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Bis(imino)pyridine Ligand Deprotonation Promoted by a Transient Iron Amide

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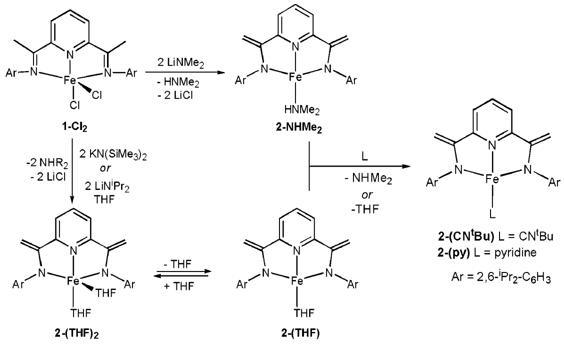
Addition of 2 equiv of $LiNMe_2$ to the bis(imino)pyridine ferrous dichloride, $(^{iPr}PDI)FeCl_2$ ($^{iPr}PDI = (2,6\text{-}^iPr_2–C_6H_3N═CMe)_2C_5H_3N$), resulted in deprotonation of the chelate methyl groups, yielding the bis(enamide)pyridine iron dimethylamine adduct, $(^{iPr}PDEA)Fe(NHMe_2)$ ($^{iPr}PDEA = (2,6\text{-}^iPr_2–C_6H_3NC═CH_2)_2C_5H_3N$). Performing a similar procedure with $KN(SiMe_3)_2$ in THF solution afforded the corresponding bis(THF) adduct, $(^{iPr}PDEA)Fe(THF)_2$. $(^{iPr}PDEA)Fe(NHMe_2)$ has also been prepared by addition of the free amine to the iron dialkyl complex, $(^{iPr}PDI)Fe(CH_2SiMe_3)_2$, implicating formation of a transient iron amide that is sufficiently basic to deprotonate the bis(imino)pyridine methyl groups. Deprotonation of the amine ligand in $(^{iPr}PDEA)Fe(NHMe_2)$ has been accomplished by addition of amide bases to afford the ferrous amide-ate complexes, $[(^{iPr}PDEA)Fe(\mu\text{-}NMe_2)M]$ (M = Li, K).

Bis(imino)pyridine complexes of iron(II) are of interest given their high productivities for ethylene and α-olefin polymerization upon activation with methylalumoxane (MAO).[1] While extensively studied,[2−4] little is known about the role of MAO in the activation process, and hence, key details such as the oxidation state of the propagating iron species remain speculative. The recent synthesis of bis(imino)pyridine iron(II) dialkyl complexes[5−7] and the corresponding alkyl cations has established the catalytic competency of iron(II).[8] As part of our continuing investigations with iron complexes for catalytic bond-forming reactions,[9,10] we are exploring alternative synthetic routes to iron dialkyls and ultimately the resulting alkyl cations.

Scheme 1



On the basis of observations from early transition metal chemistry,[11] we targeted the synthesis of iron amide complexes with the goal of treating these compounds with alkyl aluminums to furnish the desired iron dialkyls. Addition of 2 equiv of $LiNMe_2$ to a diethyl ether slurry of $(^{iPr}PDI)FeCl_2$ (**$1\text{-}Cl_2$**; $^{iPr}PDI = (^iPr_2{-}C_6H_3N{═}CMe)_2C_5H_3N$) followed by filtration and recrystallization from ether at −35 °C yielded a red-brown solid identified as $(^{iPr}PDEA)Fe(NHMe_2)$ (**$2\text{-}NHMe_2$**; $^{iPr}PDEA = (2,6\text{-}^iPr_2{-}C_6H_3NC{═}CH_2)_2C_5H_3N$), arising from deprotonation of the two bis(imino)pyridine methyl groups rather than amidation (Scheme 1).

