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Multimetallic Cooperativity in Activation of Dinitrogen at Iron-Potassium Sites

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Abstract

The reaction of soluble iron-oxygen-potassium assemblies with N₂ gives insight into the mechanisms of multimetallic N₂ coordination. We report a series of very electron-rich three-coordinate, β-diketiminato-supported iron(I) phenoxide complexes, which are metastable but have been characterized under Ar by both crystallography and solution methods. Both monomeric and dimeric Fe-OPh-K compounds have been characterized, and their iron environments are very similar in the solid and solution states. In the dimer, potassium ions hold together the phenoxide oxygens and aryl rings of the two halves, to give a flexible diiron core. The reactions of the monomeric and dimeric iron(I) compounds with N₂ are surprisingly different: the mononuclear iron(I) complexes give no reaction with N₂, but the dimeric Fe₂K₂ complex reacts rapidly to give a diiron-N₂ product. Computational studies show that the key to the rapid N₂ reaction of the dimer is the preorganization of the two iron atoms. Thus, cooperation between Fe (which weakens the N-N bond) and K (which orients the Fe atoms) can be used to create a low-energy pathway for N₂ reactions.

Introduction

Multimetallic complexes offer the opportunity for metals to cooperate in small-molecule activation.^{1–4} There has been a resurgence in the design of architectures for holding two or more redox-active metals in close proximity for multimetallic reactivity.^{5–11} This strategy is particularly compelling for the reactions of N₂ with transition metals (nitrogen fixation).¹²

Part of the motivation for multimetallic N₂ fixation is that the Haber-Bosch process takes place at metal surfaces.^{13, 14} Several zerovalent transition metals catalyze N₂ reduction,¹³ but the most common catalyst comes from iron oxide that contains potassium oxide promoters.^{14–16} The highest-activity zerovalent iron surfaces have subsurface “C7 sites” at which N₂ is surrounded by multiple Fe atoms.¹⁷ Steps on Fe(110) surfaces have also been implicated as reactive sites.¹⁸ This experimental work has been complemented by computations on possible structures for N₂ adducts on single-crystal iron.¹⁹ However, these models for M-N₂ surface structures do not yet incorporate potassium promoters.^{16, 20–23}

A multi-iron coordination site for N₂ is also implicated in nitrogenases, the enzymes that perform natural N₂ reduction.^{24–26} The active-site cluster of molybdenum-dependent nitrogenase (FeMoco) has seven iron atoms and one molybdenum in a cage.^{27, 28} The reactivity patterns of nitrogenase variants with changes in the amino acids near the FeMoco imply that N₂ binds to one or more of the iron atoms on a four-iron face of the FeMoco.^{29, 30}

It is notable that multimetallic iron sites are important in both natural and industrial N₂ fixation.

We have studied a number of iron/potassium complexes in an effort to elucidate the fundamental factors underlying N₂ fixation at multimetallic sites.^{31–33} The most common way for transition and alkali metals to cooperate in N₂ coordination is for N₂ to bind end-on to the transition metal and side-on to the alkali metal.^{34, 35} Precedents for this binding mode go back to the work of Jonas in the 1970's,^{36, 37} and in the case of iron include recent examples from Gambarotta and Peters.^{38, 39} We have reported reduced iron compounds in which the β -diketiminato aryl substituents interact with alkali metals,^{32, 40–42} and related cobalt and nickel compounds have been reported by us and by Limberg.^{43–48} However, it is still not clear *why* heterobimetallic cooperation is so beneficial in terms of specific interactions between N₂ and the multimetallic precursors.^{49, 50} We know of only one study that directly quantitates the differences in N₂ complexing ability between analogous monometallic and multimetallic species.⁵¹

In an earlier report,³² we described the KC₈ reduction of a diketiminato-supported iron(II) chloride precursor under argon to give a transient green iron(I) intermediate that is capable of coordinating N₂ (Scheme 1). It was assigned as “LFe(μ -Cl)K(THF)_n” based on the fact that addition of 18-crown-6 gave the crystallographically characterized green LFe(μ -Cl)K(18-crown-6). However, the isolated 18-crown-6 complex *did not* react with N₂. Our inability to determine the structural difference between the two iron-potassium species prevented us from explaining the surprising difference in reactivity between (presumably) similar species.

