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Rearrangement of the Tris(2-pyridylthio)methanido Ligand in an Iron(II) Complex Containing an Fe−C Bond

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Iron(II) tris(2-pyridylthio)methanido (**1**) containing an Fe−C bond, obtained from the reaction of tris(2-pyridylthio)methane (HL^1) and iron(II) triflate, reacts with protic acid to generate iron(II) bis(2-pyridylthio)carbene (**1a**). The carbene complex is converted to an iron(II) complex (**2**) of the 1-[bis(2-pyridylthio)methyl]pyridine-2-thione ligand (L^3) upon treatment with a base. Complex **2** reversibly transforms to **1a** in the presence of an acid. During the transformation of **1** to **2**, a novel rearrangement of L^1 to L^3 takes place. The iron(II) complexes are reactive toward dioxygen to form the corresponding iron(III) complexes.

Metal−carbon bonds play an important role in biology and chemistry. With the crystallographic and spectroscopic characterization of new enzymes, the role of metal−carbon bonding interaction in the catalytic reaction has received considerable attention in the field of bioorganometallic chemistry.[1] Fe−C bonding interactions have been invoked in catalytic oxidation processes in iron porphyrin systems and also as intermediates in lipoxygenases.[2−5] Recently, the active site structure of [Fe]hydrogenase (Hmd) revealed an iron(II) center coordinated by a facial triad consisting of a pyridine nitrogen, a thiolate sulfur, and an acyl carbon.[6,7] Model organoiron complexes containing iron−acyl bonds have been reported.[8−14]

We have recently reported the synthesis and structure of an iron(II) carbene complex derived from tris(2-pyridylthio)methane (HL^1).[15] The sulfur-stabilized ligand anion of HL^1 has been shown to form a metal−carbon bond in complexes with transition-metal ions.[16−22] We report herein the dioxygen reactivity and acid/base-dependent rearrangement of the tris(2-pyridylthio)methanido ligand in Fe−C-bonded complexes.

The reaction of Fe(OTf)$_2$·2CH$_3$CN and pyridine-2-thiol (PySH) with a basic (triethylamine) solution of HL^1 in dichloromethane affords a rose-red complex [(L^1)Fe^{II}(PyS)] (**1**). On the other hand, the reaction of Fe(OTf)$_2$·2CH$_3$CN, HL^1, and PySH in dichloromethane, followed by treatment with triethylamine (Et$_3$N), yields a dark-red complex [(L^3)Fe^{II}(PyS)] (**2**; Scheme 1). The electrospray ionization mass spectrometry (ESI-MS) spectra of both complexes in acetonitrile show signals at *m*/*z* 508.1 and 398.1 with the expected isotope distribution patterns calculated for [(L^1)Fe(PyS)]$^+$ and [(L^1)Fe]$^+$, respectively. The ESI-MS

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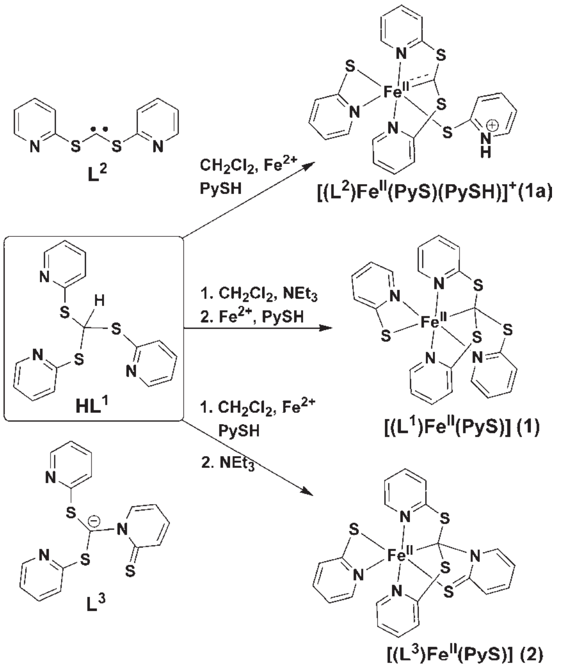
Scheme 1. Synthesis of Iron(II) Complexes



data indicate an isomeric relationship between the two complexes. The diamagnetic complexes were further characterized by ^{1}H NMR spectroscopy in CD_2Cl_2, which shows (Figures S1 and S2 in the Supporting Information, SI) peaks for pyridine protons without any paramagnetic shift of these resonances. Both **1** and **2** show the same number of proton resonances with a slight difference in their peak positions.

