Iron Nitrido Complexes

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Formation of Ammonia from an Iron Nitrido Complex **

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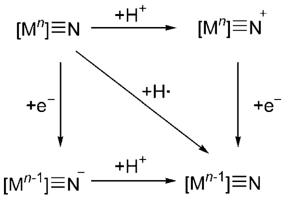
Iron nitrido complexes have attracted interest due to their possible involvement in the catalytic cycle of the nitrogenase enzyme.[1] Iron complexes with terminal nitrido ligands have been spectroscopically characterized in the +4,[2] +5,[3,4] and +6[4,5] oxidation states, although it is only recently that isolable iron(IV) nitrido complexes have been discovered.[6,7] Our group recently reported the electronic structure and preliminary reactivity of an electrophilic tris(carbene)borate iron(IV) nitrido complex.[7]

Nitrido complexes are also proposed as intermediates in cycles for the reduction of N_2 to NH_3 (e.g. the Chatt cycle).[8] Catalytic formation of ammonia by a nitrido complex requires that ammonia production be coupled to regeneration of the nitrido ligand. Therefore, in addition to the protons required to create the N−H bonds, electrons are also needed to reduce the metal center for further N_2 cleavage and nitrido ligand regeneration. Achieving catalysis requires reaction conditions that avoid undesired side reactions, particularly the reduction of protons by the electron source. In the catalytic formation of ammonia by bulky molybdenum tris(amido)amine complexes, this aim is achieved by using a proton source that has limited solubility in the reaction medium as well as by slowly delivering the reducing agent to the reaction mixture.[9]

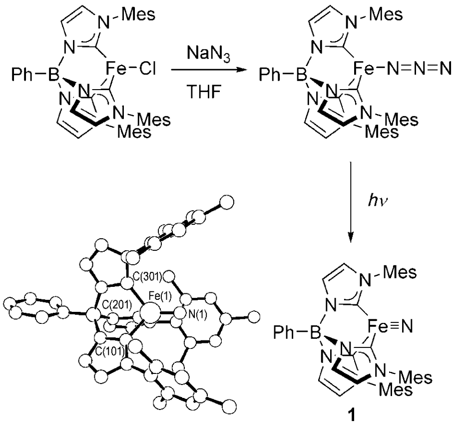
From a thermodynamic perspective, the addition of a single proton and a single electron to a metal nitrido complex is equivalent to the transfer of a hydrogen atom (Scheme 1).[10] With this in mind, we reasoned that reaction with a hydrogen-atom donor could result in the formation of NH_3 from a metal nitrido complex in solution. However, hydrogen-atom transfer reactions involving metal nitrido complexes in solution appear to be without precedent,[11] despite being well-known for other metal–ligand multiple bonds (e.g. Fe=O and Fe=NR).[12]



Scheme 1. Thermodynamic cycle for the formation of $[M^{(n-1)}]{=}NH$ from $[M^n]{\equiv}N$. Concerted HAT follows the diagonal pathway, while stepwise proton and electron transfers follow the horizontal and vertical pathways. [M] represents a metal center and its ancillary ligands.

Herein we report the formation of ammonia from a terminal iron(IV) nitrido complex by reaction with a hydrogen-atom donor. Mechanistic investigations suggest that at least one HAT step is involved in the reaction. A related reaction between the iron nitrido complex and an organic radical results in the reductive formation of a C−N bond.

Synthesis of the iron(IV) nitrido complex $[PhB(MesIm)_3Fe{\equiv}N]$ (**1**), where $PhB(MesIm)_3^-$ is a bulky tris(carbene)borate ligand, was achieved in a similar manner to other recently reported iron(IV) nitrido complexes (Scheme 2).[6,7] Reaction of the iron chloride complex $[PhB(MesIm)_3FeCl]$[13] with excess NaN_3 yields the crystallographically characterized azido complex $[PhB(MesIm)_3Fe{-}N{=}N{=}N]$ ($\nu_{N=N=N} = 2078\ cm^{-1}$), which is then photolyzed to form **1** in high yield. The X-ray crystal structure of **1** shows similar structural features to our related $[PhB(t\text{BuIm})_3Fe{\equiv}N]$ complex (Scheme 2, inset).[7] Thus, the Fe−N (1.499(5) Å) and Fe−C bond lengths (1.885(6)–1.921(6) Å) as well as the N-Fe-C bond angles (120.7(3)–123.3(3)°) are similar to those in $[PhB(t\text{BuIm})_3Fe{\equiv}N]$. Both the ^1H and ^{15}N NMR spectra are consistent with the solid-state structure.



Scheme 2. Synthesis of $[PhB(MesIm)_3Fe{\equiv}N]$ (**1**; Mes = 2,4,6-trimethylphenyl). Inset: X-ray crystal structure of **1**; solvent molecules and hydrogen atoms are omitted for clarity.