Here, we report the characterization and reactivity of analogous complexes that have aryloxides in place of the chlorides in the earlier work. This substitution has enabled us to characterize the intermediate iron(I) species in more detail, and to elucidate the mechanism of N₂ fixation. The results teach a general lesson about the kinetic and thermodynamic factors that can control N₂ reactivity in multimetallic complexes, which may assist in the future design of multimetallic complexes for N₂ reduction.

Results and discussion

Synthesis and properties of iron(I) phenoxide complexes

The monomeric three-coordinate iron(II) phenoxide complex LFeOPh (L = 2,2,6,6-tetramethyl-3,5-bis(2,6-diisopropylphenylimido)heptyl; Ph = phenyl) was previously reported.⁵² This iron(II) complex reacts rapidly with a slight excess of potassium graphite (KC₈) under argon to reduce the iron(II) complex to an iron(I) product (Scheme 2). Interestingly, the iron(I) products have a different form depending on the solvents used during the synthesis and crystallization. When the reaction is performed in toluene and the product is crystallized from pentane, the **dimeric (D)** product [KLFeOPh]₂ is isolated in 63% yield. If the reduction and crystallization are done in diethyl ether (Et₂O), then **monomeric (M)** (Et₂O)₂KLFeOPh is isolated in 92% yield.

X-ray crystallography (Figure 1) shows that **M** and **D** have the same coordination at each iron, with two diketiminato N and a phenoxide O in a planar geometry. Charge counting shows that the iron centers in both complexes are iron(I). The Fe-O distances of 1.92–1.93 Å in these iron(I) compounds are about 0.1 Å longer than the analogous distances in the iron(II) phenoxide complex LFeOTol (Table 1).⁵² On the other hand, the Fe-N distances are shorter in the reduced iron(I) complexes, which can be attributed to π -backbonding from iron into the diketiminato π -system. The backbonding also explains the slightly longer N-C distances within the diketiminato backbone for the iron(I) complexes. Iron(I) backbonding

into diketiminates has been supported by computations in related hydride and sulfide complexes.^{41, 42}

In both **M** and **D**, the potassium cations interact with the phenoxide oxygen atom, and also engage in a cation- π interaction with one of the aromatic rings of the β -diketiminato supporting ligand. In dimeric **D**, the potassium coordination is completed by a second cation- π interaction with the phenyl group of the opposing phenoxide, whereas in monomeric **M** the potassium binds to two molecules of diethyl ether to complete its coordination.

Thus, the iron coordination is the same in **M** and **D**, and the differences only pertain to the potassium coordination. Since **D** does not have diethyl ether to complete its K coordination, the second cation- π interaction gives a dimeric structure with bridging to another Fe-OPh-K unit. The FeNN planes are not parallel; rather they are at an angle of $112.38(7)^\circ$ to give a “bowl” with exposed Fe and K ions on the inside face (Figure 2).

