Nitrogen Fixation

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# Low-Temperature $N_2$ Binding to Two-Coordinate $L_2Fe^0$ Enables Reductive Trapping of $L_2FeN_2^-$ and $NH_3$ Generation**

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**Abstract:** *The two-coordinate [(CAAC)$_2$Fe] complex [CAAC = cyclic (alkyl)(amino)carbene] binds dinitrogen at low temperature (T < −80°C). The resulting putative three-coordinate $N_2$ complex, [(CAAC)$_2$Fe($N_2$)], was trapped by one-electron reduction to its corresponding anion [(CAAC)$_2$Fe$N_2$]$^-$ at low temperature. This complex was structurally characterized and features an activated dinitrogen unit which can be silylated at the β-nitrogen atom. The redox-linked complexes [(CAAC)$_2$Fe$^I$][BAr$^F_4$], [(CAAC)$_2$Fe$^0$], and [(CAAC)$_2$Fe$^{-I}$$N_2$]$^-$ were all found to be active for the reduction of dinitrogen to ammonia upon treatment with $KC_8$ and HBAr$^F_4$·2 $Et_2O$ at −95°C [up to (3.4 ± 1.0) equivalents of ammonia per Fe center]. The $N_2$ reduction activity is highly temperature dependent, with significant $N_2$ reduction to $NH_3$ only occurring below −78°C. This reactivity profile tracks with the low temperatures needed for $N_2$ binding and an otherwise unavailable electron-transfer step to generate reactive [(CAAC)$_2$Fe$N_2$]$^-$.*

While hundreds of transition metal/$N_2$ complexes have been prepared and studied,[1] comparatively few systems afford access to productive $N_2$ functionalization.[2] This is particularly true for the case of $N_2$ functionalization by protons and electrons to produce $NH_3$ (or $N_2H_4$). Building on extensive early molybdenum and tungsten model work,[3] Yandulov and Schrock[4] and Nishibayashi and co-workers[5] have reported molybdenum-containing coordination complexes (**A** and **B**; Figure 1) which facilitate catalytic $N_2$ reduction to $NH_3$ in the presence of suitable acids and reductants. Because iron is 1) the only transition metal known to be essential to enzymatic nitrogenase function,[6] and 2) the predominant transition-metal catalyst used in the Haber–Bosch ammonia synthesis,[7] studying $N_2$ reduction chemistry for well-defined iron model complexes is of interest.[8,9] Recently, our lab demonstrated that iron coordination complexes (**C**) are capable of modest catalytic $N_2$ reduction to $NH_3$.[10]

The functional Fe−$N_2$ reduction systems we have studied to date are phosphine-supported, five-coordinate $XL_3$Fe-$N_2$ adducts. It is of interest to explore whether other donor ligands and geometries might expose similar reactivity patterns for Fe−$N_2$ species.[11,12] For example, Holland and co-workers recently reported a solution characterization of a three-coordinate iron complex with an $N_2$ ligand linearly bridged between iron and a solvated magnesium cation (**D**; Figure 1).[13,14] The $N_2$ ligand in this complex is highly activated. However, only trace amounts of $NH_3$ (< 2% per Fe) could be detected upon attempts to mediate its reductive protonation. Related low-coordinate Fe−$N_2$ species can undergo reductive $N_2$ cleavage and, when followed by a separate acidic work-up, can achieve higher ammonia yields (ca. 35% overall).[8c] Understanding subtle factors that lead to productive reactivity at $N_2$ is essential to improving molecular nitrogen fixation catalysts.

