Nitrogen Fixation

New Insights into the Biological and Synthetic Fixation of Nitrogen**

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The production of biomass is limited by the availability of chemically accessible nitrogen. The synthesis of ammonia from dinitrogen requires efficient catalysis owing to the high bond energy and kinetic inertness of N_2. In contrast to biological nitrogen fixation, the industrial Haber–Bosch process operates at high pressures and temperature. Hence, synthetic NH_3 generation under milder reaction conditions defines a highly desirable target. Some recent reports on both biological and synthetic nitrogen fixation might help to close in on that goal.

In nature, ammonia is produced by soil microorganisms. Even with the most efficient enzyme, [Fe,Mo]-nitrogenase (N_2-ase), this reaction is energetically quite costly and hydrogenase activity cannot be fully suppressed, resulting in the limiting stoichiometry [Eq. (1)].[1]

$$N_2 + 8 H^+ + 8 e^- + 16 ATP \rightarrow 2 NH_3 + H_2 + 16 ADP + 16 P_i \qquad (1)$$

The catalytic site is defined by a complex cofactor, a sulfide-bridged cluster with seven iron and one molybdenum ions (FeMo-co). Two synthetic, monomeric Mo complexes, which catalyze the reduction of N_2 to NH_3 in the presence of Brønsted acid and organometallic reducing agents,[2] were reported as functional models, and alternating e^- and H^+ transfer was proposed as the mechanism ("Schrock cycle").[3] Theoretical studies assumed such stepwise mechanisms for the biological prototype as well, yet favored iron-centered N_2 activation.[4] However, N_2-ase models suffer from some uncertainty regarding the structure of the FeMo-co: X-ray diffraction analysis (1.16 Å resolution) indicated the presence of a light atom X (O, N, or C) in the center of the cluster.[5] N was widely assumed, but later disfavored: the ^{14}N hyperfine coupling (HFC) detected by electron spin-echo envelope modulation (ESEEM) and electron nuclear double resonance (ENDOR) experiments is very small after extraction of the FeMo-co from the protein environment.[6]

Lancaster et al. now examined nitrogenase with X-ray emission spectroscopy, specifically analyzing the spectroscopic region that originates from several superimposed electronic ligand(ns/np)→Fe core level transitions and comparing that with the apo-(FeMo-co)-enzyme, synthetic model clusters, and DFT predicted data.[7a] The authors concluded that the energy of the 2s(X)→1s(Fe) transition is significant enough to distinguish between X = O^{2-}, N^{3-}, and C^{4-} and obtained the best fit of the experimental data for carbide. This proposal is further supported by Spatzal et al. with a new structural model recorded at higher resolution (1.0 Å)[7b] (Figure 1). In this study, ^{13}C HFC was also reported based on ESEEM measurements of isotopically labeled N_2-ase. However, ^{13}C HFC was already observed earlier by ENDOR but absent for the free FeMo-co after extraction.[6b]
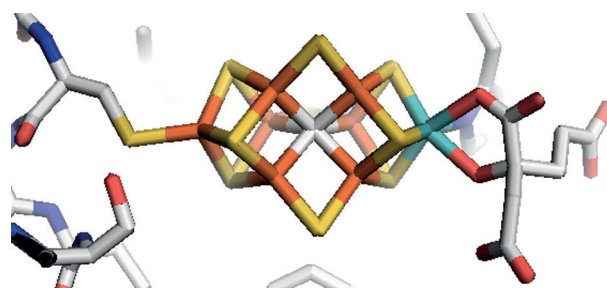

Figure 1. The latest structural model for the FeMo-co (PDB: 3U7Q; Fe orange, Mo cyan, S yellow, O red, N blue, C gray).

Several questions will have to be addressed, such as the biosynthesis, compatability with physiological conditions, and chemical role of the carbido ligand, which is unprecedented in bioinorganic chemistry. However, the intriguing and chemically least intuitive solution for X possibly implies the transition from the "Interstitial Atom Era"[8] to the "Organometallic Era" in N_2-ase research and stimulates future experimental and theoretical studies.

In comparison, the Haber–Bosch process, arguably the most extensively studied catalytic large-scale reaction, follows a different mechanistic path.[9] After 100 years, iron oxides, with promotors such as K_2O, are still the precatalysts of choice. In situ activation to "ammonia iron" affords a complex, nanostructured Fe catalyst. Spectroscopic studies on iron single-crystal surfaces and theoretical work provided a detailed model which explains the microkinetics under "real" conditions. Turnover-limiting dissociative N_2 chemi-

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sorption is followed by stepwise hydrogenation to NH_3. Promotion lowers the local catalyst work function by injection of electron density into the conduction band, thereby increasing charge transfer to adsorbed nitrogen near the potassium sites.

In comparison, the cleavage of the N_2 triple bond in the coordination sphere of early- and mid-transition-metal complexes was demonstrated several times, yet not with metals beyond Group 6.[10] Holland and co-workers now reported an iron diketiminato complex that mediates N_2 cleavage, which is striking compared with previous studies as only moderate N_2 activation was achieved with bulkier ligands (Scheme 1).[11]

1. The general trend of decreasing bond energies for diatomic $[M\equiv N]^+$ (M = Ti-Cu) is reflected in the scarcity of terminal, late-transition-metal (TM) nitrido complexes.[12] High-valent iron nitrides depend on bulky ligand frameworks which enforce suitable coordination geometries to stabilize $Fe\equiv N$ π bonding and prevent decomposition, for example, by reductive N–N coupling.[13] In the present case, the less bulky ligand enables the formation of bridging nitrido ligands with high coordination numbers, thus avoiding M–N multiple bonding and high oxidation states for Fe. Likewise, high rates of N_2 chemisorption are observed for single-crystal surfaces which afford N_{ad} interactions also with subsurface Fe atoms, namely Fe(111).[9] Furthermore, one nitrido ligand in **1** is stabilized by coordination to Lewis acidic K^+ ions, suggesting that K–N interactions might be relevant also for promoted catalyst surfaces.

