N-Heterocyclic Pincer Dicarbene Complexes of Iron(II): C-2 and C-5 Metalated Carbenes on the Same Metal Center

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Summary: Six- and five-coordinate Fe(II) complexes with the pincer ligand 2,6-bis(imidazolylidene)pyridine (C−N−C), [(C−N−C)Fe(MeCN)$_3$][BPh$_4$]$_2$ and [(C−N−C)FeBr$_2$], respectively, were synthesized. Substitution of tmeda in [FeCl$_2$(tmeda)]$_2$ by C−N−C gave the six-coordinate {[Fe(C−N−C)(C−N−C)][FeCl$_4$]}, in which one of the pincer ligands is bound to the metal via the 2- and 5-imidazole carbons.*

We[1] and others[2] have recently used 2,6-bis(imidazol-2-ylidene)pyridine and -lutidine ligands for the stabilization of catalytically active palladium, rhodium, and ruthenium complexes. The common synthetic routes, i.e., transmetalation from the corresponding silver carbene complexes[1a,b,2c] or deprotonation of the bis(imidazolium) salts in the presence of metal precursors,[1d,e,2a,b] lead to complexes in which the N-heterocyclic carbene (NHC) ring is metalated via the C-2 atom. Direct metalation of imidazolium salts with basic (acetate or alkoxide)[2a] or low-oxidation-state metal complexes[1b,2f] leads also to C-2 bonded NHCs. Crabtree was the first to observe "abnormal" C-5 metalation of the NHC ring in bidentate picolyl- and pyridyl-NHC dihydrides of iridium(III), prepared by metalation of imidazolium salts with IrH$_5$(PPh$_3$)$_2$.[3] Detailed studies of this system by experimental and theoretical methods[3b] have shown that the C-5 bound NHC is the kinetic product of direct metalation, assisted by secondary interactions of the C-2 bound hydrogen atom and the imidazolium counteranions.

In the course of our continuing work involving the use of isolated, thermally stable pincer 2,6-pyridyl−dicarbene (C−N−C) ligands[1c,4] for the synthesis of reactive organometallics, we tried to prepare simple iron(II) pincer NHC complexes, (C−N−C)FeX$_2$ (X = Cl$^-$, Br$^-$, alkyl etc.), which may exhibit interesting catalytic activity in oligomerization, polymerization, C−C bond formation or oxidation reactions.[5] Herein, we report preliminary data showing that the nature of the isolated iron(II) pincer NHC complexes is dependent on the choice of the synthetic method and the iron(II) precursors (see Scheme 1).

Surprisingly, we also observed and fully characterized the first complex in which the C-2 and C-5 metalation modes coexist on the same metal center, in a system where (C-2)−H−anion interactions are not possible. Finally, we describe a new high-yield method leading to (C−N−C)FeBr$_2$, based on the direct metalation of imidazolium salts by {Fe[(N(SiMe$_3$)$_2$]$_2$}. Homoleptic NHC complexes of Fe(III) have been studied and characterized by Fehlhammer[6] and were found to be very inert, due to the low lability of the NHC functionality.

Interaction of FeCl$_2$·1.5THF[7] or FeCl$_2$(PPh$_3$)$_2$[8] in THF with **L^a** or **L^b** at −78 °C resulted in the formation of red-purple solutions, which on slow warming to room temperature gave purple microcrystalline air- and moisture-sensitive precipitates. These were insoluble in THF, ether, and toluene, gave orange solutions in MeCN or DMF and brown unstable solutions in CH$_2$Cl$_2$. Due to their low solubility in organic solvents, their identity was difficult to establish. However, microanalytical and reactivity data discussed below support the formulation {[(C−N−C)FeClL]$_2$(FeCl$_4$)} (L = thf, PPh$_3$).

Anion exchange with BPh$_4$$^-$ in MeCN followed by crystallization from MeCN/ether gave air-stable diamagnetic orange prisms of **1a** and **1b**. The identity of **1a** was unequivocally established by a single-crystal X-ray diffraction study. An ORTEP plot of the cation is