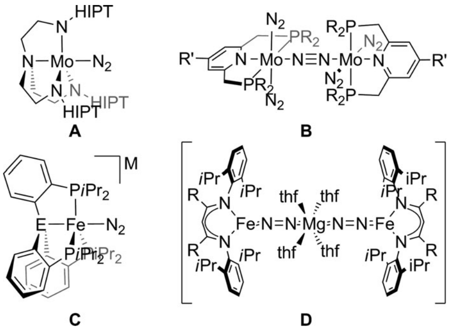

*Figure 1.* Representative molybdenum and iron complexes studied for catalytic $N_2$ reduction to $NH_3$. E = B, C; M = K, Na; R = *t*Bu; R′ = H, OMe. HIPT = hexaisopropylterphenyl.

We recently reported the utilization of a π-accepting cyclic (alkyl)(amino)carbene (CAAC)[15] to synthesize a structurally unusual two-coordinate, formally [$L_2Fe^0$] complex by reduction of its corresponding two-coordinate iron(I) cation.[16] We reasoned that the polarizability of the CAAC ligand, by comparison to typical N-heterocyclic carbenes (NHCs),[17] might better facilitate $N_2$ binding and productive functionalization. Note that low-valent iron/carbene complexes[18] have, to date, been surprisingly resistant to $N_2$ binding, with the tripodal NHC-containing systems reported by the groups of Meyer[19] and Smith[20] underscoring this point. To our knowledge, a bis(imidazol-2-ylidene)pyridine scaffold is the only iron/carbene derivative where $N_2$ binding has been established.[21] Here we show that the two-coordinate [(CAAC)$_2$Fe] complex binds $N_2$, but only at low temperature, and that this binding event exposes an otherwise unavailable one-electron reduction step to form three-coordinate [(CAAC)$_2$Fe($N_2$)]$^-$ and desirable reactivity at the coordinated $N_2$.

Under an atmosphere of $N_2$, a solution of [(CAAC)$_2$Fe] in pentane exhibited drastic changes in the absorption spectrum

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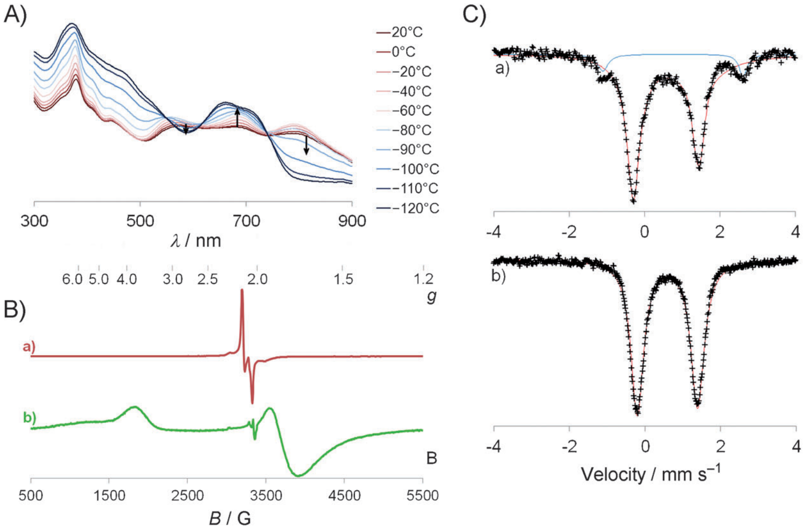
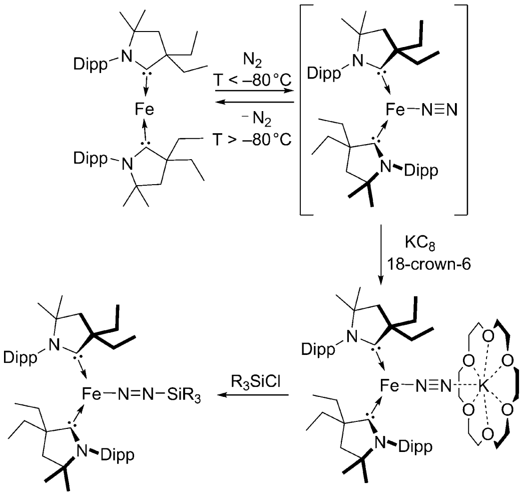