The solution magnetic moment of **M** is $4.1(2) \mu_B$, and for **D** is $6.5(3) \mu_B$ (per dimer). Each value is consistent with high-spin ($S = 3/2$) iron(I) ions, as found in other three-coordinate iron(I) diketiminato complexes.^{32, 41, 42} The paramagnetically shifted ^1H NMR spectra of **D** under argon in C_6D_6 , C_6D_{12} , Et_2O , and $\text{THF}-d_8$ (Figure S2) give peak integrations consistent with local C_{2v} symmetry around each iron atom. This indicates that the core of **D** is fluxional, though the high solubility suggests that the potassium ions remain surrounded by bound arenes. Dissolving crystals of **M** in C_6D_6 under an Ar atmosphere gives a ^1H NMR spectrum identical to **D** (Figures 3 and S2), except for the observation of free Et_2O in the solution from **M**. This indicates that the Et_2O molecules are lost from **M** in benzene solution; the fact that the compound remains soluble suggests that the potassium ions are still part of the structure, and presumably the predominant solution structure in benzene is related to the crystallographic structure of **D**. Attempts to measure the solution molecular weight through cryoscopy gave irreproducible results (likely because of the extreme sensitivity of the compound to slight traces of moisture). However, as shown below, *the reactivity of M (in Et₂O or THF) and D (in C₆D₆ or C₆D₁₂) toward N₂ are very different (see below), indicating that their solution structures are different.* The most reasonable model is thus that **M** (in Et_2O or THF) and **D** (in C_6D_6 or C_6D_{12}) each have solution structures much like their crystallographic structures. The core of **D** must be highly flexible (consistent with computations below), but remains dimerized because of the inability to lose K^+ into the nonpolar solvent.

The most significant shift in the ^1H NMR spectrum when changing the solvent from C_6D_6 (**D**) to Et_2O (**M**) is that the most upfield peak shifts further upfield by about 10 ppm (Figure S-2). Addition of 18-crown-6 or cryptand-2.2.2 to **D** in C_6D_6 gives larger upfield shifts of the same resonance, as shown in Figure 4. This indicates the formation of ionic compounds (denoted **M-18C6** and **M-crypt**, respectively) in which the potassium ions are increasingly separated from the iron-phenoxide. It has not been possible to isolate the chelate compounds in pure form, because of their exceptionally high sensitivity to trace air or moisture. We note that the related iron(I) hydride complex, $\text{K}_2[\text{LFeH}]_2$, can similarly be broken up into monomers with potassium chelating agents.⁴¹ In the hydride system, breaking up the dimer gave upfield shifts in the same resonance of the supporting ligand, with the amount of shift increasing from 18-crown-6 to cryptand-2.2.2.

Differential reactivity of iron(I) phenoxides with N_2

Exposing solutions of the four iron(I) compounds **D** (in C_6D_6), **M** (in Et_2O), **M-18C6**, and **M-crypt** to an atmosphere of purified dinitrogen (N_2) at room temperature provides a direct

comparison of their solution reactivity toward N_2 . Out of the four species, *only D reacts with N_2* (Scheme 3, top). In contrast, the electronically similar complexes **M**, **M-18C6** and **M-crypt** each remain unchanged under N_2 after 1 h. Though a solution of **M** in Et_2O does not react, when the Et_2O is evaporated from this solution and C_6D_6 is added to convert it into **D**, the reaction with N_2 occurs, again showing that **M** and **D** have different behaviors in solution as well as the solid state.

The reaction of N_2 with a C_6D_6 solution of **D** is complete within 2 minutes at room temperature, as evidenced by complete disappearance of the 1H NMR peaks for **D** and the growth of new paramagnetically shifted peaks. The 1H NMR spectrum of the product shows that it is a roughly 1:1 mixture of the formally diiron(0) **nitrogen (N)** complex $K_2[LFenNFeL]$ and the new iron(II) **phenoxide (P)** complex $[KLFe(OPh)_2]_2$ (Scheme 3, bottom). An internal integration standard shows that these two products account for 91% of the iron introduced into the reaction as **D**, indicating the iron stoichiometry in Scheme 3. note that this reaction formally represents a disproportionation of iron(I) into equal amounts of iron(0) and iron(II).