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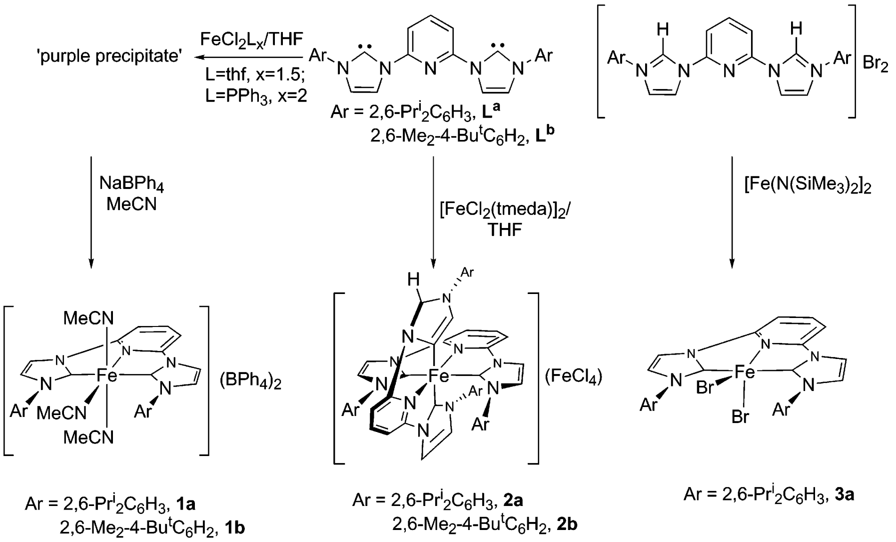
Scheme 1. Synthesis of the Iron (II) Complexes 1−3

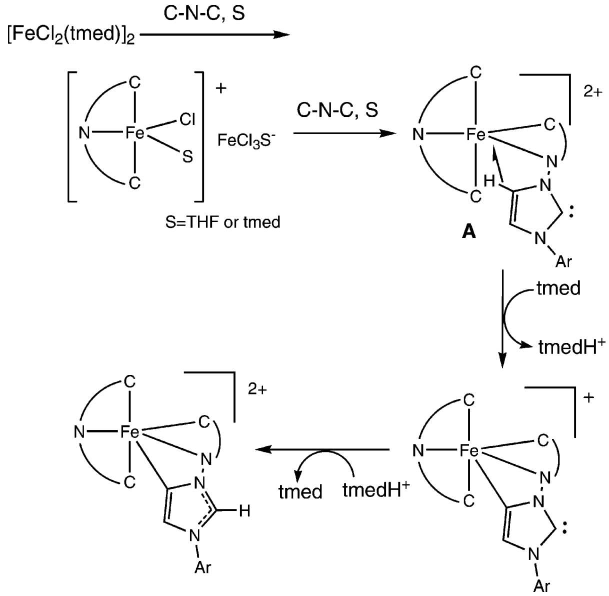


shown in Figure 1. The iron center in **1a** is distorted octahedral. The imidazole and pyridine rings of the pincer ligand are almost coplanar; the bite angles are in the range of 79.6−80.7°. The bulky $2,6\text{-Pr}^{i}{}_{2}\text{C}_{6}\text{H}_{3}$ rings are rotated by 87.8 and 88.3° out of the plane of the heterocyclic rings to which they are attached. The Fe−carbene bond lengths (1.944(5)−1.947(5) Å) are slightly shorter than the previously reported values for Fe(III)[9] (1.983(4)−2.004(3) Å), showing the expected trend.

In an effort to prepare $(\text{C}{-}\text{N}{-}\text{C})\text{FeX}_2$ complexes (X = Cl^-, Br^-) we decided to explore alternative iron(II) starting materials with labile ligands. Reaction of $\mathbf{L^a}$ or $\mathbf{L^b}$ with $[\text{FeCl}_2(\text{tmeda})]_2$[9] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) in THF at low temperatures gave red-purple precipitates, insoluble in most common organic solvents but easily soluble in DMF, from which they were crystallized, giving the complexes **2a** and **2b**. The reactions were not sensitive to the ratio of the reactants. The identity of the products obtained was established by an X-ray diffraction study of **2b**.

Compound **2b** is a salt, the cation of which is shown in Figure 2. Its most remarkable structural feature is the occurrence on the same metal center of two pincer ligands adopting different coordination modes. The first involves symmetrical binding by two C-2 metalated NHC rings and the second nonsymmetrical binding by two NHC rings metalated at C-2 and C-5 (crystallographic C46), respectively. All four Fe−C bond lengths are virtually equal (1.933(8)−1.938(8) Å). Comparison of the system leading to **2a** and **2b** with the above-mentioned iridium systems, which also give rise to C-5 metalation, shows the following important differences. (i) It has a base (tmeda) as an essential component. (ii) The metalation of C-5 becomes favorable in the presence of three C-2 metalations; no fully C-2 metalated species has been detected. (iii) Imidazolium salts are not used as starting materials. Although the mechanism seems to be very complicated and will be the subject of further investigations, we propose a plausible sequence as shown in Scheme 2.