***Figure 2.*** A) Variable-temperature UV/Vis spectra of [(CAAC)$_2$Fe] in a pentane solution under N$_2$. B) X-Band EPR spectra at 10 K: a) [(CAAC)$_2$Fe(N$_2$)][K(18-crown-6)] in a frozen Et$_2$O glass; b) [(CAAC)$_2$Fe(N$_2$SiEt$_3$)] in a frozen methylcyclohexane glass. C) $^{57}$Fe Mössbauer spectra for microcrystalline samples obtained at 80 K in boron nitride pellets. a) [(CAAC)$_2$Fe(N$_2$)][K(18-crown-6)]; b) (CAAC)$_2$Fe(N$_2$SiEt$_3$). The solid red line corresponds to the simulated data. The solid blue line in (a) corresponds to a minor species (ca. 9% of Fe); parameters of $\delta = 0.74$ mm s$^{-1}$ and $\Delta E_Q = 3.79$ mm s$^{-1}$. D) Structure of [(CAAC)$_2$Fe(N$_2$)][K(18-crown-6)] in the solid state. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.[23] Selected bond lengths [Å] and angles [°]: C1–Fe1 1.924(2), C2–Fe1 1.919(2), C1–N1 1.386(3), C2–N2 1.411(3), Fe1–N3 1.778(3), N3–N4 1.035(4), N4–K1 2.726(4); C1-Fe1-C2 140.81(10), C1-Fe1-N3 101.91(11), C2-Fe1-N3 117.08(11), Fe1-N3-N4 175.5(3).

upon cooling to temperatures below −80 °C (Figure 2 A). This temperature-dependent change in the optical profile of [(CAAC)$_2$Fe] under N$_2$ was reversible over several cooling-warming cycles. To confirm that the change in the optical spectrum was indeed related to the presence of N$_2$, the solution was thoroughly degassed by five freeze-pump-thaw cycles and variable-temperature UV/Vis spectra were re-collected (see Figure S7 in the Supporting Information). In this case, the standard spectrum of [(CAAC)$_2$Fe] was recovered. Re-exposing the solution to N$_2$ resulted in the previously observed temperature-dependent profile. Thermodynamic parameters were extracted from a van't Hoff plot of the experimental data (see the Supporting Information). As expected, binding of dinitrogen is exothermic ($\Delta H = -22.1$ kcal mol$^{-1}$) and is associated with negative entropy ($\Delta S = -8.1$ cal K$^{-1}$ mol$^{-1}$). These parameters are similar to those recently reported for N$_2$ coordination at cobalt.[22] The N$_2$ binding constant at room temperature is very low ($K_{eq} = 0.2$) and consistent with our initial report of a two-coordinate [(CAAC)$_2$Fe] complex.[16]



***Scheme 1.*** Reduction of [(CAAC)$_2$Fe] and subsequent trapping with silylating reagents. R = Me, Et. Dipp = 2,6-diisopropylphenyl.

To structurally confirm the binding of dinitrogen at low temperature, we sought to trap the putative complex [(CAAC)$_2$Fe(N$_2$)] (Scheme 1). The presence of an additional π-accepting ligand (N$_2$) facilitates the further reduction of [(CAAC)$_2$Fe$^0$] to a formal Fe$^{-I}$. Hence, reduction of [(CAAC)$_2$Fe] with KC$_8$ at −95 °C in diethyl ether in the presence of 18-crown-6 yielded, after work-up, dark brown crystals of [(CAAC)$_2$Fe(N$_2$)][K(18-crown-6)] in moderate yield (42 %). Temperature control was crucial: reduction at room temperature resulted instead in decomposition of the starting material to intractable products, and at −78 °C, only traces of [(CAAC)$_2$Fe(N$_2$)]$^-$ could be detected by IR spectroscopy. An XRD study of crystals of [(CAAC)$_2$Fe(N$_2$)][K(18-crown-6)] confirmed the binding of N$_2$ to a three-coordinate iron center in an end-on fashion with an additional ion-pair of the β-nitrogen atom to the K(18-crown-6) cation (Figure 2 D).

