Conversion of atmospheric N₂ into NH₃ is one of the most important chemical processes, because ammonia is the industrial precursor to many nitrogen-containing compounds. Large-scale transformation of N₂ and H₂ into ammonia is important chemical processes, because ammonia is the industrial N₂ reduction catalysis.

Paradoxically, synthetic iron/N₂ complexes are viewed as “unactivated” despite the importance of iron in the catalytic processes described above. Examples of stepwise metal-promoted N₂ cleavage reactions use metals in groups 5 and 6 of the periodic table. The driving force for these N–N cleavage reactions is the formation of extremely strong metal–nitride bonds. The only synthetic Fe/N₂ complex in which the N–N bond is stretched is the unusual complex Fe[NNMo(N₂N₃)]. Some iron/N₂ complexes produce ammonia on decomposition, but the intermediates in this process are not known. In this report we describe three-coordinate iron complexes that bind N₂ and weaken its N–N bond in a stepwise fashion. A combination of synthetic, structural, spectroscopic, and theoretical studies shows that a low coordination number at iron correlates with the ability to weaken N₂.

In the following discussion, L represents the anion shown at the right of Chart 1. Reduction of the three-coordinate iron(II) complex LFeCl₃ with naphthalenide under a purified N₂ atmosphere gives a highly air-sensitive, dark red, paramagnetic compound, for which the structure LFeN(NMe₂)Cl was revealed by X-ray crystallography (Figure 1a). This is a rare example of a three-coordinate transition-metal dinitrogen complex. Consistent with the low coordination number at iron and/or multiple bonding (see below) between iron and N₂, the Fe–N₂ distances are extremely short (1.77–1.78 Å). The most interesting feature of this structure is that the bridging N₂ ligand is stretched substantially (N–N = 1.182(5) Å; N–N in free N₂ = 1.098 Å). The cis-N–N elongation by almost 0.1 Å distinguishes this compound from other crystallographically characterized iron–N₂ complexes, which have N–N distances within about 0.03 Å of that in free N₂.

An intense band at 1778 cm⁻¹ was observed in the resonance Raman spectrum of LFeN(NMe₂)Cl with 514.5 nm excitation. This band shifted to 1718 cm⁻¹ in the spectrum of a sample prepared from ¹⁵N₂, consistent with a diatomic N–N oscillator whose force constant is substantially smaller than that of free N₂ (2331 cm⁻¹). Thus, structural and spectroscopic evidence shows that iron binding has weakened the N–N bond in LFeN(NMe₂)Cl relative to N₂.

To evaluate the effects of coordination number on the geometry of bound N₂, we performed DFT calculations on five- and three-coordinate iron complexes. Geometry optimization of [Fe(CO)₂(Ph₃P)₂(µ-N₂)] gave bond lengths of Fe–N = 1.893 Å and N–N = 1.122 Å, in excellent agreement with the experimental structures of [Fe(CO)₅(PR₃)₂(µ-N₂)] (R = C₅H₅; Fe–N = 1.871(1), 1.892(2) Å; N–N = 1.13(2) Å; R = OCH₃; Fe–N = 1.876(9) Å; N–N = 1.13(1) Å). Removal of all PH ligands to give three-coordinate iron (Scheme 1), followed by geometry

**Scheme 1. Five-Coordinated and Three-Coordinated Models Evaluated by Density-Functional Theory**

ADF calculations of Fe(N₂)Cl₃, FeCl₅, and Fe(N₂)Cl₅ model the active site for N₂ activation. The binding constants of N₂ to Fe(N₂)Cl₃ and FeCl₅ are calculated to be 1.2 × 10⁵ and 1.2 × 10⁶, respectively. The binding constant of N₂ to Fe(N₂)Cl₅ is calculated to be 4.2 × 10⁷, which is significantly higher than the binding constants of N₂ to Fe(N₂)Cl₃ and FeCl₅.

**Chart 1**

![Chart 1](image-url)

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Population of these back-bonding orbitals is expected to give \( \pi \)
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Further reaction of \( \text{LFeNNFeL} \) with sodium or potassium

Key bond distances for \( \text{Na}_2 \text{LFeNNFeL} \): Fe–N = 1.773 Å; Na–N = 1.173 Å. It is apparent from the

Key bond distances for \( \text{K}_2 \text{LFeNNFeL} \): Fe–N = 1.750(3), 1.744(3) Å; N–N = 1.239(4) Å; Na–N = 2.483(3), 2.488(3), 2.495(3), 2.484(3) Å.

The specific reasons for N–N bond weakening in \( \text{LFeNNFeL} \) were elucidated by using MCSCF calculations to determine its electronic structure. For simplicity, calculations were done on \( \text{LFeNNFeL} \) (not shown here; see Figure S-3): Fe–N = 1.239 Å; Na–N = 2.483 Å. Key bond distances for \( \text{Na}_2 \text{LFeNNFeL} \) are consistent with N–N double bonds. Examination of the molecular orbital diagram in Figure 2 shows that N2 is weakened because two additional electrons fall into the 11b1,2 orbitals with N–N antibonding character. The complex \( \text{K}_2 \text{LFeNNFeL} \) in Figure 1b, which has two iron and two potassium atoms each coordinated to N2, reminds one that the Haber–Bosch catalyst typically contains potassium “promoter” that is known to contribute to N2 binding.