Compound **N** was characterized previously, using crystallography, solution magnetism, NMR spectroscopy, resonance Raman spectroscopy, and elemental analysis.⁵³ Its 1H NMR spectrum serves as the clearest identifying feature in mixtures of **N** and **P**, because it has seven distinct resonances of known chemical shifts. In **N**, N_2 is surrounded by two Fe bound end-on and two K bound side-on. The N-N bond in **N** is substantially lengthened (1.23 Å) and weakened (stretching frequency 1589 cm^{-1}) relative to that in N_2 (1.11 Å and 2331 cm^{-1}).^{32, 35} Therefore, it is reasonable to consider the bridging ligand as N_2^{2-} , in analogy to its neutral analogue $LFenNFeL$ that has been extensively characterized using variable-field Mössbauer spectroscopy and computations.⁵⁴ Thus the reaction of **D** with N_2 leads to significant structural activation of the N-N bond.

The iron(II) bis-phenoxide complex $[KLFe(OPh)_2]_2$ (**P**) can be synthesized independently by adding one equivalent of $KOPh$ to a solution of $LFenOPh$ in tetrahydrofuran (THF). Phenoxide **P** may be crystallized in 81% yield by vapor diffusion of Et_2O into a toluene solution of **P**. The X-ray crystal structure of **P** (Figure 5) shows a dimeric species with two pseudotetrahedral iron centers. The two halves of this molecule are *not* related by symmetry. One K cation lies near the centroid of the four phenoxide oxygen atoms with K–O distances of 2.657(2), 2.674(3), 2.677(2), and 2.818(2) Å (Table S1). The second K cation associates with the aryl rings of a β -diketiminato ligand, one O atom of a phenoxide ligand, and is also coordinated to a THF solvent molecule. Other crystallographic details may be found in the ESI.

While the solid-state structure of **P** shows no symmetry elements, the 1H NMR spectrum of **P** in C_6D_6 (Figure S1) contains eleven signals suggesting averaged D_{2h} or D_{2d} symmetry from a rapid fluxional process. Nine of the signals are assigned to the product (one of the aryl peaks integrating to 8 H is presumed to be underneath the solvent peak) based on integrations. Two of the peaks (δ 42 ppm and -29 ppm) belong to the starting material, $LFenOPh$, which exists in equilibrium with the product as shown in Scheme 4. This equilibrium prevents detailed solution characterization and thorough purification. It is not possible to drive the equilibrium all the way to **P** using an excess of $KOPh$, presumably due to the poor solubility of $KOPh$ in THF. Despite these difficulties, the amassed spectroscopic and crystallographic characterization clearly establish the identity of **P**, and the observation of the same 1H NMR spectrum during the reaction of **D** with N_2 shows that it is the product of this reaction.

Proposed mechanism for formation of **N** and **P** from **D**

We suggest the mechanism in Scheme 5 to account for the formation of **N** and **P** from the reaction of **D** with N_2 . The first step in this mechanism is the reaction of N_2 with one equivalent of **D** to form a complex; the possible geometry of this complex will be discussed below. Loss of two equivalents of KOPh would give the known N_2 complex LFeNNFeL. This in turn could be reduced by the second equivalent of **D** to give the observed product **N** and the known iron(II) phenoxide complex LFeOPh. This is a net disproportionation of iron(I) to iron(0) (in **N**) and iron(II) (in LFeOPh). Finally, the iron(II) product LFeOPh could react with KOPh (released in the earlier step) to give the observed product **P**.

This mechanism is supported by the independent experimental study of several of the steps; these are indicated by solid lines in Scheme 5. LFeNNFeL (the bottom compound in Scheme 5) has been characterized previously.^{32, 53, 54} Reaction of independently synthesized LFeNNFeL with a stoichiometric amount of **D** indeed gives **N** and LFeOPh in the expected 1:2 stoichiometry in 83% yield, as judged by 1H NMR integrations. As illustrated in Scheme 4, reaction of LFeOPh with KOPh gives **P**, verifying the feasibility of the final step. The steps indicated with dotted lines are too rapid to study using kinetics. Thus, we use computations to evaluate mechanistic possibilities for the early steps in the reaction.