The structure of [(CAAC)$_2$Fe(N$_2$)][K(18-crown-6)] reveals a distorted trigonal-planar iron center ($\Sigma_{angle} = 359.8°$), with a very wide C-Fe-C angle [140.81(10)°]. The C−N distances of the CAAC ligand are substantially elongated: they are 1.386(3) and 1.411(3) Å, compared with 1.315(3) Å for the free ligand.[15c] This C−N lengthening is indicative of a substantial amount of spin leakage from the highly reduced iron center to the supporting CAAC ligand.[16] Complex [(CAAC)$_2$Fe(N$_2$)][K(18-crown-6)] represents a rare example of a structurally characterized pseudoterminally bonded, three-coordinate Fe$-$N$_2$ complex.[13,14]

A sharp band was observed in the IR spectrum of [(CAAC)$_2$Fe(N$_2$)][K(18-crown-6)] at 1850 cm$^{-1}$ (ATR-IR; thin film), and attributed to the $\nu_{NN}$ stretch. This value is higher in energy than the transiently observed [{β-diketimidatoFe(N$_2$)}$_2$Mg(thf)$_4$] species reported by Holland and co-workers (1818 cm$^{-1}$),[13] but lower than other anionic terminal Fe$-$N$_2$ complexes where the iron center resides in higher coordination numbers (1905–1927 cm$^{-1}$).[9,10a] As expected for a formal Fe$^{-1}$ species, a room temperature solution magnetic moment for [(CAAC)$_2$Fe(N$_2$)][K(18-crown-6)] of 1.9 $\mu_B$ in C$_6$D$_6$ was measured, and is consistent with its frozen glass (Et$_2$O) EPR spectrum (Figure 2B,a) and indicative of an $S = 1/2$ ground state.

Exposure of [(CAAC)$_2$Fe(N$_2$)][K(18-crown-6)] to trimethylsilylchloride in diethyl ether resulted in a rapid color change from dark brown-red to dark green. A diagnostic broad band at 1675 cm$^{-1}$ was observed in the IR spectrum of the crude reaction mixture, and is reminiscent of previously observed $\nu_{NN}$ stretches for iron/silyldiazenido complexes.[9,10a] The presumed diazenido product [(CAAC)$_2$Fe(N$_2$SiMe$_3$)] rapidly decomposed to the [(CAAC)$_2$Fe] complex upon attempted work-up. A bulkier silylating reagent led to a more stable product. Hence, a similar change of color from dark brown-red to dark green was observed when triethylsilylchloride was added to the [(CAAC)$_2$Fe(N$_2$)][K(18-crown-6)] complex (Scheme 1). The diazenido product, [(CAAC)$_2$Fe(N$_2$SiEt$_3$)] was isolated as an analytically pure, dark-green solid in moderate yield (52 %). Its IR spectrum exhibits a broad band at 1690 cm$^{-1}$. The complex [(CAAC)$_2$Fe(N$_2$SiEt$_3$)] is high-spin with $S = 3/2$ (room temperature solution magnetic moment of 3.9 $\mu_B$), and consistent with its frozen glass EPR spectrum at 10 K showing broad signals at low field (Figure 2B,b). Its electronic structure is therefore distinct from previously characterized five-coordinate [XL$_3$Fe(N$_2$SiR$_3$)] species which are low spin. For instance, (TP$^{iPr}$B)Fe(N$_2$SiMe$_3$) is an $S = 1/2$ species.[9b]