The benzene-d_6 ^1H NMR spectrum of **$2\text{-}NHMe_2$** exhibits nine paramagnetically broadened and shifted resonances over

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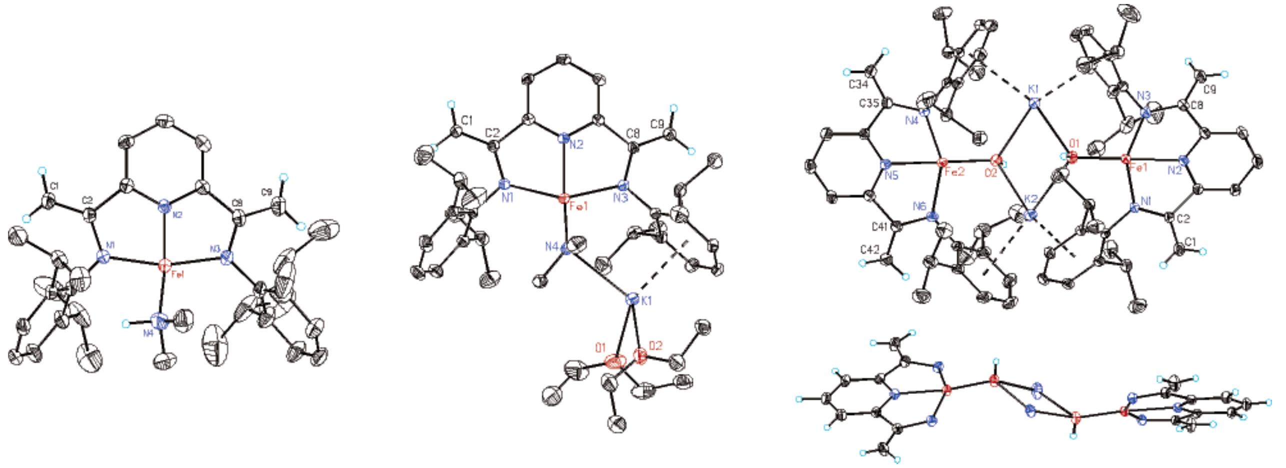

Figure 1. ORTEP represenations of **2-NHMe$_2$**, **2-NMe$_2$K**, and **2-OHK**. Hydrogen atoms except for those attached to the methylene backbone carbons, the dimethylamine ligand in **2-NHMe$_2$**, and the hydroxy ligand in **2-OHK** are omitted for clarity. Included is a side-view of **2-OHK** (bottom right) revealing the geometry of the [Fe(OH)]$_2$[μ-K]$_2$ framework.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **2-NHMe$_2$**, **2-NMe$_2$K**, and **2-OHK**

	2-NHMe$_2$	**2-NMe$_2$K**	**2-OHK**
Fe(1)−X[a]	2.040(3)	1.9773(16)	1.9347(17)
Fe(1)−N(1)	1.931(3)	2.0746(15)	2.0035(19)
Fe(1)−N(2)	1.906(2)	2.1113(14)	2.0900(18)
Fe(1)−N(3)	1.944(3)	2.0780(15)	2.0162(17)
Fe(1)−O(5)			1.9333(18)
Fe(1)−N(4)			2.0252(18)
Fe(1)−N(5)			2.0683(19)
Fe(1)−N(6)			2.0366(18)
N(1)−C(2)	1.386(4)	1.370(2)	1.371(3)
N(3)−C(8)	1.378(4)	1.380(2)	1.360(3)
N(4)−C(35)			1.375(3)
N(6)−C(41)			1.379(3)
C(1)−C(2)	1.350(5)	1.355(3)	1.335(4)
C(8)−C(9)	1.345(5)	1.346(3)	1.340(4)
C(34)−C(35)			1.333(4)
C(41)−C(42)			1.336(4)
X−Fe(1)−N(2)[a]	164.32(14)	165.05(6)	175.56(8)
N(1)−Fe(1)−N(3)	161.88(11)	148.18(6)	150.77(7)
O(5)−Fe(1)−N(5)			172.40(8)
N(4)−Fe(1)−N(6)			151.22(8)

[a] For **2-NHMe$_2$** and **2-NMe$_2$K**: X = N(4); for **2-OHK**: X = O(1).

a 170 ppm chemical shift range, consistent with a C_{2v}-symmetric ligand environment. Notably, two singlets are observed at −58.9 and −39.4 ppm for the methylene protons on the tridentate ligand backbone, indicating their coplanarity with the chelate. Although not located in the ^{1}H NMR spectrum, an N−H stretch was observed at 3258 cm^{-1} in the solid-state (KBr) infrared spectrum, confirming a neutral NHMe$_2$ ligand.