The greater reactivity of **D** results from a low-energy bimetallic pathway for N_2 activation

We envisioned two hypotheses for explaining the difference in reaction rates between **M** and **D**. In *hypothesis 1*, N_2 binds cooperatively to Fe and K, and backbonding into N_2 is enhanced by the positive charge on the potassium cation(s). In this hypothesis, N_2 would bind more strongly to **D** because there are *two* K^+ in the bowl-shaped cavity of **D** (Figure 2), but only *one* nearby K^+ in **M**. In *hypothesis 2*, both **M** and **D** initially form Fe- N_2 adducts, but the N_2 adduct of **D** is more rapidly trapped by N_2 coordination to the second iron atom, leading ultimately to the final products.

In order to evaluate the unobserved, transient reactions of **M** and **D** with N_2 , we used density-functional theory (DFT) calculations performed with the ORCA computational package, using the BP86 functional and the def2-SVP basis set; computational details are described in the ESI. In order to provide reasonable starting points, we optimized the geometries of **M** and of **D** starting from the crystallographic coordinates (Figure 6), using a high-spin (quartet) electronic configuration at each iron atom.

The optimized geometry of **M** agrees well with the crystallographic structure (Table 2). For **D**, the optimized geometry has very similar Fe-N and Fe-O distances and an similar overall geometry. However, the geometry optimization gives a significant contraction of the molecular core (O...O calcd. 4.15 Å; obs. 5.01 Å) and lengthening of the K-O interactions (calcd. 2.68, 2.74 Å; obs. 2.586(2) Å) relative to the crystallographic structure. In an effort to gauge the importance of this core distortion, the computation was repeated on a model in which the Fe...Fe distance was constrained to the crystallographic distance of 8.17 Å. This shortens the K-O distances to be closer to the experimentally observed values (2.65, 2.68 Å), and gives an electronic energy that is the same as the unconstrained model within 1 kcal/mol. This suggests that the potential energy surface for distortion of the potassium interactions with the arenes and oxygens is quite flat, indicating flexibility in the core of the molecule consistent with the NMR studies above. It also suggests that the energy of the molecule is not significantly influenced by the precise geometry of the K-arene and K-O interactions.

The calculations also predict that reaction of **D** with four molecules of Et_2O to split the dimer and form two molecules of **M** has ΔG° of only 2 kcal/mol, which is indistinguishable

from zero within the expected accuracy of the computations. This agrees with the experimental observations of the ability of **D** to transform into **M** in pure diethyl ether, and the ability to return **M** to **D** by evaporation of diethyl ether. The similar energies of **M** and **D** indicate that *the difference in reactivity between **M** and **D** is not due to **D** having a greater thermodynamic driving force to give the products **N** and **P**.*

Next, we introduced N₂ to the computational models of **M** and of **D**, trying several potential binding modes on each side of the iron coordination plane, and both iron atoms of **D**. The lowest-energy N₂ adducts of **M-N₂** and of **D-N₂** are shown in Figure 7, and *no stable isomers were observed with significant K-N₂ interactions*. In both **M-N₂** and **D-N₂**, the N₂ molecule binds end-on and the N-N bond is slightly lengthened, to 1.155 Å in **M-N₂** and to 1.166 Å in **D-N₂**. The lengthening comes from π -backbonding from the iron center into the π^* orbital of N₂, as shown by the somewhat shorter Fe-N(N₂) distance in **D-N₂** (1.772 Å) than in **M-N₂** (1.797 Å) and from the occupation of frontier molecular orbitals with π bonding interactions between Fe and N and π^* interactions between the two N atoms (see Supporting Information). The extent of backbonding into N₂ is somewhat greater in **D-N₂**, which might be explained by the approach of the terminal N atom of the N₂ to the two K⁺ ions (K-N = 2.79 and 2.88 Å). However, *the binding energy of N₂ is similar for both **M-N₂** and **D-N₂*** (Table 3), with enthalpies and free energies for binding that are indistinguishable within the expected accuracy of DFT calculations.