The $^{57}$Fe Mössbauer spectra of [(CAAC)$_2$Fe(N$_2$)][K(18-crown-6)] and [(CAAC)$_2$Fe(N$_2$SiEt$_3$)] were recorded at 80 K in the solid state (Figure 2C) and fits to the data provided isomer shifts at $\delta = 0.56$ and $\delta = 0.59$ mm s$^{-1}$, respectively, with corresponding quadrupole splittings of $\Delta E_Q = 1.67$ and $\Delta E_Q = 1.60$ mm s$^{-1}$. The isomer-shift value is in line with previously reported three-coordinate bis(carbene) iron complexes.[16,24] For example, [(CAAC)$_2$FeCl] has an isomer shift of 0.52 mm s$^{-1}$. The spectrum of [(CAAC)$_2$Fe(N$_2$)][K(18-crown-6)] displays an asymmetrical doublet presumably caused by anisotropy in the polycrystalline sample.[25] A minor component (ca. 9 % of the total iron content), whose parameters fit the oxidation product [(CAAC)$_2$Fe]$^+$,[16] was also detected (Figure 2C,a).

In previous studies of five-coordinate Fe$-$N$_2$ species, we have empirically determined that the ability to successfully silylate the β-nitrogen atom of an Fe$-$N$_2$ derivative can translate to efficacy of the system towards reductive protonation.[9c,10] Attempts to fix N$_2$ to NH$_3$ at room temperature using [(CAAC)$_2$Fe] in the presence of excess KC$_8$ and HBAr$^F_4$·2 Et$_2$O in diethyl ether, regardless of the order of addition, proved largely ineffective (Table 1; see Figure S12). This observation is consistent with a very limited degree of N$_2$ binding to [(CAAC)$_2$Fe] at room temperature, and the requirement that a [(CAAC)$_2$Fe(N$_2$)] species be present to facilitate N$_2$ fixation. Indeed, when [(CAAC)$_2$Fe] was treated at −95 °C with an excess of KC$_8$ (50 equiv), followed by an excess of HBAr$^F_4$·2 Et$_2$O (50 equiv), the formation of (3.3 ± 1.1) equivalents of NH$_3$ per iron center was observed. Similar yields [(3.4 ± 1.0) equiv] were obtained by employing the two-coordinate iron(I) cation [(CAAC)$_2$Fe][BAr$^F_4$] under the same conditions at −95 °C. The enhancement of the N$_2$-to-NH$_3$ reduction yield at very low temperature correlates with the variable-temperature optical data for [(CAAC)$_2$Fe], which shows that N$_2$ binding to [(CAAC)$_2$Fe] becomes favorable only at low temperature. Indeed, the yield of NH$_3$ is negligible at −50 °C (0.3 equiv) and is still quite low at −78 °C (0.9 equiv). Note that significantly lower temperature (−113 °C) was examined but did not improve the NH$_3$ yield beyond that obtained at −95 °C.

***Table 1:*** Catalytic reduction of N$_2$ to NH$_3$.[a]

$$N_2 + KC_8 + HBAr^F{}_{24}\cdot 2\,Et_2O \xrightarrow[Et_2O]{cat.} NH_3$$

| Run | Catalyst | $T$ [°C] | Equiv NH$_3$ per Fe |
|---|---|---|---|
| 1 | [(CAAC)$_2$Fe] | −113 | 3.0 ± 0.7 |
| 2 | [(CAAC)$_2$Fe] | −95 | 3.3 ± 1.1 |
| 3 | [(CAAC)$_2$Fe] | −78 | 0.9 ± 0.3[b] |
| 4 | [(CAAC)$_2$Fe] | −50 | 0.3 ± 0.2[b] |
| 5 | [(CAAC)$_2$Fe] | 23 | 0.4 ± 0.2[b] |
| 6 | [(CAAC)$_2$Fe][BAr$^F_4$] | −95 | 3.4 ± 1.0 |
| 7 | [(CAAC)$_2$FeN$_2$][K(18-c-6)] | −95 | 2.6 ± 0.6 |
| 8 | CAAC[c] | −95 | < 0.1 |
| 9 | none | −95 | < 0.1 |

[a] Catalytic conditions: catalyst (0.002 mmol), KC$_8$ (0.1 mmol), HBAr$^F_4$·2 Et$_2$O (0.1 mmol), Et$_2$O, 45 min. Yields are an average of 8 independent runs and were determined by the indophenol method (See the Supporting Information). [b] Average of 4 runs. [c] 0.004 mmol of CAAC used.

