Nitrogen Atom Transfer

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Snapshots of Complete Nitrogen Atom Transfer from an Iron(IV) Nitrido Complex**

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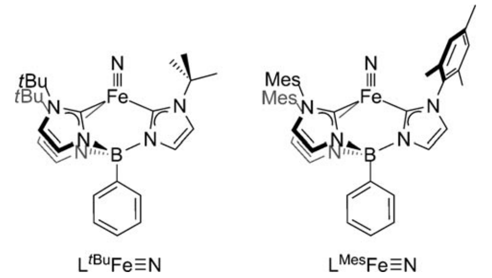
The oxidation of organic hydrocarbons by oxygen atom transfer from metal oxo complexes has been well studied, and numerous methods of epoxidation by oxo transfer are routinely utilized in organic synthesis.[1,2] In contrast to oxygen atom transfer, methods for transferring nitrogen atoms to organic substrates are not as well-developed. Such methods would be of great utility owing to the value of the anticipated end products (e.g. aziridines)[3] and the potential for using N_2 as the nitrogen atom source.[4]

In analogy to oxygen atom transfer, metal nitrido complexes may be expected to serve as intermediates in nitrogen atom transfer. However, with one notable exception, in which the isocyanate anion is formed by two electron nitrogen atom transfer from a vanadium nitrido complex to CO,[5] complete nitrogen atom transfer leading to substrate functionalization is unknown. An alternative approach to achieving complete nitrogen atom transfer from nitrido complexes is to activate the nitrido ligand with trifluoroacetic anhydride, which results in the formation of an imido ligand that is reactive in nitrene transfer.[6]

The incomplete transfer of nitrogen atoms to organic substrates is more prevalent. For example, while the formation of new N−C bonds by two electron nitrogen atom transfer to alkene,[7] diene,[8] CO,[5,9] isonitriles,[9,10] carbene,[11] and carbanion[12] substrates has been reported, the functionalized substrate remains bound to the metal in the form of a new ligand. To achieve cycles for substrate functionalization by nitrogen atom transfer, methods for evicting the nitrogenated substrate and regenerating the nitrido ligand need to be developed.

We have previously reported the four-coordinate iron(IV) nitrido complexes [$L^{tBu}Fe{\equiv}N$] and [$L^{Mes}Fe{\equiv}N$] (Scheme 1).[13,14] Our initial survey of their reactivity revealed that the nitrido ligands in these complexes have electrophilic character, as evidenced by their reactions with triphenylphosphine, resulting in the formation of iron(II) phosphoraniminato complexes.[13,15] Furthermore, [$L^{Mes}Fe{\equiv}N$] reacts with hydrogen atom donors, such as 2,2,6,6-tetramethylpiperidinol (TEMPO-H), ultimately yielding NH_3 by a mechanism that involves hydrogen atom transfer to the nitrido ligand.[14] Inspired by these observations, which show that the reactive nitrido ligand that can be released from the metal center, we sought to develop methods for substrate functionalization by complete nitrogen atom transfer.



Scheme 1. Tris(carbene)borate iron(IV) nitrido complexes.

Herein we present the transfer of nitrogen atoms from these iron nitrido complexes to the unsaturated substrates $C{\equiv}O$ and $C{\equiv}NtBu$, resulting in the formation of new N−C bonds. The architecture of the tris(carbene)borate supporting ligand controls the extent of nitrogen atom transfer, with [$L^{Mes}Fe{\equiv}N$] undergoing complete nitrogen atom transfer from iron to $C{\equiv}NtBu$. Although incomplete atom transfer occurs for [$L^{tBu}Fe{\equiv}N$], an additional group transfer step completes a nitrogen atom transfer cycle for the synthesis of an unsymmetrical carbodiimide.

