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# Molecular and Electronic Structure of a Nonheme Iron(II) Model Complex Containing an Iron−Carbon Bond

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The synthesis and molecular structure of a novel iron(II) complex of an acyclic non-NHC bis(2-pyridylthio)carbene ligand containing a S−N−C facial triad are discussed. The iron carbene complex is formed in situ during the reaction of tris(2-pyridylthio)methane with an iron(II) salt. In the six-coordinate iron(II) complex, a strong Fe−C interaction (1.776 Å) is observed crystallographically and the complex exhibits a singlet-spin ground state. Density functional theory calculations that reproduce the geometry as well as the spin ground state indicate that the electronic structure of the complex is best described as an iron(II) carbene. The carbene center is stabilized by extensive backbonding from iron(II) and delocalization into the adjacent thiopyridine units.

Transition-metal carbenes are an important class of compounds in organic and organometallic chemistry.[1] Generally, metal carbene complexes (both N-heterocyclic and acyclic carbenes) are normally supported by $\pi$-acceptor ancillary ligands like CO, Cp, and phosphines.[2,3] There are reports of N-heterocyclic carbene complexes with $\pi$-donor ligands;[3−7] such complexes for acyclic carbene complexes are hard to find.

Metal−carbon bonding interactions have been shown to play an important role in biological systems. In iron porphyrin systems, they have been invoked in catalytic oxidative processes.[8] Structurally characterized model iron carbene complexes of porphyrins,[9] calix[4]arene,[10,11] and azamacrocyclic ligand[12] have been reported in the literature. In most of the cases, the carbenes were generated in situ from diazoalkanes, followed by their complexation with iron. In nonheme systems, an organoiron-mediated oxygenation of polyunsaturated fatty acids by lipoxygenases has been proposed.[13−15] Recently, the crystal structure of Fe−S cluster-free mononuclear iron hydrogenase (Hmd) revealed an Fe−C bond in the active site.[16,17] The enzyme was crystallized, and the structure showed an octahedral iron center with a facial triad consisting of a thiolate sulfur, a pyridine nitrogen, an acyl carbon. A water and two CO donors complete its coordination sphere.[17] So far, there are only a few reports of related model complexes, but none of them successfully models the S−N−C facial triad.[18]

During the course of our study on the C−H bond activation of tris(2-pyridylthio)methane ($L^1$)[19−22] by iron(II), we have isolated a mononuclear iron(II) complex of an acyclic bis(2-pyridylthio)carbene ($L^2$) ligand (Scheme 1). The reported iron complexes of the dithiocarbene ligand [$C(SR)_2$ ; R = alkyl or aryl], with either a terminal or bridging carbene, are

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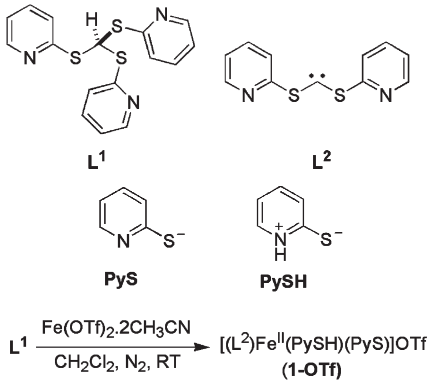
**Scheme 1.** Ligands and Synthesis of Complex **1**



all supported by $\pi$-acceptor ligands.[23-26] They show a wide range of reactivity, but structurally characterized dithiocarbene complexes are rare.[25] We report in this Communication the synthesis, molecular and electronic structure of a novel low-spin iron(II) complex of a new tridentate dithiocarbene ligand that mimics the S−N−C facial triad present in the active site of Hmd.

