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Iron Pyridine-2-thiolate Complexes: Interconversion of $[Fe^0(CO)_4(SC_5H_4N)]^-$, *cis*-$[Fe^{II}(CO)_2(SC_5H_4N)_2]$, and $[Fe^{II}(SC_5H_4N)_3]^-$

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Summary: The reaction of bis(2-pyridyl) disulfide with $[HFe(CO)_4]^-$ *affords* $[Fe(CO)_4(SC_5H_4N)]^-$*, in which the pyridine-2-thiolate ligand is bound in a monodentate (S-bonded) mode. Oxidative addition of bis(2-pyridyl) disulfide to* $[Fe(CO)_4(SC_5H_4N)]^-$ *and concomitant displacement of* $[SC_5H_4N]^-$ *leads to the neutral monomeric compound cis-*$[Fe(CO)_2(SC_5H_4N)_2]$*. In the presence of* $[SC_5H_4N]^-$ *in* CH_3CN *at 60 °C, cis-*$[Fe(CO)_2(SC_5H_4N)_2]$ *undergoes facile conversion to* d^6 *Fe(II) high-spin* $[Fe(SC_5H_4N)_3]^-$*. Reduction of cis-*$[Fe(CO)_2(SC_5H_4N)_2]$ *and* $[Fe(SC_5H_4N)_3]^-$ *under CO at room temperature with* $[BH_4]^-$*/[Na][benzophenone] affords the monodentate (S-bonded) complex* $[Fe(CO)_4(SC_5H_4N)]^-$*. The results are consistent with sulfur-donor atom stabilization of the lower oxidation states of iron, while the S,N-chelating pyridine-2-thiolate ligand enhances the stability of iron in the higher oxidation state.*

Introduction

Metal pyridine-2-thiolate complexes have been studied because of their structural diversity,[1] important biological roles,[2] and potential application as precursors for metal−sulfide materials.[3]

We previously reported investigations into the biomimetic nickel-site structures of [NiFeSe] hydrogenase (nickel is ligated to one Se atom, one to two S/Cl atoms, and three to four N/O atoms)[4] and CO dehydrogenase[5a] and the oxidative addition of RE−ER (E = Te, Se; R = Ph, alkyl) to anionic metal carbonyl fragments.[5b−e] In this work, we report a study of the interconversion of the pyridine-2-thiolate complexes $[Fe^0(CO)_4(SC_5H_4N)]^-$, *cis*-$[Fe^{II}(CO)_2(SC_5H_4N)_2]$, and $[Fe^{II}(SC_5H_4N)_3]^-$ (Scheme 1).

Results and Discussion

As illustrated in Scheme 1a, the reaction of bis(2-pyridyl) disulfide with the anionic iron hydride $[HFe(CO)_4]^-$ leads to cleavage of the sulfur−sulfur bond and concomitant addition of the pyridine-2-thiolate to the iron−carbonyl fragment to yield $[Fe^0(CO)_4(SC_5H_4N)]^-$, with liberation of HSC_5H_4N.[6] The thermally unstable product, monodentate (S-bonded) $[Fe^0(CO)_4(SC_5H_4N)]^-$, was isolated as an oily compound. Treatment of 1 equiv of $[Fe(CO)_4(SC_5H_4N)]^-$ with bis(2-pyridyl) disulfide in THF led to the formation of the neutral *cis*-$[Fe(CO)_2(SC_5H_4N)_2]$ and elimination of $[PPN][SC_5H_4N]$. The anionic $SC_5H_4N^-$ ligands in *cis*-$[Fe(CO)_2(SC_5H_4N)_2]$ bind to the metal in a bidentate manner, forming four-membered chelate rings (Scheme 1b,c). The proposed mechanism, shown in Scheme 1b,c, involves oxidative addition of bis(2-pyridyl) disulfide to the anionic $[Fe(CO)_4(SC_5H_4N)]^-$,[5b,c,7a−c] possibly via the intermediate *fac*-$[Fe^{II}(CO)_3(SC_5H_4N)_3]^-$. (In a similar fashion, the reaction of $[HFe(CO)_4]^-$ with 2 equiv of $(S(C_4H_3S))_2$ in THF at ambient temperature leads to a thermally stable crystalline solid *fac*-$[Fe^{II}(CO)_3(SC_4H_3S)_3]^-$ characterized by X-ray crystallography.[7d]) Subsequent elimination of $SC_5H_4N^-$ and concomitant dissociation of CO and coordination of the nitrogen atom of the $SC_5H_4N^-$ ligands to the Fe(II) result in formation of *cis*-$[Fe^{II}(CO)_2$-