Although these NH$_3$ yields are low compared with our two previously reported iron catalysts,[10] Schrock's original molybdenum system,[4] and especially Nishibayashi's recently improved molybdenum system,[5a] [(CAAC)$_2$Fe] is nevertheless a very modest catalyst for nitrogen fixation to ammonia and the yields of NH$_3$ per iron equivalent reported here are far greater than those which have been observed for previously studied three-coordinate Fe$-$N$_2$ complexes (< 0.2 equiv per Fe), including [{β-diketimidatoFe(N$_2$)}$_2$Mg(thf)$_4$] species (Figure 1).[13] We speculate that the ability of [(CAAC)$_2$Fe]/[(CAAC)$_2$Fe(N$_2$)] to perform nitrogen fixation may arise from the relative flexibility of the system, which is capable of switching between two- and three-coordinate geometries, and allows the formation of highly covalent Fe$-$N$_x$ multiple-bond interactions. The recent isolation of a three-coordinate iron/bis(imide) complex supported by CAAC by Deng and co-workers is noted in the latter context.[26]

For comparison, we also explored [(CAAC)$_2$Fe] in the context of catalytic N$_2$ silylation. Catalytic silylation reactions of $N_2$ under strongly reducing conditions have been known for many years using metals such as chromium,[27] titanium,[28] and molybdenum,[29] and recently, such silylations were extended to systems using iron precatalysts including $[Fe(CO)_5]$ and $[Cp_2Fe]$.[30] For example, $[Fe(CO)_5]$ was shown to produce up to 25 equivalents of $N(SiMe_3)_3$ per iron in the presence of a vast excess sodium metal and TMSCl at room temperature.[30] These silylation reactions remain mechanistically ill-defined. Only trace yield of $N(SiMe_3)_3$ could be detected using Nishibayashi's conditions (Na as reductant, in THF)[30] with $[(CAAC)_2Fe]$ as precatalyst. However, when a catalytic amount of $[(CAAC)_2Fe]$ was instead treated with a large excess of $KC_8$ (600 equiv) and trimethylsilylchloride (600 equiv), the formation of $(24.4 \pm 2.7)$ equivalents of $N(SiMe_3)_3$ was observed (see Table S1). Slightly lower TONs $(19.4 \pm 3.0)$ were obtained using $[(CAAC)_2Fe][BAr^F_4]$ as a precatalyst instead. The catalytic activity was significantly reduced $(7.0 \pm 1.0)$ when the reaction was performed at $-78\,°C$. The attenuation in $N(SiMe_3)_3$ product is presumably related to slower generation of trimethylsilyl radical at low temperature.

Although it is presently unclear what the mechanistic requirements are for the $N_2$ to $N(SiMe_3)_3$ catalysis mediated by various iron precursors, including $[(CAAC)_2Fe]$, the $N_2$ to $NH_3$ chemistry described herein appears to require a well-defined molecular Fe−$N_2$ species. Indeed, significant $N_2$ to $NH_3$ conversion is observed only at the low temperatures where $N_2$ binds $[(CAAC)_2Fe]$ sufficiently favorably. The low-temperature $N_2$ binding event facilitates subsequent electron transfer as evidenced by the very low temperature required to synthetically reduce $[(CAAC)_2Fe(N_2)]$ and isolate highly reactive $[(CAAC)_2Fe(N_2)]^-$.

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