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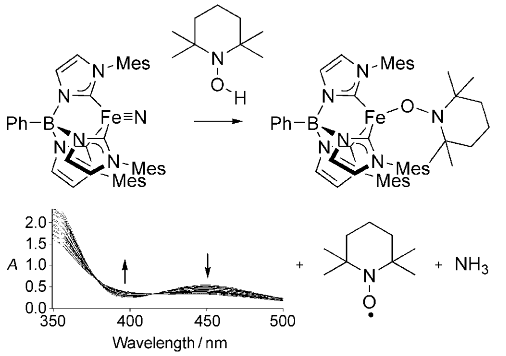
Reaction of **1** with excess TEMPO-H (TEMPO-H = 1-hydroxy-2,2,6,6-tetramethylpiperidine) results in quantitative formation of the yellow iron(II) complex [PhB(MesIm)$_3$Fe(tempo)].[14] The other products of this reaction are ammonia (up to 74% based on Fe) and TEMPO (greater than 95%), which was characterized by EPR spectroscopy (Scheme 3).



Scheme 3. Reaction of **1** with TEMPO-H. Inset: Spectral evolution of the reaction in THF at 299 K. [Fe] = 0.354 mM, [TEMPO-H] = 21.3 mM. Traces are shown at 230 s intervals.

The reaction of **1** with TEMPO-H is notable for its selectivity and mildness, producing ammonia while simultaneously reducing the iron center. As mentioned above, the formation of ammonia from a nitrido complex coupled with reduction of the metal center is typically achieved using separate proton and electron sources.[2a,15]

Formation of ammonia from [PhB(MesIm)$_3$Fe≡N] and TEMPO-H requires multiple steps. At least three possible mechanisms for the first step of the reaction between **1** and TEMPO-H are possible. The iron(IV) nitrido complex could react by electron transfer (ET) to form an anionic iron(III) nitrido complex [PhB(MesIm)$_3$Fe^{III}≡N]$^-$ and TEMPO-H$^+$. A second possibility is initial proton transfer (PT) to **1** to yield the iron(IV) imido complex [PhB(MesIm)$_3$Fe^{IV}≡NH]$^+$ and TEMPO$^-$. Finally, HAT from TEMPO-H leads to the formation of the iron(III) imido complex [PhB(MesIm)$_3$Fe≡NH] and TEMPO.

Thermodynamic and kinetic investigations were undertaken to determine the mechanism by which **1** reacts with TEMPO-H. The thermodynamics of electron transfer to **1** were determined by cyclic voltammetry. No reduction waves are observed at potentials greater than −2.5 V (vs. ferrocene/ferrocenium (Fc/Fc$^+$) in MeCN) in the cyclic voltammogram of **1**. Consistent with this result, no reaction was observed between **1** and [Cp*$_2$Co] ($E_{1/2} = -1.91$ V vs. Fc/Fc$^+$ in MeCN; Cp* = C$_5$Me$_5$).[16] Since TEMPO-H is not strongly reducing ($E_{1/2} \approx 0.71$ V vs. Fc/Fc$^+$ in MeCN),[17] initial electron transfer to **1** is thermodynamically uphill ($\Delta G_{ET} > 74$ kcal mol^{-1}).

Direct measurement of the free energy for proton transfer to **1** is complicated by the fact that the nitrido complex is decomposed by acids (e.g. HOAc). The upper limit for the pK_a for the conjugate acid of **1**, [PhB(MesIm)$_3$Fe^{IV}≡NH]$^+$, was determined by evaluating the reactivity of **1** towards a series of acids. Complex **1** was found to react with PhCH$_2$SH (pK_a = 15.4 in DMSO)[18] but not with phenol (pK_a = 18.0 in DMSO).[18] Therefore proton transfer from TEMPO-H (pK_a = 31.0 in DMSO)[19] to **1** is also thermodynamically uphill, with $\Delta G_{PT} > 18$ kcal mol^{-1}.

The free energy for hydrogen-atom transfer to **1** was estimated in a similar manner. While **1** reacts with TEMPO-H (O–H bond dissociation energy (BDE) = 69.7 kcal mol^{-1})[19] to produce ammonia, no reaction is observed between **1** and 9,10-dihydroanthracene (C–H BDE = 78 kcal mol^{-1})[20] or xanthene (C–H BDE = 76 kcal mol^{-1}).[20] This result provides an upper limit for the N–H BDE of the parent imido complex [PhB(MesIm)$_3$Fe^{III}≡NH], and therefore for hydrogen-atom transfer from TEMPO-H to **1**, $\Delta G_{HAT} > -7$ kcal mol^{-1}.