Addition of excess $C{\equiv}NtBu$ to a THF solution of [$L^{Mes}Fe{\equiv}N$] immediately results in the formation of a white precipitate, which was established to be the diamagnetic complex [$L^{Mes}Fe(CNtBu)_3$]$^+$[$N{=}C{=}NtBu$]$^-$ on the basis of structural and spectroscopic studies (Figure 1a). The structure of the cation was determined from crystals of [$L^{Mes}Fe(CNtBu)_3$]$^+$[$B(C_6F_5)_4$]$^-$, which is prepared by metathesis of [$L^{Mes}Fe(CNtBu)_3$]$^+$[$N{=}C{=}NtBu$]$^-$ with $LiB(C_6F_5)_4$ (Figure 1b). The solid-state structure reveals a six-coordinate iron center that is facially bound by the tris(carbene)borate ligand and three isonitrile ligands. The geometry at the metal ion is distorted from octahedral, as seen in the C-Fe-C angles. Despite the higher coordination number, the Fe−C(carbene) bond lengths are slightly shorter than in other iron(II) tris(carbene)borate complexes,[13] which is most likely a consequence of the low spin state. No other unusual structural features are observed.

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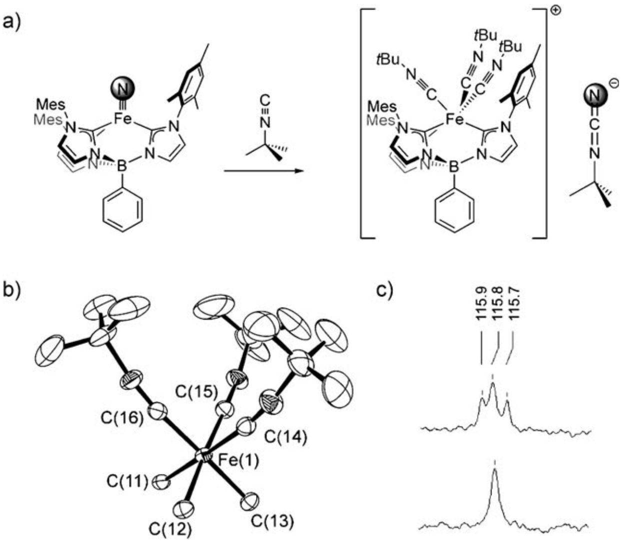


Figure 1. a) Synthesis of $[L^{Mes}Fe(CNtBu)_3]^+[N{=}C{=}NtBu]^-$. b) X-ray crystal structure of $[L^{Mes}Fe(CNtBu)_3]^+[B(C_6F_5)_4]^-$. Ellipsoids set at 50% probability; hydrogen atoms, most of the tris(carbene)borate ligand, and the borate anion are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–C12 2.009(2), Fe1–C13 2.033(2), Fe1–C11 2.036(2), Fe1–C16 1.882(2), Fe1–C15 1.884(2), Fe1–C14 1.882(2); C12-Fe1-C11 88.23(7), C11-Fe1-C13 84.63(7), C12-Fe1-C13 85.41(7), C16-Fe1-C15 86.38(8), C16-Fe1-C14 86.71(8), C15-Fe1-C14 84.24(8). c) Carbodiimido resonance in the ^{13}C NMR spectrum (33% ^{13}C enrichment). Bottom: $[L^{Mes}Fe(^{13}CNtBu)_3]^+[N{=}^{13}C{=}NtBu]^-$; top: $[L^{Mes}Fe(^{13}CNtBu)_3]^+[^{14/15}N{=}^{13}C{=}NtBu]^-$, with 50% ^{15}N enrichment.

The most striking feature in the ^1H NMR spectrum of $[L^{Mes}Fe(CNtBu)_3]^+[N{=}C{=}NtBu]^-$ is a singlet at $\delta = 1.12$ ppm. This resonance is absent in the ^1H NMR spectrum of $[L^{Mes}Fe(CNtBu)_3]^+[B(C_6F_5)_4^-]$ and is therefore assigned to the *tert*-butylcarbodiimido anion. As expected for threefold symmetry, two $\nu_{C\equiv N}$ bands are observed in the IR spectrum of $[L^{Mes}Fe(CNtBu)_3]^+[N{=}C{=}NtBu]^-$ at 2133 cm^{-1} and 2094 cm^{-1}. A strong absorption band is also observed at 2253 cm^{-1}. This band is not observed in the IR spectrum of $[L^{Mes}Fe(CNtBu)_3]^+[B(C_6F_5)_4]^-$, and is therefore assigned as $\nu_{N=C=N}$. The comparative spectral data of these two complexes establish that $[N{=}C{=}NtBu]^-$ is not bound to the metal.