Scheme 2. Plausible Mechanism Leading to 2a and 2b



In this, the intermediate **A** formed by the initial substitutions of the labile ligands by the NHC and pyridine functionalities undergoes base-assisted metalation at the C5 of the dangling NHC, which is protonated at the C2 by $(\text{tmedaH})^+$. It is plausible that the reaction pathway leading to $[\text{Fe}(\text{C}{-}\text{N}{-}\text{C})(\text{C}{-}\text{N}{-}\text{C}^*)]^{2+}$ is favored over the formation of $[\text{Fe}(\text{C}{-}\text{N}{-}\text{C})_2]^{2+}$ for steric reasons;[3a] $[\text{Ru}(\text{C}{-}\text{N}{-}\text{C})_2]^{2+}$ with less bulky 3-alkylimidazoles has recently been characterized.[10] A possible alternative mechanistic proposal may involve base (tmeda)-catalyzed 1,3-H shifts of the dangling NHC ring and coordination of the C5 metalated NHC on the metal center.

The ^{1}H NMR spectra of the BPh_4^- analogues of **2a** and **2b** (prepared by anion exchange with NaBPh_4) show the C5 and C2 protons at 5.4 and 7.9 ppm, in agreement with previous observations.[3a]

The five-coordinate iron(II) pincer $(\text{C}{-}\text{N}{-}\text{C})\text{FeBr}_2$ (**3a**) was obtained cleanly and in good yields by direct metalation (aminolysis) from $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$[11] and 2,6-

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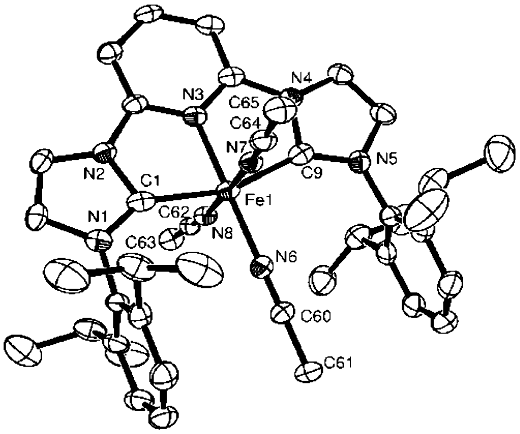

Figure 1. ORTEP representation of the cation in **1a** showing 50% probability ellipsoids. H atoms, three distorted MeCN ligands, and two water molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)−Fe(1) = 1.944(5); C(9)−Fe(1) = 1.947(5); Fe(1)−N(3) = 1.911(4); Fe(1)−N(7) = 1.920(4); Fe(1)−N(6) = 1.921(4); Fe(1)−N(8) = 1.939(4); N(3)−Fe(1)−C(1) = 79.68(17); N(6)−Fe(1)−C(1) = 100.39(17); N(8)−Fe(1)−C(1) = 89.10(17); N(3)−Fe(1)−C(9) = 80.75(18); N(6)−Fe(1)−C(9) = 99.18(17); N(3)−Fe(1)−C(9) = 80.75(18); N(3)−Fe(1)−N(8) = 89.22(15).

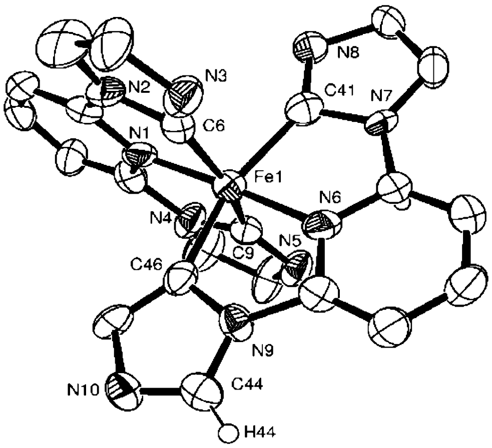

Figure 2. ORTEP representation of the cation in **2b** showing 50% probability ellipsoids. H atoms (except H44) and the 2,6-Me$_2$-4-Bu^t-C$_6$H$_3$ rings are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(6)−Fe(1) = 1.938(8); N(1)−Fe(1) = 1.909(7); N(6)−Fe(1) = 1.902(6); C(9)−Fe(1) = 1.938(8); C(46)−Fe(1) = 1.938(7); C(41)−Fe(1) = 1.933(8); N(1)−Fe(1)−C(6) = 81.0(4); N(6)−Fe(1)−C(41) = 80.8(3); N(6)−Fe(1)−C(46) = 81.2(3); N(1)−Fe(1)−C(9) = 79.3(4); N(1)−Fe(1)−C(6) = 81.0(4).