The iron(II) complexes are sensitive toward dioxygen. During the reaction with dioxygen in the presence of triethylammonium triflate (Et_3NHOTf), the charge-transfer bands of the iron(II) complexes at 480 and 530 nm[23] slowly disappear, with a concomitant appearance of a peak at around 755 nm (Figures S3 and S4 in the SI). The latter peak may be attributed to a thiolate-to-iron(III) charge-transfer transition.[24] The X-band electron paramagentic resonance (EPR) spectrum (at −150 °C in a dichloromethane−hexane solvent mixture) of the oxidized solution of **1** (i.e., **1-OTf**) shows a rhombic signal with g values at 1.91, 2.32, and 2.51. The oxidized solution of **2** (**2-OTf**) exhibits similar EPR signals at g = 1.91, 2.32, and 2.50. The EPR spectra (Figures S5 and S6 in the SI) support the formation of low-spin iron(III) species during the reaction of **1** and **2** with dioxygen.

All attempts to grow X-ray-quality single crystals of iron(II) complexes were unsuccessful. However, the corresponding iron(III) complexes were crystallized for the structural verification of iron(II) complexes. The oxidized solutions of **1** and **2** containing Et_3NHOTf were kept for vapor diffusion of ether in an inert atmosphere at 0 °C to isolate deep-green X-ray-quality single crystals of **1-OTf** and **2-OTf**, respectively (Table S1 in the SI). The crystal structure of the complex cation of **1-OTf**[25] reveals the iron center octahedrally coordinated with the monoanioinic N_3C-donor ligand (L^1) and a monoanionic PyS anion (Figures 1a and S7 in the SI). Three pyridine nitrogen atoms from the tripodal ligand and the nitrogen donor of PyS occupy the equatorial plane in such a way that they are positioned alternating up and down from the mean plane consisting of iron and nitrogen atoms. The anionic carbon (C6) and anionic sulfur (S4) coordinate to the iron center trans to each other in the axial position with a C6−Fe1−S4 angle of 171.11(12)° and a Fe1−C6 distance of 1.986(4) Å. The Fe1−S4 bond [2.3427(12) Å] is longer most likely because of the trans influence of the carbanioinic ligand (Table S2 in the SI). The Fe−N bond distances are in the range of low-spin iron(III) complexes.[26]

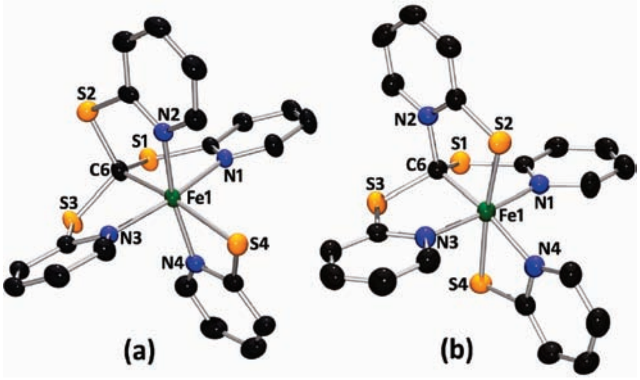


Figure 1. Molecular structures of the complex cations of (a) **1-OTf** and (b) **2-OTf**. All hydrogen atoms have been omitted for clarity.

