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Dinitrogen Complexes of Sulfur-ligated Iron

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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, $[\text{SiP}^{\text{R}}_3]$ ($[\text{SiP}^{\text{R}}_3] = [(2\text{-R}_2\text{PC}_6\text{H}_4)_3\text{Si}]$; $\text{R} = \text{Ph}, i\text{Pr}$), 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.

The intimate mechanism of nitrogen fixation by the nitrogenase enzymes remains a fascinating puzzle. Recent theoretical and experimental studies on the FeMo nitrogenase cofactor have suggested N_2 binding at iron (Figure 1),¹ and have resulted 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 owing to 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 ligands⁹ that typically yield high-spin complexes with long Fe-L bonds.¹⁰ Such a scenario is undesirable with respect to the favorable π -backbonding 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 for cases where N_2 is terminally bonded. Thioethers are particularly appealing since they are σ -donating and (weakly) π -accepting¹¹ and, thus, would favor lower spin states relative to thiolates and sulfides. To test this idea we targeted hybrid thioether/phosphine relatives of a tetradentate tris(phosphino)silyl ligand, $[\text{SiP}^{\text{R}}_3]$ ($\text{R} = \text{Ph}, i\text{Pr}$), that has proven exceptionally successful in stabilizing terminal, trigonal bipyramidal $\{[\text{SiP}^{\text{R}}_3]\text{Fe-N}_2\}^n$ 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.

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Supporting Information Available Synthetic and spectroscopic details and data, computational details, solid state structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Precursors to the desired ligands have been conveniently synthesized by lithiation of the aryl bromides, 2-*i*Pr₂P(C₆H₄Br) (**1**) and 2-AdS(C₆H₄Br) (**2**), with *n*-BuLi, followed by quenching with 0.5 equiv of HSiCl₃ to yield the chlorosilanes, (2-*i*Pr₂PC₆H₄)₂Si(H)(Cl) (**3**) and (AdSC₆H₄)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, affords the hybrid ligands, [SiP^{*i*Pr}₂S^{Ad}]H (**5**) ([SiP^{*i*Pr}₂S^{Ad}]H = (2-*i*Pr₂PC₆H₄)₂(2-AdSC₆H₄)SiH) and [SiP^{*i*Pr}S^{Ad}]₂H (**6**) ([SiP^{*i*Pr}S^{Ad}]₂H = (2-*i*Pr₂PC₆H₄)(2-AdSC₆H₄)₂SiH), in high yield. The tris(thioether)silane ligand, [SiS^{Ad}]₃H ([SiS^{Ad}]₃H = {(AdS(C₆H₄)Si)₃H} (**7**), is also synthesized by addition of 0.33 equiv of HSiCl₃ to the lithiation product of **2**.¹³

Metallation with iron is found to be facile for **5** and **6**. Addition of two equiv of MeMgCl to a solution of FeCl₂ and **5** or **6** at -78 °C yields the paramagnetic (*S* = 1) iron(II) methyl complexes, [SiP^{*i*Pr}₂S^{Ad}]FeMe (**8**) and [SiP^{*i*Pr}S^{Ad}]₂FeMe (**9**), respectively (Scheme 2). The tris(thioether)silane **7** is not metallated under similar conditions, perhaps underscoring the need of a phosphine donor to aid a chelate-assisted Si-H bond activation.^{12b}

Complexes **8** and **9** serve as convenient entry points into the FeN₂ chemistry of interest. Protonation of the methyl ligand in **8** and **9** with HBar^F₄ (Bar^F₄ = tetrakis(3,5-trifluoromethylphenyl)borate) in Et₂O results in loss of methane. For complex **8**, loss of methane is followed by binding of N₂ to yield the cationic, paramagnetic *S* = 1 dinitrogen complex **10**, {[SiP^{*i*Pr}₂S^{Ad}]Fe(N₂)}Bar^F₄, as evident from the N₂ stretch in its IR spectrum at ν_{N2} = 2156 cm⁻¹. Consistent with the high IR frequency, the N₂ ligand is appreciably labile and a rapid color change from green to orange occurs under reduced pressure.

The solid-state structure of **10** (Figure 2.) reveals a distorted trigonal bipyramidal (TBP) geometry (τ = 0.73¹⁴) with a terminal N₂ ligand.¹⁵ The distorted structure is in contrast to that of the corresponding {[SiP^{*i*Pr}₃]Fe(N₂)}[Bar^F₄] 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** compared to {[SiP^{*i*Pr}₃]Fe(N₂)}[Bar^F₄].

For the bis(thioether) complex **9**, protonation in Et₂O leads instead to the solvent adduct {[SiP^{*i*Pr}S^{Ad}]₂Fe(Et₂O)}Bar^F₄, **11**. The lack of N₂ binding is likely dictated by the slightly reduced electron density at the iron center chelated by **6** relative to that by **5**, owing to the fewer number of phosphine donors. To increase the electron-richness of the iron center, the addition of a hydride donor was explored.