A dual-label NMR experiment confirms the formulation of the carbodiimido anion $[N{=}C{=}NtBu]^-$. The ^{13}C NMR spectrum of $[L^{Mes}Fe(^{13}CNtBu)_3]^+[N{=}^{13}C{=}NtBu]^-$, prepared using $^{13}C{\equiv}NtBu$ (33% enrichment), shows two singlets at $\delta = 162.2$ and 115.8 ppm in a 3:1 ratio. The resonance at $\delta = 115.8$ ppm develops ^{15}N satellites ($J_{CN} = 16$ Hz) when the experiment is repeated with 50% ^{15}N-enriched $L^{Mes}Fe{\equiv}N$, which is consistent with formation of the doubly labeled anion $^{15}N{=}^{13}C{=}NtBu^-$ (Figure 1c). This result convincingly demonstrates C–N bond formation between the nitrido ligand and $C{\equiv}NtBu$, ultimately leading to formation of the carbodiimido anion. This is a rare example of a two-electron nitrogen atom transfer reaction involving complete atom transfer from the metal to the substrate.[5]

Interestingly, when $L^{Mes}Fe{\equiv}N$ is treated with CO, complete nitrogen atom transfer does not occur, but instead the diamagnetic six-coordinate complex $[L^{Mes}Fe(NCO)(CO)_2]$ is obtained (Figure 2). The solid-state structure of this complex reveals that an isocyanate ligand is formed by nitrogen atom transfer from $[L^{Mes}Fe{\equiv}N]$ to CO. In contrast to the reaction with $C{\equiv}NtBu$, the newly formed ligand remains bound to the metal center, with the remaining two coordination sites occupied by carbonyl ligands (Figure 2).[16] The Fe–N distance in $[L^{Mes}Fe(NCO)(CO)_2]$ is similar to other structurally characterized iron(II) isocyanide complexes and is consistent with two-electron nitrogen atom transfer from $[L^{Mes}Fe{\equiv}N]$ to CO.

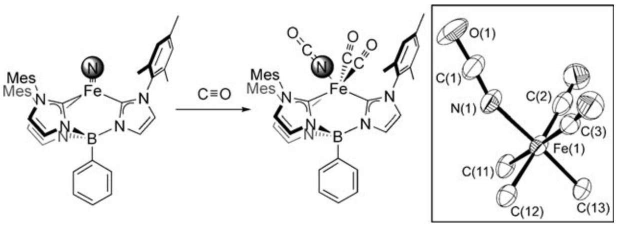


Figure 2. Synthesis of the isocyanate complex $L^{Mes}Fe(NCO)(CO)_2$. Inset: X-ray crystal structure. Ellipsoids set at 50% probability; hydrogen atoms and most of the tris(carbene)borate ligand omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–N1 1.987(2), N1–C1 1.156(4), C1–O1 1.210(4); Fe1-N1-C1 159.8(3), N1-C1-O1 177.0(4).

Spectroscopic characterization of $[L^{Mes}Fe(NCO)(CO)_2]$ reveals that the solid-state structure is maintained in solution. Eleven resonances with appropriate integration for C_s symmetry are observed in the ^1H NMR spectrum, while two ν_{CO} bands (2036 cm^{-1} and 1983 cm^{-1}) and a single $\nu_{N=C=O}$ band (2223 cm^{-1}) are observed in the IR spectrum.