If **D** does not bind N₂ more tightly than **M** in an intermediate, why does it specifically give a net reaction with N₂? Further computational exploration of geometries for **D-N₂** revealed a second isomer (**D-N₂-bridge**), which has N₂ bridging between the two iron atoms (Figure 7, bottom). In **D-N₂-bridge**, the N-N bond is weakened more significantly, with an N-N distance of 1.204 Å, due to backbonding from both iron atoms. The free energy of **D-N₂-bridge** is 22 kcal/mol lower than the initially studied **D-N₂** isomer that had N₂ bound to only one iron atom. Therefore, bimetallic **D-N₂** is special because it can relax into a much more stable isomer with bridging N₂. The ability to form a lower-energy isomer would provide a significant driving force for N₂ reaction with **D** (Figure 8), and clearly implicates the preorganization of the two Fe ions (*hypothesis 2*) as the key enabling factor for the rapid reaction of N₂ with **D**. On the other hand, **M** does not benefit from the ability to make a stable FeNNFe unit, and does not show an overall reaction with N₂.

The calculated structure of **D-N₂-bridge** (Figure 7, bottom) has K-O interactions that presage the loss of KOPh, as proposed in Scheme 5. Consistent with this idea, optimization of some geometries near **D-N₂-bridge** led to spontaneous loss of KOPh molecules and contraction of the FeNNFe core (see ESI). Exoergic addition of KOPh to LFeOPh could subsequently drive the reaction through formation of **P**. Overall, the computational results support the feasibility of the proposed mechanism in Scheme 5, and shed light upon key interactions in the proposed reaction intermediates.

Conclusions and Implications

Mononuclear K[LFeOPh] (**M**) and dinuclear K₂[L₂Fe₂(OPh)₂] (**D**) have iron atoms with the same oxidation state, the same coordinating donors, and the same coordination geometry. Despite these similarities, and the fact that **M** and **D** are nearly isoenergetic, they react at very different rates with N₂. No reaction is observed from **M** (in Et₂O or THF) within 1 h, while **D** (in benzene or cyclohexane) reacts with N₂ within 2 min to give a formally diiron(0) N₂ complex (**N**). The product K₂LFeNNFeL (**N**) has an N-N bond that is significantly stretched and weakened compared to that in free N₂.^{32, 35} Therefore, the formation of multimetallic intermediates can play a key role in trapping N₂ and weakening its N-N bond.

This work shows the detailed structures through which multiple iron atoms react with N₂. In **D**, oxygen bridges between the iron and potassium play a key role in holding the iron and potassium ions in place, which may mimic the oxygen bridges between iron and potassium in the widely used Mittasch catalyst for the Haber-Bosch process. Therefore, these solution studies suggest that oxygen-bridged iron/potassium sites could be N₂ binding locations on iron-based Haber-Bosch catalysts. In addition, the N₂-binding ability of multiiron assemblies may be relevant to the mechanism of nitrogenase enzymes, which use iron clusters as their active sites.^{55, 56}

These studies also address the potential intermediates in potassium reduction of diketiminate-bound iron(II) chloride complexes to give N₂ complexes.³² The current results suggest that a *dimeric* Fe₂K₂ assembly would be very reactive toward N₂ (Scheme 6). This hypothesis explains why the N₂-binding ability of the iron(I) species was lessened in the presence of 18-crown-6 in the earlier studies: the chelating agent broke up the N₂-reactive bimetallic complex.