Accordingly, addition of NaEt₃BH to **10** and **11** results in clean conversion to the corresponding neutral and diamagnetic hydride-N₂ complexes, [SiP^{*i*Pr}₂S^{Ad}]Fe(H)(N₂) (**12**) and [SiP^{*i*Pr}S^{Ad}]₂Fe(H)(N₂) (**13**), with ν_{N2} of 2055 and 2060 cm⁻¹, respectively. While isomers in which the hydride ligand is either *trans* to a thioether or to a phosphine are conceivable, only one hydride signal (triplet for **12** and doublet for **13**) is observable in their respective ¹H NMR spectra at ca. δ = -19 ppm. The solid-state structure of **13**, featuring two thioether donors, has been obtained and illustrates a hydride ligand *trans* to one of the thioether ligands, as would be expected based on the greater *trans* influence of a phosphine.¹⁶ DFT calculations indicate an energy difference of 17.5 kcal/mol in favor of the observed isomer (see SI for details). The structure of **12** is presumed to be similar in light of the equivalence of the P atoms in the ³¹P{¹H} spectrum.

Despite the stability of [SiP^{*i*Pr}₃]Fe^I(N₂),^{12 a,b,d} corresponding iron(I) complexes using ligands **5** and **6** have not proven accessible. For **10**, strong reductants such as KC₈ and Na/Hg result in a mixture of products. One of these products has been determined by X-ray diffraction to be a dimeric complex, in which cleavage of an S-C(alkyl) bond of a thioether arm yields a thiolate ligand that bridges two iron centers (Scheme 3). Related dimeric iron

cores with bridging thiolates, chelated by tripodal tris(thiolate) ligands, have been reported elsewhere.¹⁷ In contrast, addition of CoCp₂ to **10** unexpectedly leads to transmetallation of one Cp ligand, with concomitant displacement of a thioether arm (See SI). These observations underscore some of the problems associated in stabilizing dinitrogen complexes with thiolates/thioethers, as thiolates tend to bridge metal centers and occupy sites that may otherwise be available for N₂ binding, and thioethers can be labile by comparison to phosphines, or undergo reductive S-C cleavage.

Reduction of the solvent adduct **11** using CoCp₂ or Cr(C₆H₆)₂ proved more interesting and led to a mixed-valent Fe(II)/Fe(I) complex with a bridging dinitrogen ligand, $[[\text{SiP}^{\text{Pr}}\text{S}^{\text{Ad}}_2]\text{Fe}]_2(\text{N}_2)[\text{BAr}^{\text{F}}_4]$ (**14**) (Scheme 4).¹⁸ The combustion analysis data and stoichiometry of the reaction is consistent with our formulation of **14**, the latter requiring 0.5 eq each of reductant and N₂ (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** reveals a weak IR stretch (Figure 3) at 1881 cm⁻¹ that shifts to 1819 cm⁻¹ upon performing the reaction under ¹⁵N₂ (calc'd harmonic oscillator model: 1818 cm⁻¹). This ν(N₂) stretch is much lower in energy and significantly weaker in intensity than the terminal Fe(I) dinitrogen complex $[\text{SiP}^{\text{Pr}}_3]\text{Fe}(\text{N}_2)$ (2008 cm⁻¹); the frequency is closer in value to the corresponding Fe(0) complex, $[(\text{SiP}^{\text{Pr}}_3)\text{Fe}^0(\text{N}_2)]^-$ (1891 cm⁻¹), highlighting the influence of a second metal center.^{12d} Since a molecule with an inversion center cannot yield an IR active N₂ stretch, complex **14** must be asymmetric on the IR timescale, presumably via an asymmetric orientation of the phosphine/thioethers (Scheme 4). Additionally, an inter-valence charge transfer band, characteristic of mixed valent species, is observed in the NIR spectrum at 1360 nm in Et₂O in **14**, whose assignment is supported by a λ_{max} that is solvent dependent. The 20 K EPR spectrum of **14** exhibits 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 moment are consistent with the EPR spectrum, supporting an S = 3/2 spin state arising from ferromagnetic coupling between 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 other spin states. The diiron μ-N₂ complex, $\{[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{Fe}\}_2(\text{N}_2)[\text{BAr}^{\text{F}}_4]$ (**15**) ($[\text{SiP}^{\text{Ph}}\text{S}^{\text{Ad}}_2]\text{H} = (2\text{-PPh}_2\text{C}_6\text{H}_4)(2\text{-AdSC}_6\text{H}_4)_2\text{SiH}$), featuring phenyl groups on the phosphine donors, has been synthesized analogously to **14** and exhibits similar spectroscopic features (see 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 iron N₂ adducts **12**, **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. 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, use of thioethers in the present synthetic context provides steric protection while conserving a low valent iron center.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Hypothetical binding mode of N_2 at the FeMoco (left) and a hypothetical model complex (right). Whether any of the S-atoms shown in red for FeMoco (left) are protonated during catalysis is unknown.

Figure 2.

Solid-state structures of **10** and **13** (50 % probability; H atoms and solvent for **10** and **13**, BArF_4^- for **10** removed). Selected bond lengths (Å) and angles (°): **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). **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).

Figure 3. Variable temperature SQUID data (fit in black), and EPR data (20 K, 2-Me-THF), for **14**.

Scheme 1.

Scheme 2.

Scheme 3.