The reaction of $Fe(OTf)_2 \cdot 2CH_3CN$ and ligand $L^1$ in dichloromethane at room temperature yields a red iron(II) complex $[(L^2)Fe^{II}(PySH)(PyS)]^+$ (**1**).[27] The X-ray crystal structure of the monocationic complex **1**[28] reveals a six-coordinate distorted octahedral coordination geometry at the iron center consisting of the tridentate $L^2$ ligand, a bidentate monoanioic PyS, and a neutral monodentate PySH (Figure 1). In the meridional arrangement of $L^2$, two pyridine nitrogens are coordinated to the iron center trans to each other, occupying the axial position with a N1−Fe1−N2 angle of 173.64(6)°. In the equatorial plane, a four-membered chelate ring is formed at the iron center through the coordination of S4 and N4 of the 2-pyridinethiolate anion with a N4−Fe1−S4 angle of 70.36(4)°. The other sulfur donor, S3, from the monodentate PySH ligand occupies the equatorial position trans to S4 at a S3−Fe1−S4 angle of 162.93(2)°. This leaves the carbon donor C6 of $L^2$ to occupy the equatorial position trans to the pyridine nitrogen donor N4 with a N4−Fe1−C6 angle of 161.74(6)°. The equatorial Fe1−N4 bond distance (2.05 Å) is longer than the axial Fe−N(pyridine) bond distances (average 1.967 Å) most likely because of the trans influence of the carbene ligand.

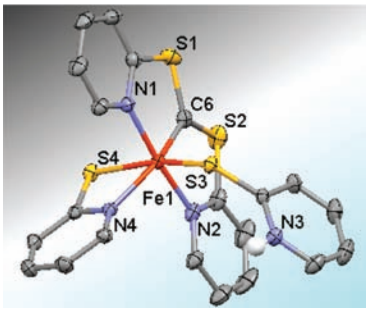


**Figure 1.** Molecular structure of **1**. All hydrogen atoms except that attached to N3 on **1** have been omitted for clarity. Selected bond lengths [Å] and angles [deg] for **1**: Fe1−N1 1.9756(13), Fe1−N2 1.9594(14), Fe1−N4 2.0501(14), Fe1−S3 2.3160(4), Fe1−S4 2.3279(4), Fe1−C6 1.7762(17), C6−S1 1.7319(18); N1−Fe1−N2 173.64(6), C6−Fe1−N4 161.74(6), N4−Fe1−S4 70.36(4), C6−Fe1−S3 105.56(5).

The Fe1−C6 bond distance of 1.776(2) Å is a clear indication of a strong Fe−C interaction, and the trigonal-planar geometry at C6 strongly suggests that it is a carbene carbon (Table S1 in the Supporting Information, SI). The Fe−C bond length is among the shortest reported for iron carbene complexes.[2,11] The average Fe−N and Fe−S bond distances are comparable to those reported for low-spin iron(II) complexes[2,29] rather than high-spin iron(II) complexes.[30] The C−S bond lengths in the tridentate carbene ligand are shorter than the C−S single bond for thioethers. The shortening of C(carbene)−S bonds and concomitant elongation of C(py)−S bond suggest the involvement of a sulfur atom in stabilizing the carbene center. The triflate counterion is in hydrogen-bonding interaction with the protonated pyridine nitrogen (N3) of the monodentate PySH ligand [N3···O2 distance of 2.831(2) Å; Table S2 and Figure S1 in the SI).

The electrospray ionization mass spectrometry spectrum of **1** in acetonitrile shows signals at *m*/*z* 508.12 and 398.10 with the expected isotope distribution pattern calculated for $[\{(L^2)Fe(PySH)(PyS)\}-H]^+$ and $[(L^2)Fe(PyS)]^+$, respectively (Figure S2 in the SI). The diamagnetic complex was further characterized by $^1H$ NMR spectroscopy in $CD_2Cl_2$ at room temperature, which shows sharp peaks for the pyridine protons without any paramagnetic shift of these resonances (Figure S3 in the SI).