The X-ray crystal structure of **2-OTf**[27] reveals a six-coordinate distorted octahedral coordination geometry at the iron center. The iron is coordinated by a monoanionic tetradentate tripodal N_2CS-donor ligand and a bidentate PyS anion (Figures 1b and S8 in the SI). The bond parameters and donor environment comfirm the isomerization of ligand L^1 during the reaction with iron(II) triflate to form L^3 as a result of C−S bond cleavage, followed by C−N bond formation. Ligand L^3 is coordinated to the iron center through two pyridine nitrogen atoms trans to each other occupying the axial position with a N1−Fe1−N3 angle of 174.18(9)° and Fe1−N1 and Fe1−N3 distances of 1.976(2) and 1.981(2) Å, respectively (Table S3 in the SI). In the equatorial plane, a four-membered chelate ring is formed at the iron center through coordination of S4 and N4 of PyS with a N4−Fe1−S4 angle of 71.60(7)°. The other sulfur donor, S2, trans to S4 at a S2−Fe1−S4 angle of 173.14(3)° and carbon donor C6 occupy the trans to pyridine nitrogen donor N4 with a N4−Fe1−C6 angle of 169.25(10)°. The Fe1−C6 distance of 1.951(3) Å is shorter than the Fe−C distance in **1-OTf**. A short Fe1−S2 bond [2.2247(8) Å] is observed in the

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(25) Crystal data of **1-OTf:** M_r = 657.54, triclinic, space group $P\bar{1}$, a = 8.9779(5) Å, b = 10.8480(6) Å, c = 13.2027(8) Å, α = 97.436(5)°, β = 94.259(5)°, γ = 92.101(5)°, V = 1270.11(13) Å^3, Z = 2, ρ = 1.719 mg m^{-3}, μ(Mo Kα) = 1.062 mm^{-1}, F(000) = 666, GOF = 1.093. A total of 11 995 reflections were collected in the range 1.56° ≤ θ ≤ 25.00°, 4477 of which were unique (R_{int} = 0.0223). R1 (wR2) = 0.0527 (0.1528) for 343 parameters and 3931 reflections [$I > 2\sigma(I)$].

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(27) Crystal data of **2-OTf·CH$_2$Cl$_2$**: M_r = 742.46, monoclinic, space group $P2_1/n$, a = 11.7123(15) Å, b = 11.1622(14) Å, c = 21.735(3) Å, β = 101.507(3)°, V = 2784.4(6) Å^3, Z = 4, ρ = 1.771 mg m^{-3}, μ(Mo Kα) = 1.165 mm^{-1}, F(000) = 1500, GOF = 1.073. A total of 29 210 reflections were collected in the range 1.84° ≤ θ ≤ 27.00°, 6058 of which were unique (R_{int} = 0.0612). R1 (wR2) = 0.0394 (0.1024) for 370 parameters and 4787 reflections [$I > 2\sigma(I)$].