Slow evaporation of a diethyl ether solution of **2-NHMe$_2$** produced single crystals suitable for X-ray diffraction. A representation of the molecular structure is presented in Figure 1, while selected metrical parameters are reported in Table 1. The data were of sufficient quality such that all of the hydrogen atoms were located and refined, reaffirming the presence of a neutral dimethylamine ligand and methylene carbons at C(1) and C(9). The C(1)−C(2) and C(8)−C(9) bond distances of 1.350(5) and 1.345(5) Å are in the range expected for a C═C bond, while the C−N bond lengths of 1.386(4) and 1.378(4) Å are elongated from the value typically encountered in bis(imino)pyridine ligands (~1.30 Å).[1,5]

Performing the deprotonation of **1-Cl$_2$** in THF with larger amide bases such as KN(SiMe$_3$)$_2$ or LiN^{i}Pr$_2$ furnished the bis-THF compound, (^{iPr}PDEA)Fe(THF)$_2$ (**2-(THF)$_2$**) as a green-brown solid (Scheme 1). Exposure of **2-(THF)$_2$** to vacuum, either in solution or the solid state, yielded **2-(THF)** arising from THF loss. Substitution of the amine or THF ligands in **2-NHMe$_2$** and **2-(THF)$_2$** has been accomplished by addition of more potent ligands. Treatment of either compound with pyridine resulted in isolation of a brown solid identified as **2-(py)** while addition of ^{t}BuNC formed **2-(CN^{t}Bu)** (Scheme 1). All of these compounds have similar spectroscopic features to **2-NHMe$_2$**, although **2-(CN^{t}Bu)** has only been observed in solution as formation of an unidentified brown precipitate occurred over time.

Each adduct prepared in this study is paramagnetic. For the complex containing the strongest-field ligand, **2-(CN^{t}Bu)**, a magnetic moment (Evans method, C$_6$D$_6$, 23 °C) of 2.9 μB was measured, consistent with the spin-only value for two unpaired electrons and an intermediate-spin iron(II) center. Weaker-field ligands such as THF yielded a high-spin complex with a μ_{eff} of 4.7 μB. A solution and solid-state magnetic moment of 3.6 μB was repeatedly (nine independent trials) measured for **2-NHMe$_2$**, suggesting an admixture of high- and intermediate-spin complexes at 23 °C.

It is now well-documented that bis(imino)pyridine chelates are "non-innocent" ligands, participating in redox processes with the metal[9,12] or reaction chemistry including alkylation at the pyridine[6,13] or imine positions[14] and C−C dimeriza-

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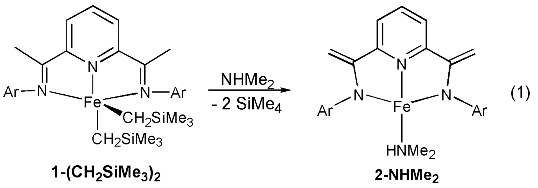
tion.[15] Deprotonation of the methyl positions in the chelate backbone has also been previously observed during low-temperature alkylation of **1-Cl$_2$** with LiCH$_2$SiMe$_3$,[6] in related manganese chemistry,[13b] and upon treatment of the free ligand with alkyllithium bases[16] and alkali metal reductants.[17]

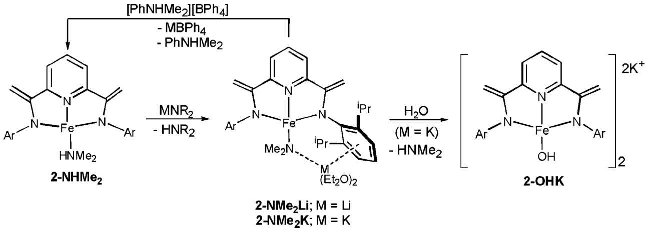
To gain insight into the ligand-deprotonation reaction with amide bases, additional experiments were conducted. Addition of 1 equiv of NHMe$_2$ to **1-(CH$_2$SiMe$_3$)$_2$**[5] resulted in clean conversion to **2-NHMe$_2$** along with liberation of SiMe$_4$ (eq 1). Formation of **2-NHMe$_2$** by this procedure is much slower than the corresponding salt metathesis reaction. The analogous experiment with NDMe$_2$ again formed **2-NHMe$_2$** along with deuterated SiMe$_4$. These observations suggest that the base in these reactions is a transient ferrous amide complex, either ($^{i\mathrm{Pr}}$PDI)Fe(NMe$_2$)(CH$_2$SiMe$_3$) or ($^{i\mathrm{Pr}}$PDI)Fe(NMe$_2$)$_2$, that promotes the ligand deprotonation, either intramolecularly by imine dissociation and bond rotation or through a bimolecular process. Precedent for such chemistry has been provided by Group 8 amide complexes, such as (dmpe)$_2$M(NH$_2$)H (M = Fe, Ru; dmpe = 1,2-bis(dimethylphosphino)ethane), which are known to deprotonate weak carbon acids such as fluorene.[18]