It is likely that complete nitrogen atom transfer from $[L^{Mes}Fe{\equiv}N]$ to $C{\equiv}NtBu$ is facilitated by the topology of the tris(carbene)borate ligand; that is, the planar mesityl substituents make the $[Fe{\equiv}N]$ unit accessible to incoming substrates. In support of this idea, the bulkier iron nitrido complex $[L^{tBu}Fe{\equiv}N]$ reacts with $C{\equiv}NtBu$ to yield the four-coordinate iron complex $[L^{tBu}Fe\text{-}N{=}C{=}NtBu]$, even in the presence of excess $C{\equiv}NtBu$ (Figure 3). A notable feature of the solid state structure is the Fe1–N41 bond length (1.936(3) Å), which is substantially longer than the corresponding bond in $[L^{tBu}Fe{\equiv}N]$ (1.512(1) Å)[13] and is consistent with incomplete two electron nitrogen atom transfer from

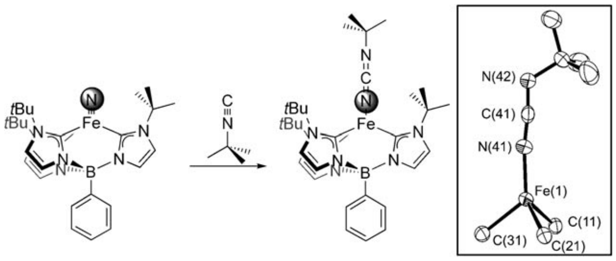
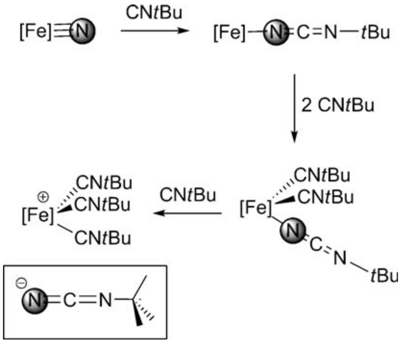


Figure 3. Synthesis of $L^{tBu}Fe\text{-}N{=}C{=}NtBu$. Inset: X-ray crystal structure. Ellipsoids set at 50% probability; hydrogen atoms and most of the tris(carbene)borate ligand omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–N41 1.936(3), N41–C41 1.186(4), C41–N42 1.242(5); C41-N41-Fe1 169.8(3), N41-C41-N42 173.7(3).

iron to $\mathrm{C{\equiv}N}t\mathrm{Bu}$. This bond length is similar to that observed in other iron(II) carbodiimido complexes.[17]

The ^{1}H NMR spectrum of $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{Fe{-}N{=}C{=}N}t\mathrm{Bu}]$ shows seven paramagnetically shifted resonances with appropriate integration ratios for a threefold-symmetric complex. The magnetic moment of this complex, as determined by the Evans method ($\mu_{\mathrm{eff}} = 4.8(3)\ \mu_{\mathrm{B}}$), is consistent with a high-spin $S = 2$ iron(II) center. A strong absorption band at 2115 cm^{-1} in the IR spectrum is assigned to the $\nu_{\mathrm{N{=}C{=}N}}$ stretching frequency, which is similar to other *tert*-butylcarbodiimido ligands.[18] In an analogous reaction, $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{Fe{\equiv}N}]$ also undergoes nitrogen atom transfer to CO, providing the high spin isocyanate complex $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{Fe{-}NCO}]$ ($\nu_{\mathrm{N{=}C{=}O}} = 2194\ \mathrm{cm}^{-1}$).

