^{Ph}S^{Ad}_2]H = (2-Ph_2PC_6H_4)(2-AdSC_6H_4)_2SiH$) featuring phenyl groups on the phosphine donors was synthesized analogously to **14** and exhibited similar spectroscopic features (see the SI).

To conclude, a class of dinitrogen complexes of iron chelated by hybrid silyl ligands that include sulfur and phosphine donors has been characterized. Noteworthy are the iron−N_2 adducts **13**, **14**, and **15**, which possess multiple sulfur donors per Fe; these complexes are unique in this regard. Additionally, **14** and **15** represent unusual examples of formally Fe(I)/Fe(II) mixed-valent dinitrogen complexes. The work herein illustrates that mononuclear and dinuclear dinitrogen complexes of sulfur-ligated iron are accessible in various spin states ($S = 3/2$, S = 1, and S = 0) using sulfur-containing scaffolds that induce relatively electron-rich metal centers. The structural relevance of thioether donors as models of the local environment of the iron centers in the FeMo cofactor in part depends on whether inorganic sulfide is protonated during catalytic turnover,[20] which in turn could result in HS → Fe dative interactions (Figure 1). Regardless, the use of thioethers in the present synthetic context provides steric protection while conserving a low-valent iron center.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Synthetic and spectroscopic details and data, computational details, solid-state structures, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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