(1)

Treatment of **2-NHMe$_2$** with additional KN(SiMe$_3$)$_2$ or LiNMe$_2$ resulted in formation of the ferrous amide-ate complexes, [($^{i\mathrm{Pr}}$PDEA)Fe(μ-NMe$_2$)M] (**2-NMe$_2$K**; M = K; **2-NMe$_2$Li**; M = Li) (Scheme 2). Interestingly, **2-NMe$_2$Li** was also prepared from treatment of **1-(CH$_2$SiMe$_3$)$_2$** with 1 equiv of LiNMe$_2$. The potassium derivative, **2-NMe$_2$K**, has been characterized by X-ray diffraction (Figure 1) and reveals an essentially square planar iron center with a dimethylamide ligand occupying one of the coordination sites. Both the olefinic and C−N bond distances (Table 1) are comparable to those found in **2-NHMe$_2$**, confirming a doubly deprotonated tridentate ligand. The Fe(1)−N(4) bond distance of 1.9773(16) Å is contracted from the value of 2.040(3) Å found in the neutral precursor. The potassium cation is ligated by two molecules of diethyl ether and is also coordinated to the amide nitrogen and to one of the aryl groups of the tridentate chelate.

Scheme 2



In benzene-d_6 solution, both **2-NMe$_2$M** complexes exhibit the number of resonances for C_{2v}-symmetric compounds along with free diethyl ether, suggesting dissociation of the cation. It should be noted that a symmetric dimeric structure (vide infra), while unlikely, has not been ruled out. The solution magnetic moment of 4.3 μB measured for **2-NMe$_2$K** is consistent with high-spin iron(II).

The protonation of the iron amide-ate complexes was also studied. Addition of an acid with a weakly coordinating conjugate base, [PhNHMe$_2$][BPh$_4$], to **2-NMe$_2$K** cleanly and quantitatively regenerated **2-NHMe$_2$**. However, when a more-nucleophilic conjugate base is present, displacement of the amide ligand was observed. Treatment of **2-NMe$_2$K** with water resulted in isolation of the dimeric bis(hydroxy) iron compound, [($^{i\mathrm{Pr}}$PDEA)FeOH]$_2$(μ-K)$_2$ (**2-OHK**, Scheme 2). The solid-state structure of **2-OHK** (Figure 1) reveals a dimeric molecule with bridging potassium ions ligated by the hydroxide oxygen and aryl rings from the $^{i\mathrm{Pr}}$PDEA ligand. The data were of sufficient quality such that the hydrogen atoms on the hydroxide ligands were located and refined. The metrical parameters (Table 1) of the $^{i\mathrm{Pr}}$PDEA ligand are comparable to those found in the solid-state structures of **2-NHMe$_2$** and **2-NMe$_2$K**.

In summary, a series of ferrous complexes bearing a bis(enamide)pyridine ligand has been prepared via double deprotonation of the corresponding bis(imino)pyridine iron dichloride complex by reaction with amide bases. Similar products are obtained by addition of free amine to the related ferrous dialkyl, implicating a transient iron-amide as the base for chelate deprotonation. Direct attack by an external amide base in the salt metathesis procedures is also plausible. Using this ligand motif, iron-amide- and hydroxy-“ate” complexes have also been isolated and crystallographically characterized, demonstrating the rich coordination chemistry associated with this class of molecules.

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Supporting Information Available: Complete experimental detail and crystallographic data for **2-NHMe$_2$**, **2-NMe$_2$K**, and **2-OHK**. This material is available free of charge via the Internet at http://pubs.acs.org.

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