We have reported that electronically similar iron complexes with smaller diketiminate ligands can break the triple bond of N₂.⁴⁰ The N₂-cleaving species in that system is also generated by KC₈ reduction of an iron(II) chloride complex. Though its structure is not yet known, some possible structures were proposed through computations.⁵⁷ The compounds described in the current study may serve as isolable mimics of the fleeting intermediates in N₂-cleaving reactions of diketiminate-iron clusters. Further studies will take advantage of the stabilizing power of phenoxides, which can bind K⁺ through both the O atom and the phenyl group, to trap key intermediates in N₂-activating reactions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
(Top) Thermal ellipsoid plot of **M**; (Bottom) Thermal ellipsoid plot of **D**

Figure 2.
Thermal ellipsoid plot showing only the core of **D**; 2,6-diisopropylphenyl groups are omitted in order to reveal the core of the molecule

Figure 3. ^1H NMR spectra of **D** in C_6D_6 (top) and **M** dissolved in C_6D_6 to give **D** (bottom); asterisks (*) indicate peaks from released Et_2O

Figure 4. ^1H NMR spectra of (a) **D**, (b) **M-18C6**, and (c) **M-crypt** in C_6D_6 ; shifting peaks are indicated

Figure 5.
Thermal ellipsoid plot of **P**

Figure 6. Computational models of (top) **M** and (bottom) **D** with full geometry optimization

Figure 7. Computational models of (top) $\mathbf{M-N_2}$, (middle) $\mathbf{D-N_2}$ with terminal $\mathbf{N_2}$, and (bottom) $\mathbf{D-N_2}$ with bridging $\mathbf{N_2}$

Figure 8.

Relative free energies for computed species in kcal/mol; free diethyl ether and N₂ molecules were included in the thermodynamic calculations, but are not shown for clarity

Scheme 1.

Previous work on iron-potassium- N_2 chemistry (see also Scheme 6 below)³²

Scheme 2. Preparation of monomer **M** and dimer **D** by reduction of LFeOPh

Scheme 3.

(Top) Reactivity of iron(I) complexes with N_2 ; (Bottom) Structures of the **nitrogen** complex $\text{K}_2[\text{LFeNNFeL}]$ (**N**), which is formally diiron(0), and the **phenoxide** complex $[\text{KFe}(\text{OPh})_2]_2$ (**P**), which is formally diiron(II)

Scheme 4.

Equilibrium between LFeOPh and **P** in THF solution

Scheme 5.

Proposed mechanism for formation of **N** and **P** in the reaction of **D** and N_2 . The figure uses *formal* oxidation states for electron counting, though these may not reflect the physical oxidation levels of the metal ions.

Scheme 6.

Reinterpretation of the data in Scheme 1,³² in light of the current results.

Table 1Key bond lengths and angles in **M**, **D**, and an iron(II) analogue

	M	D	LFeOTol
Fe-O (Å)	1.9220(9)	1.929(2)	1.833(2)
Fe-N (Å)	1.913(1), 1.926(1)	1.926(2), 1.936(2)	1.965(2), 1.972(2)
N-C (Å)	1.356(2), 1.368(2)	1.344(3), 1.352(2)	1.342(3), 1.335(3)
K-OAr (Å)	2.609(1)	2.586(2)	
K-OEt ₂ (Å)	2.726(1), 2.753(1)		
N-Fe-N (°)	100.92(4)	98.09(9)	94.76(8)
N-Fe-O (°)	142.28(4), 116.80(4)	139.61(8), 122.28(8)	140.20(8), 125.01(9)
Fe-O-C (°)	133.13(8)	132.5(2)	138.8(2)

Table 2

Comparison of calculated and experimental (in parentheses) bond distances

	M	D
Fe-N (Å)	1.904, 1.915 (1.913, 1.926)	1.915–1.944 (1.926, 1.936)
Fe-O (Å)	1.915 (1.922)	1.938, 1.951 (1.929)
K··OAr (Å)	2.636 (2.609)	2.684, 2.742 (2.586)
K··OEt ₂ (Å)	2.74, 2.754 (2.726, 2.753)	

Table 3Calculated thermodynamics for N₂ reactions

Reactants	Products	ΔH° (kcal/mol)	ΔG° (kcal/mol)
M + N ₂	M-N ₂	-17	-5
D + N ₂	D-N ₂	-19	-6
D-N ₂	D-N ₂ -bridge	-20	-22
D + N ₂	D-N ₂ -bridge	-39	-28