This work shows that low-coordinate iron is adept at the binding and weakening of N2, and provides the first well-characterized example of stepwise reduction of N–N bond order by reduction of an iron complex. We are currently attempting to evaluate the N2 reactivity brought about by the structural and electronic effects of low-coordinate metal atoms.

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Further reaction of \( \text{LFeNNFeL} \) with sodium or potassium metal in diethyl ether gave blue (Na) or green (K) products \( \text{M}_2 \text{LFeNNFeL} \) (M = Na; M = K, Figure 1b) that were characterized by X-ray crystallography. In these compounds, the [FeNNFe]1+ core of \( \text{LFeNNFeL} \) is reduced by two electrons to \[\text{FeNNFe}^0\], and the alkali metal cations coordinate to the N2 fragment and the aryl rings of the ligand. In each compound, the combination of reduction and alkali metal coordination has lengthened the N–N bond to 1.23–1.24 Å. Vibrations at 1589 and 1123 cm\(^{-1}\) with substantial N–N stretching character were observed in \( \text{K}_2 \text{LFeNNFeL} \) by resonance Raman spectroscopy (\( \lambda_{ex} = 406.7 \) nm). These bond lengths and stretching frequencies are consistent with N–N double bonds.

The frontier orbitals of \( \text{LFeNNFeL} \), from MCSCF calculations under \( D_2 \) symmetry. The left side shows the relative energies of the orbitals and their occupancies; the right has contour plots of the singly occupied MO’s, viewed along a 2-fold rotation axis. Both 11b1,2 and 12b1,2 are pairs of corresponding, orthogonal partners with Fe–N \( \pi \)-bonding and N–N \( \pi \)-antibonding character.

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Figure 1. Thermal ellipsoid diagrams (50% probability). In each compound, the Fe–N–N–Fe core is virtually linear. (a) Key bond distances for \( \text{LFeNNFeL} \): Fe–N(N1) = 1.770(5), 1.779(5) Å; N–N = 1.182(5) Å. (b) Key bond distances for \( \text{K}_2 \text{LFeNNFeL} \): Fe–N(N2) = 1.763(6), 1.765(6) Å; N–N = 1.233(6) Å; K–N = 2.697(6), 2.697(5), 2.701(5), 2.706(6) Å. Key bond distances for \( \text{Na}_2 \text{LFeNNFeL} \) (not shown here; see Figure S-3): Fe–N(N) = 1.750(3), 1.744(3) Å; N–N = 1.239(4) Å; Na–N = 2.483(3), 2.488(3), 2.495(3), 2.484(3) Å.

Optimization of the resulting \( \{\text{Fe(CO)}_2\} _2(\mu-\text{N}_2) \) complex, gave Fe–N = 1.773 Å and N–N = 1.173 Å. It is apparent from the significant shortening of the Fe–N bonds (\( \Delta \text{FeN} \approx -0.12 \) Å) and lengthening of the N–N bond (\text{ANN} \approx +0.05 \) Å) that the lower coordination number correlates with N2 stretching.

The specific reasons for N–N bond weakening in \( \text{LFeNNFeL} \) were elucidated by using MCSCF calculations to determine its electronic structure. For simplicity, calculations were done on \( \text{LFeNNFeL} \) (L′ = C(NH)3), a model of \( \text{LFeNNFeL} \) in the crystallographically determined geometry stripped of alky1 and aryl groups and symmetrized to \( D_{2h} \) symmetry. The lowest energy spin state of \( \text{LFeNNFeL} \) has six unpaired electrons (7B3 in the point group \( D_{2h} \)), consistent with the solution magnetic moment (8.4 \( \mu_B \)). The nature of the orbitals in which these six electrons lie is informative (Figure 2). Each of the b1/b2 pairs has \( \pi \)-bonding character between the iron atoms and the N2 ligand, and \( \pi \)-antibonding character between the nitrogen atoms of N2. Population of these back-bonding orbitals is expected to give stronger Fe–N bonds and a weakened N–N bond, as observed experimentally.

Further reaction of \( \text{LFeNNFeL} \) with sodium or potassium metal in diethyl ether gave blue (Na) or green (K) products \( \text{M}_2 \text{LFeNNFeL} \) (M = Na; M = K, Figure 1b) that were characterized by X-ray crystallography. In these compounds, the [FeNNFe]1+ core of \( \text{LFeNNFeL} \) is reduced by two electrons to [FeNNFe]0, and the alkali metal cations coordinate to the N2 fragment and the aryl rings of the ligand. In each compound, the combination of reduction and alkali metal coordination has lengthened the N–N bond to 1.23–1.24 Å. Vibrations at 1589 and 1123 cm\(^{-1}\) with substantial N–N stretching character were observed in \( \text{K}_2 \text{LFeNNFeL} \) by resonance Raman spectroscopy (\( \lambda_{ex} = 406.7 \) nm). These bond lengths and stretching frequencies are consistent with N–N double bonds. Examination of the molecular orbital diagram in Figure 2 shows that N2 is weakened because two additional electrons fall into the 11b1,2 orbitals with N–N antibonding character. The complex \( \text{K}_2 \text{LFeNNFeL} \) (Figure 1b), which has two iron and two potassium atoms each coordinated to N2, reminds one that the Haber–Bosch catalyst typically contains potassium “promoter” that is known to contribute to N2 binding.

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(17) Nitrogen-15 labeling caused these bands to shift into apparent Fermi doublets at 1565/1536 and 1108/1087 cm\(^{-1}\). See Supporting Information for details.