The electronic structure of complex **1** could be an ferrous carbene ($Fe^{II}-C^+$), an antiferromagnetically coupled ferric methylene radical ($Fe^{III}-C\cdot$), or an iron(IV) carbanion ($Fe^{IV}-C^-$), all of which can have a diamagnetic ground state (GS). Geometry-optimized, spin-unrestricted, density functional theory (DFT) calculations[32] have been performed to evaluate these possibilities. The $S = 0$ GS is predicted to be more stable relative to the $S = 2$ GS by 31.7 and 3.8 kcal

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[27] **1-OTf.** To a rapidly stirred solution of $Fe(OTf)_2 \cdot (CH_3CN)_2$ (0.436 g, 1 mmol) in dichloromethane (8 mL) was added a dichloromethane solution (2 mL) of ligand (0.235 g, 1 mmol). The red solution was stirred overnight at room temperature. To the solution was added dropwise diethyl ether (15 mL), and the resulting solution was stirred for a further 3−4 h to precipitate a red solid. The solid was filtered, washed with diethyl ether, and dried under vacuum. X-ray-quality single crystals were grown by slow vapor diffusion of diethyl ether into a dichloromethane solution of the complex. Yield: 0.16 g (44%). The complex was isolated with improved yield (ca. 90%) when the same reaction was carried out in the presence of 1 equiv of pyridine-2-thiol. Elem anal. Calcd for $C_{22}H_{17}F_3FeN_4O_3S_5$ (658.55 g mol$^{-1}$): C, 40.12; H, 2.60; N, 8.51. Found: C, 39.7; H, 2.5; N, 8.2.

[28] Crystal data of **1-OTf:** $M_r$=658.55, orthorhombic, space group *Pbca*, $a$ = 21.3743(3) Å, $b$ = 11.3697(2) Å, $c$ = 21.3828(3) Å, $\alpha = \beta = \gamma = 90.00°$, $V$ = 5196.43(14) Å$^3$, $Z$ = 8, $\rho$ = 1.684 mg m$^{-3}$, $\mu$(Mo K$\alpha$) = 1.038 mm$^{-1}$, $F(000)$ = 2672, GOF = 1.030. A total of 75 568 reflections were collected in the range $1.90 \leq \theta \leq 30.99$, 8230 of which were unique ($R_{int}$ = 0.0514). R1 (wR2) = 0.0336 (0.0757) for 411 parameters and 6283 reflections [$I > 2\sigma(I)$].

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[32] Geometry optimizations were performed using a mixed (6-311G* on Fe, S, N, and C and 6-31G* on H) basis set using BP86 and B3LYP functionals in *Gaussian 03*, version C02. The single-point calculations used for energies and the electronic structure were performed using a 6-311+G* basis set and tight convergence criteria in *Gaussian 03*, version C02.

**Table 1.** DFT Results Calculated Using *Gaussian 03*[31]

| | Fe–S (PySH), Å | Fe–S (PyS), Å | Fe–N (PyS), Å | Fe–$N_{ax}$,[a] Å | Fe–C, Å | S–C,[a] Å | $\Delta E$, kcal $mol^{-1}$ |
|---|---|---|---|---|---|---|---|
| $S = 0$ | **2.32** | **2.33** | **2.05** | **1.97** | **1.78** | **1.74** | |
| BP86 | 2.33 | 2.34 | 2.06 | 1.97 | 1.78 | 1.76 | 0 |
| B3LYP | 2.40 | 2.30 | 2.08 | 2.02 | 1.8 | 1.73 | 0 |
| $S = 2$ | | | | | | | |
| BP86 | 2.62 | 2.39 | 2.18 | 2.19 | 1.96 | 1.73 | 31.7 |
| B3LYP | 2.67 | 2.47 | 2.17 | 2.22 | 2.02 | 1.71 | 3.8 |

[a] Average distances.