2. For early-TM complexes, the side-on, bridging N_2 coordination mode (μ_2:η^2,η^2) has been associated with stronger N_2 activation than that with end-on coordination (μ_2:η^1,η^1), as a result of the increased population of orbitals with N–N antibonding character.[14] Facile N_2 functionaliza-tion (e.g. with H_2 or CO_2) and splitting were reported for Group 4 and Group 5 μ_2:η^2,η^2-N_2 complexes, respectively.[15] The reduced steric bulk of the auxiliary ligand in **1** possibly enables beneficial side-on coordination. Interestingly, only a small degree of N_2 activation was predicted for $(R_2N)_2Fe(\mu_2$:η^2,η^2-$N_2)Fe(NR_2)_2$ by DFT calculations.[14b] However, the {Fe(N)$_2$Fe} core of **1** exhibits a higher total valence electron count and further stabilization arises from coordination of a three-coordinate high-spin ferrous ion which is strongly antiferromagnetically coupled to the two four-coordinate ferric high-spin centers. It is an intriguing question whether all Fe centers and the complex spin-coupling scheme are instrumental not only for stabilization of the product but also for the kinetics of the 6 e^- N_2 reduction.

Dinitrogen functionalization through N_2 cleavage with early-TM complexes generally suffers from the high stability of the resulting d^0 nitrides.[10] In contrast, **1** reacts with H_2 at room temperature giving NH_3 in around 40% yield (Scheme 1), as one of the few examples producing substantial amounts of NH_3 directly from N_2 and H_2.[16] Partial hydro-genolysis of binuclear iron μ-nitrido to μ-imido complexes had been reported earlier and full hydrogenolysis of a termi-nal ruthenium nitride bearing a cooperating ligand for H_2 heterolysis was recently demonstrated.[17] While those nitrides had not been derived from N_2, generation of NH_3 was, in fact, achieved by cooperative N_2 and H_2 activation with separate metal centers.[16a] To date, all these examples produced only substoichiometric amounts of ammonia, but they emphasize, like the present study, that the utilization of cooperativity is a promising strategy for both jobs. Although it is not to be expected that the Haber–Bosch process will be replaced by a more efficient pathway any time soon, the recent milestones
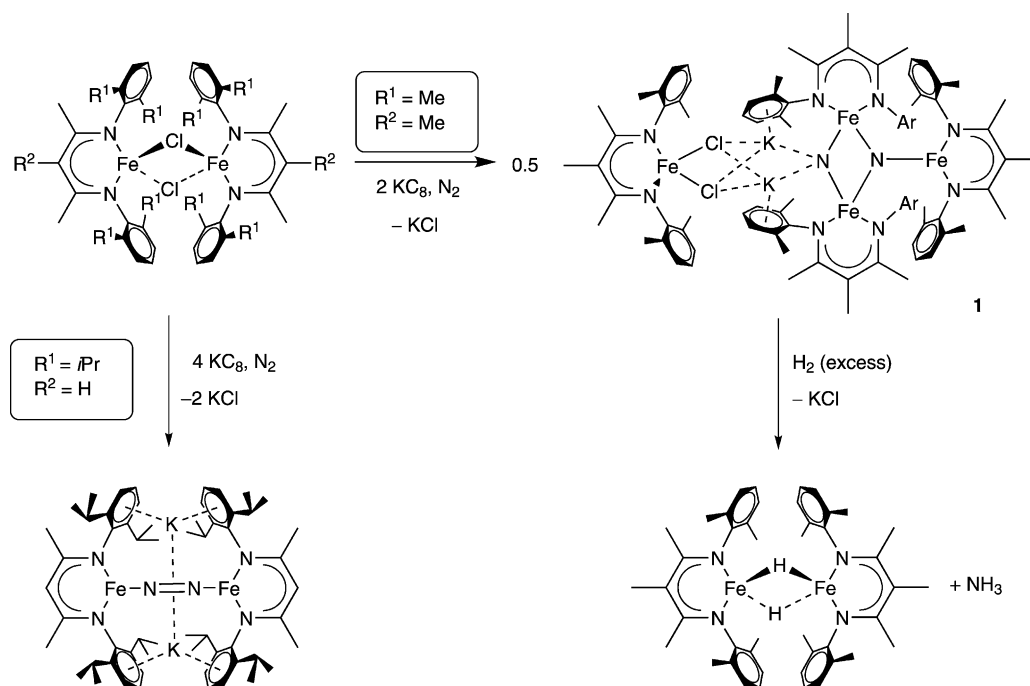
Scheme 1. Activation of N_2 with iron diketiminato complexes.

provide a basis to rationalize the mechanistic details of biological and synthetic nitrogen fixation, and therefore also for the synthesis of other useful products of N_2 functionalization.

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