Kinetic investigations were used to provide further insight into the reaction mechanism. The rate of reaction between **1** and TEMPO-H in THF, measured under pseudo-first-order conditions by UV/Vis spectroscopy, was found to be first order in both **1** and TEMPO-H, consistent with the rate law rate = k_H[Fe][TEMPO-H]. The second-order rate constant at 298 K is $k_H = 8.1(3) \times 10^{-3}$ M^{-1}s^{-1}. The kinetic isotope effect ($k_H/k_D = 3.1$) determined from the rate of reaction between **1** and TEMPO-D is consistent with either initial proton or hydrogen-atom transfer. Analysis of the temperature dependence of the rate constant gives activation enthalpy and entropy values of $\Delta H^{\ddagger} = (11.1 \pm 0.3)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -(37.4 \pm 0.8)$ e.u. (288–318 K).

The free energy of activation at 298 K is $\Delta G^{\ddagger} = (22.2 \pm 0.3)$ kcal mol^{-1}. Since $\Delta G^{\ddagger} > \Delta G_{PT}$, the combined thermodynamic and kinetic data do not clearly distinguish between mechanisms involving initial proton or hydrogen-atom transfer from TEMPO-H to **1**. However, three additional observations lead us to favor a mechanism involving initial HAT: 1) 9,10-dihydroanthracene (pK_a = 30.1 in DMSO)[20] and xanthene (pK_a = 30.0 in DMSO)[20] have similar acidities to TEMPO-H, and therefore our finding that these reagents do not react with **1** argues against initial proton transfer from TEMPO-H to **1**. 2) We find that the rate of reaction between **1** and TEMPO-H in the lower polarity solvent C$_6$H$_6$ is similar to that observed in THF.[21] 3) The rate of reaction is unaffected by the ionic strength of the solution.[21] The latter two observations suggest that charged intermediates are not involved in the rate-determining step (see Scheme 1), arguing against initial proton transfer from TEMPO-H to **1**.

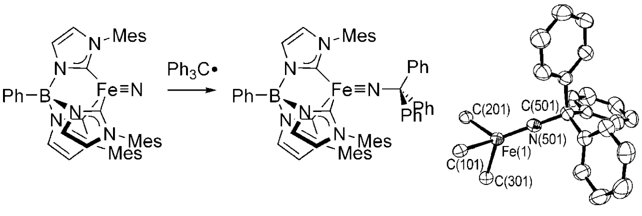
Our experimental data therefore favor a reaction mechanism in which the initial N–H bond-forming step occurs by HAT [Eq. (1)]:

$$[\mathrm{Fe^{IV}}]{\equiv}\mathrm{N} + \text{TEMPO-H} \rightarrow [\mathrm{Fe^{III}}]{\equiv}\mathrm{N{-}H} + \mathrm{TEMPO}\cdot \qquad (1)$$

Although initial proton transfer cannot be definitively excluded at present, it is significant that a hydrogen-atom donor provides both protons and electrons required for formation of N–H bonds coupled to reduction of the metal center. This strategy can be extended to other hydrogen-atom donors such as metal hydrides. For example, reaction of **1** with the weakly acidic metal hydride [Co(dppe)$_2$H] (Co–H BDE = 64 kcal mol^{-1}, dppe = 1,2-bis(diphenylphosphanyl)ethane)[22] also leads to the formation of NH$_3$ (22%, not optimized).

The feasibility of one-electron chemistry is further illustrated by the reaction of a carbon-centered radical with

1, which leads to the formation of a carbon–nitrogen bond. In particular, reaction of **1** with Gomberg's dimer,[23] a source of the triphenylmethyl radical, results in rapid formation of the dark brown iron(III) imido complex [PhB(MesIm)$_3$Fe≡N−CPh$_3$] (Scheme 4). This complex has been crystallographically characterized (Scheme 4, inset) and shows similar structural features to other four-coordinate iron(III) imido complexes, in particular the short Fe−N bond (1.653(2) Å) and linear Fe-N-C angle (177.7(2)°).[13,24] The complex has a paramagnetically shifted ^{1}H NMR spectrum that is consistent with the solid-state structure and a solution magnetic moment (2.5(3) μ_B) indicative of low-spin iron(III) ($S = 1/2$). Thus, radical capture by **1** results in C−N bond formation coupled with reduction of the metal center. This reaction provides a model for our proposed mechanism for the first step of the reaction between TEMPO-H and **1**.



Scheme 4. Reaction of **1** with the triphenylmethyl radical. Inset: X-ray crystal structure of [PhB(Mes)$_3$Fe≡N−CPh$_3$]. Thermal ellipsoids are shown at 50% probability; solvent molecules, hydrogen atoms, and most of the tris(carbene)borate ligand is omitted for clarity.

In conclusion, we find that reaction of suitable hydrogen-atom donors with an iron(IV) nitrido complex leads to the formation of ammonia. Although not conclusive, mechanistic investigations suggest a mechanism involving HAT from TEMPO-H to **1**. A similar reaction of the nitrido complex with a carbon-based radical leads to C−N bond formation. These reactions, which may generally be described as reductive radical transfers, represent a previously unexplored mode of reactivity for metal nitrido complexes.

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