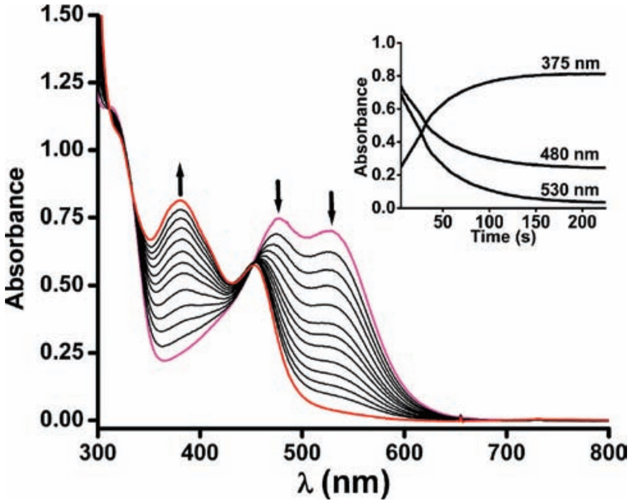


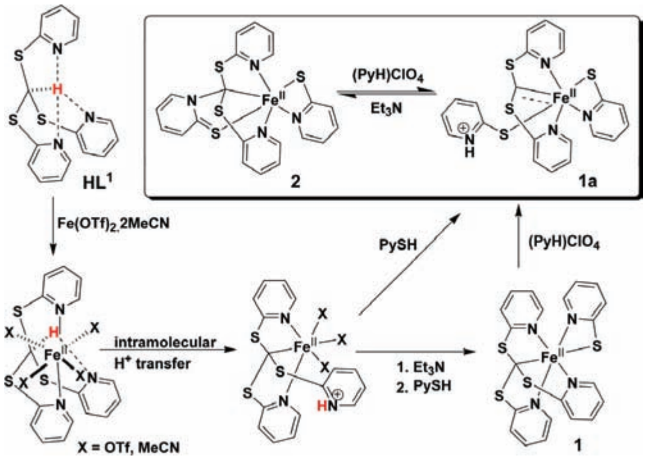
Figure 2. Optical spectral changes during the reaction of an acetonitrile solution of **1** (0.1 mM) with 5 equiv of pyridinium perchlorate.

equatorial plane possibly because of a strong in-plane bonding interaction.

During the synthesis of Fe−C-bonded complexes, it is observed that the sequence of base (Et_3N) addition gives rise to two different but isomeric iron(II) complexes. We have earlier reported the structure of an iron(II) carbene complex, $[(L^2)Fe^{II}(PyS)(PySH)]^+$ (**1a**), synthesized by the reaction of HL^1 with iron(II) triflate in the absence of a base. The presence of a base, therefore, plays a role in directing the course of the reaction between the ligand and iron(II) salts. When an acetonitrile solution (10^{-4} M) of **1** is treated with 5 equiv of pyridinium perchlorate, $(PyH)ClO_4$, in an inert atmosphere and optical spectral changes are monitored, the characteristic peaks of **1** at 480 and 530 nm slowly disappear and new peaks at 375 and 452 nm gradually appear (Figure 2). The final spectrum of the reaction solution does match with the optical spectrum of independently synthesized **1a**.[15] The carbene complex **1a**, on the other hand, is converted to **2** by reaction with 10 equiv of triethylamine (Figure S9 in the SI). Interestingly, **2** reversibly transforms to **1a** upon treatment with 5 equiv of pyridinium perchlorate (Figure S10 in the SI). The rate of formation of **1a** from **2** is faster when a stronger protic acid is used. The acid breaks the C−S bond in complex **1** and the C−N bond in complex **2** to form a common carbene species.

On the basis of the above observation, we propose a mechanism for the formation of different complexes of ligands derived from HL^1 (Scheme 2). In the reaction of ligand with iron(II) salt, initially a weak metal−ligand complex is formed that rapidly cleaves the C−H bond and the proton is transferred to one of the pyridine nitrogen atoms. As a result, a transient species is formed where the iron(II) is in direct bonding interaction with sp^3 carbon. In the absence of any base, the transient species undergoes C−S bond cleavage of the protonated pyridine arm to form carbene complex **1a**. In the presence of triethylamine, the protonated pyridine of transient species gets deprotonated to coordinate with the iron center, forming complex **1**. The pyridinium nitrogen atom in **1a** upon treatment with a base gets deprotonated and attacks the electrophilic carbene carbon to form **2**. The X-ray crystal structures of **1-OTf** and **2-OTf** support the proposal. During the transformation of **1** to **1a**, spatial rearrangement of pyridine-2-thiolate donors takes place.

Scheme 2. Proposed Mechanism for the Formation of Iron(II) Complexes with an Fe−C Bond



In summary, we have isolated and characterized two low-spin iron(II) complexes containing an Fe−C bond with the N,S,C-donor environment. The iron(II) complexes react with dioxygen to form low-spin mononuclear iron(III) complexes. While **2** shows acid−base-dependent equilibrium with iron(II) bis(2-pyridylthio)carbene (**1a**), complex **1** irreversibly transforms to **1a** in the presence of an acid. This is the first report of a novel rearrangement of tris(2-pyridylthio)methanido to 1-[bis(2-pyridylthio)methyl]pyridine-2-thione in the iron(II) complex and highlights the importance of this ligand in organoiron chemistry. The synthesis and reactivity of complexes reported in this work would provide useful insight in the design of biomimetic complexes containing an Fe−C bond. Further reactivity study in this direction is presently being carried out in our laboratory.

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Supporting Information Available: Crystallographic data for **1-OTf** and **2-OTf** in CIF format and experimental and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.