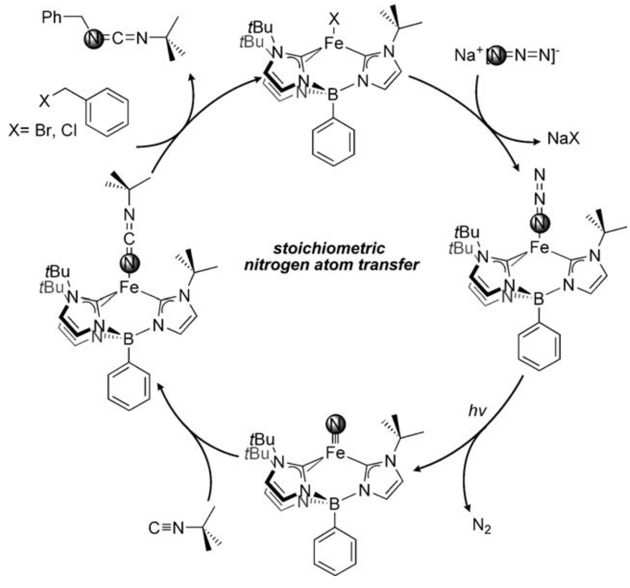
Mechanistically, these new complexes provide snapshots of the reaction pathway leading to complete nitrogen atom transfer from $[\mathrm{L}^{\mathrm{Mes}}\mathrm{Fe{\equiv}N}]$ to $\mathrm{C{\equiv}N}t\mathrm{Bu}$ (Scheme 2).[19] Thus, initial reaction of $[\mathrm{L}^{\mathrm{Mes}}\mathrm{Fe{\equiv}N}]$ with $\mathrm{C{\equiv}N}t\mathrm{Bu}$ leads to the four-coordinate iron(II) carbodiimido complex $[\mathrm{L}^{\mathrm{Mes}}\mathrm{Fe{-}N{=}C{=}N}t\mathrm{Bu}]$ that reacts with two additional $\mathrm{C{\equiv}N}t\mathrm{Bu}$ ligands to provide six-coordinate $[\mathrm{L}^{\mathrm{Mes}}\mathrm{Fe(N{=}C{=}N}t\mathrm{Bu)(CN}t\mathrm{Bu)_2}]$. Substitution of the carbodiimido ligand by $\mathrm{C{\equiv}N}t\mathrm{Bu}$ results in the final product $[\mathrm{L}^{\mathrm{Mes}}\mathrm{Fe(CN}t\mathrm{Bu)_3}]^{+}[\mathrm{N{=}C{=}N}t\mathrm{Bu}]^{-}$. Further support for this proposed pathway comes from the reaction of $[\mathrm{L}^{\mathrm{Mes}}\mathrm{FeCl}]$[20] with excess $\mathrm{C{\equiv}N}t\mathrm{Bu}$, which affords the spectroscopically characterized complex $[\mathrm{L}^{\mathrm{Mes}}\mathrm{Fe(CN}t\mathrm{Bu)_3}]^{+}\mathrm{Cl}^{-}$.



Scheme 2. Snapshots of a complete nitrogen atom transfer reaction.

Despite the fact that nitrogen atom transfer from $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{Fe{\equiv}N}]$ to $\mathrm{C{\equiv}N}t\mathrm{Bu}$ is not complete, this nitrido complex nevertheless serves as an intermediate in a nitrogen atom transfer cycle. We have found that the product of the nitrogen atom transfer reaction, $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{Fe{-}N{=}C{=}N}t\mathrm{Bu}]$, is reactive in a carbodiimido group transfer reaction that leads to complete nitrogen atom transfer. Thus, heating a solution of $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{Fe{-}N{=}C{=}N}t\mathrm{Bu}]$ and excess benzylbromide at 60 °C results in the formation of $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{FeBr}]$, along with *N*-benzyl-*N′*-*tert*-butylcarbodiimide (60 % yield, as determined by ^{1}H NMR and LC/MS).[21] A similar group-transfer reaction occurs with benzylchloride, providing $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{FeCl}]$[13] as the iron-containing product, but this reaction is substantially slower. Since the iron halide products resulting from the group-transfer reactions are starting materials for $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{Fe{\equiv}N}]$,[13] the group-transfer reaction closes a cycle for nitrogen atom transfer (Scheme 3).

In summary, the terminal iron nitrido complexes $[\mathrm{L}^{\mathrm{Mes}}\mathrm{Fe{\equiv}N}]$ and $[\mathrm{L}^{t\mathrm{Bu}}\mathrm{Fe{\equiv}N}]$ undergo nitrogen atom transfer reactions with CO and $\mathrm{C{\equiv}N}t\mathrm{Bu}$, leading to the formation of new N–C bonds. The topology of the supporting ligand allows for precise control over the extent of nitrogen atom transfer. Furthermore, coupling a group-transfer reaction with incomplete nitrogen atom transfer allows the nitrido ligand to be regenerated and a nitrogen atom transfer cycle to be completed. This cycle provides an alternate pathway for the synthesis of unsymmetrical carbodiimides.[22]



Scheme 3. A stoichiometric cycle for nitrogen atom transfer that uses $\mathrm{N_3}^{-}$ to generate an unsymmetrical carbodiimide.

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