bis(arylimidazolium)pyridine dibromide[1b] (aryl = 2,6-Pr$^i_2$C$_6$H$_3$) in THF. Paramagnetic, red-purple, air-sensitive crystals were isolated by layering the THF solution with light petroleum. In acetonitrile solution the bromide ligands in **3a** are easily displaced by MeCN, giving rise to $[(C{-}N{-}C)Fe(MeCN)_3]^{2+}$. In chlorinated solvents the complex decomposes within 5 min to as yet unidentified species. The structure of **3a** was established by X-ray diffraction. An ORTEP representation of the molecule is shown in Figure 3.

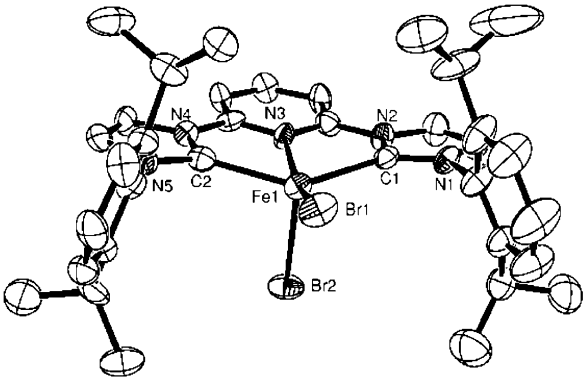

Figure 3. ORTEP representation of **3a** showing 50% probability ellipsoids. H atoms and THF molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)−Fe(1) = 2.193(10); C(2)−Fe(1) = 2.166(10); Fe(1)−Br(1) = 2.4208(17); Fe(1)−Br(2) = 2.5065(18); Fe(1)−N(3) = 2.211(8); C(2)−Fe(1)−C(1) = 141.0(4); C(2)−Fe(1)−N(3) = 73.1(3); C(1)−Fe(1)−N(3) = 71.7(3); C(2)−Fe(1)−Br(1) = 103.8(3); C(1)−Fe(1)−Br(1) = 104.0(3); N(3)−Fe(1)−Br(1) 161.0(2); C(2)−Fe(1)−Br(2) = 96.9(3); C(1)−Fe(1)−Br(2) = 99.8(3); N(3)−Fe(1)−Br(2) 90.8(2); Br(1)−Fe(1)−Br(2) = 108.19(7). The asymmetric unit contains one more molecule with slightly different metrical data.

There are two independent molecules in the asymmetric unit with slightly different metrical data. Both have approximate C_s symmetry arising from the plane containing the two bromides, the metal, and the pyridine nitrogen. The metal adopts a distorted-square-pyramidal geometry with apical bromide. The iron atom is positioned 0.3986(39) Å (0.4583(44) Å) above the basal plane. Similar structural features have been observed in 2,6-bis(imino)pyridyl iron dibromide with bulky 2,6-Pr$_2{}^i$-C$_6$H$_3$ substituents.[12] The Fe−C (carbene) bond lengths are 2.145(11)−2.193(10) Å), longer than those observed in **1a**, possibly due to the different coordination geometry and charge. The same trend is observed with the Fe−N(pyridine) bond lengths 2.211(8) and 2.241(8) Å in **3a** vs 1.911(4) Å in **1a**. The magnetic susceptibility of **3a** in the solid state (Evans balance) is 4.7 μ_B, indicating the presence of four unpaired electrons in the square-pyramidal ligand field.

In conclusion, we have developed synthetic methods leading to the first iron(II) NHC complexes by taking advantage of the inertness offered by the C−N−C pincer architecture. Elucidation of the mechanistic details leading to the formation of **2b** and **2a**, the synthesis of analogues of **3a** with other early transition metals, and the study of their organometallic chemistry and catalysis are under way.

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Supporting Information Available: Text giving experimental methods for the preparation and characterization of complexes **1**−**3** and full details of the X-ray crystal structures, including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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