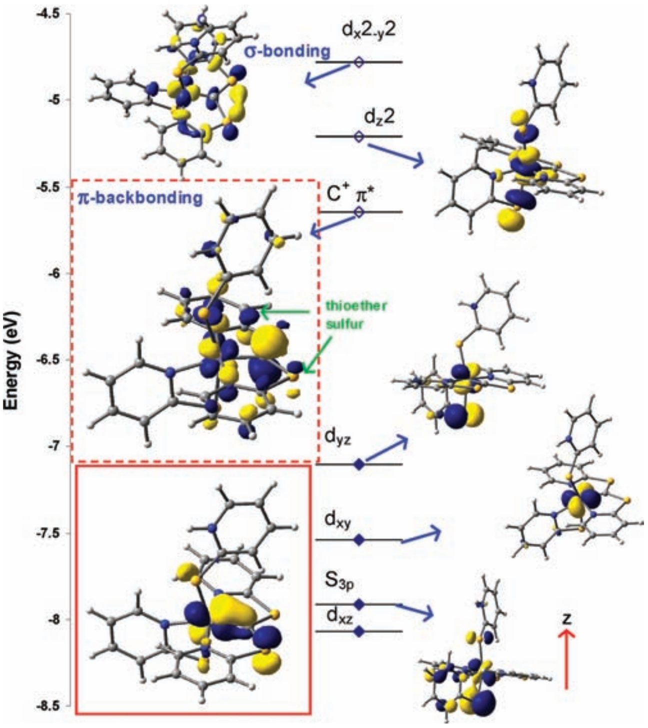

**Figure 2.** Calculated (UBP86, 6-311+G*) GS MO diagram for **1**. The orbitals involved in back-bonding are indicated using red borders. The molecular $Z$ axial is along the Fe–$S_{PySH}$ bond, and the $X$ and $Y$ axes are along Fe–S and Fe–$N_{ax}$, respectively.

$mol^{-1}$ using BP86[33,34] and B3LYP[35] functionals, respectively. However, the optimized structures indicate that the BP86 functional reproduces the experimental geometry better than the B3LYP functional (Table 1). In particular, the Fe–N bond lengths are overestimated using B3LYP.

The molecular orbital (MO) diagram of the $S = 0$ state (Figure 2) indicates a $d_{xy}{}^2 d_{xz}{}^2 d_{yz}{}^2 d_{z^2}{}^0 d_{x^2-y^2}{}^0$ configuration of the iron center. This is consistent with a tentative low-spin iron(II) assignment. Additionally, there is a low-lying unoccupied $\pi^*$ orbital on the carbon bonded to the iron (Figure 2, dashed-red border) characteristic of a carbene center. The $d_{x^2-y^2}$ orbital of the iron is involved in $\sigma$ bonding with the carbene (Figure 2, top left). There is a very strong $\pi$-back-bonding interaction between the filled $d_{xz}$ orbital on the iron and the unoccupied carbene $\pi^*$ orbital, as indicated by their contours with red and dashed-red borders, respectively. The Mulliken populations[36] indicate that 39% Fe $d_{xz}$ is mixed into the carbene $\pi^*$ orbital; i.e., 0.78e ($\alpha$ and $\beta$ orbitals summed up) charge density is shifted from the iron center to the carbene. Furthermore, the carbene is stabilized via its delocalization into the thioether sulfur atoms (Figure 2, green arrows) as well as into the aromatic pyridine ring, as indicated by the contour (Figure 2, dashed-red border). Thus, the electronic structure description of this complex is consistent with an iron(II) carbene GS for this molecule with significant $\pi$-back-bonding interaction between the iron $d_{xz}$ and the carbene $\pi^*$ orbital.

In summary, we have isolated and characterized a novel iron(II) complex of an acyclic bis(2-pyridylthio)carbene ligand. A strong Fe–C interaction is observed crystallographically, and the complex exhibits a singlet GS. DFT calculations that reproduce the geometry as well as the spin GS indicate that the electronic structure of the complex is tentatively described as an iron(II) carbene. The carbene center is stabilized by extensive back-bonding from iron(II) and delocalization into the adjacent thiopyridine units. The facial coordination of N, C, and S donors and the respective M–L bond distances closely mimic the structural aspect of an octahedral iron complex in mononuclear iron hydrogenase.[17] To the best of our knowledge, this is the only report of a stable iron(II) carbene complex of a non-NHC ligand supported by $\pi$-donor and not $\pi$-acceptor ancillary ligands. A detailed reactivity study of complex **1** is presently under investigation.

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**Supporting Information Available:** Crystallographic data in CIF format, spectroscopic data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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