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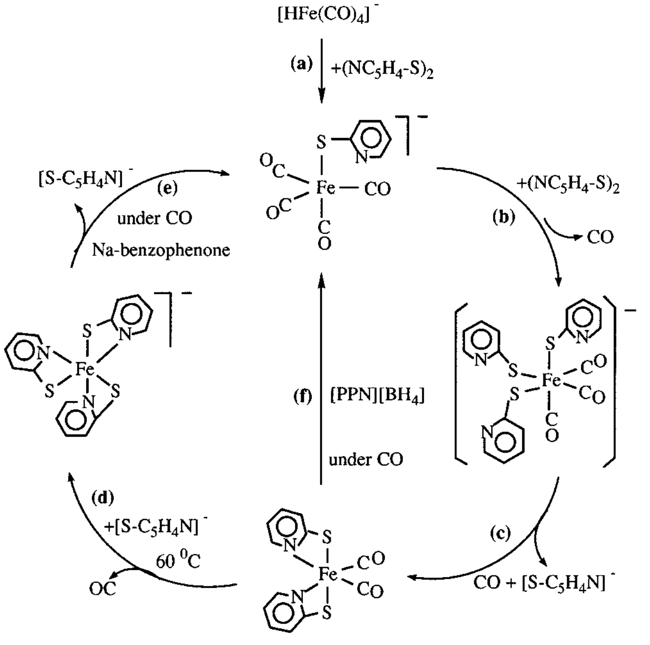
Scheme 1



$(SC_5H_4N)_2]$. This complex is soluble and stable in THF/hexane solution. The IR spectrum shows two strong CO stretching bands, which supports a cis orientation of two CO ligands. The ^{1}H and ^{13}C NMR spectra show the expected signals (^{1}H NMR (CD_3COCD_3) δ 6.83 (m), 6.97 (m), 7.60 (m), 8.28 (m) ppm; ^{13}C NMR (CD_3COCD_3) δ 119.2, 126.1, 138.4, 147.2, 179.9 ppm) for the $[SC_5H_4N]^-$ ligands in a diamagnetic d^6 Fe(II) species.

When allowed to stir in the presence of 1 equiv of the $[SC_5H_4N]^-$ ligand for 4 h in CH_3CN at 60 °C, *cis*-$[Fe(CO)_2(SC_5H_4N)_2]$ loses the carbonyl ligands to form the known d^6 high-spin tris-chelate $[Fe(SC_5H_4N)_3]^-$ (Scheme 1d).[1a] Alternatively, complete conversion of $[Fe(CO)_4(SC_5H_4N)]^-$ to $[Fe(SC_5H_4N)_3]^-$ was observed when 1 equiv of bis(2-pyridyl) disulfide was added to $[Fe(CO)_4(SC_5H_4N)]^-$ and the solution was allowed to stir for 4 h in CH_3CN at 60 °C. The results suggest that the S,N-chelating pyridine-2-thiolate ligand enhances the stability of iron complexes in higher oxidation states. In comparison, the carbon monoxide atmosphere does not promote the formation of *cis*-$[Fe(CO)_2(SC_5H_4N)_2]$ when the $[Fe(SC_5H_4N)_3]^-/CH_3CN$ solution is exposed to 1 atm of CO at room temperature.

The ring-opened complex $[Fe(CO)_4(SC_5H_4N)]^-$ was obtained upon chemical reduction of *cis*-$[Fe(CO)_2(SC_5H_4N)_2]$ and $[Fe(SC_5H_4N)_3]^-$ with $[BH_4]^-$ and [Na][benzophenone] under CO in THF at room temperature, respectively (Scheme 1e, f).[8] Apparently, the metal-centered reduction of *cis*-$[Fe^{II}(CO)_2(SC_5H_4N)_2]$ and $[Fe^{II}(SC_5H_4N)_3]^-$ labilizes the $[SC_5H_4N]^-$ chelating ligands and results in the formation of the pentacoordinate species $[Fe^0(CO)_4(SC_5H_4N)]^-$. The loss of the S,N-chelating pyridine-2-thiolate ligands from the Fe(0) center may be due to the electron density at the iron(0) center. The ligand $[SC_5H_4N]^-$ was not observed to undergo reduction, and consequently, the reduction process is assigned to the iron(II)−iron(0) couple.

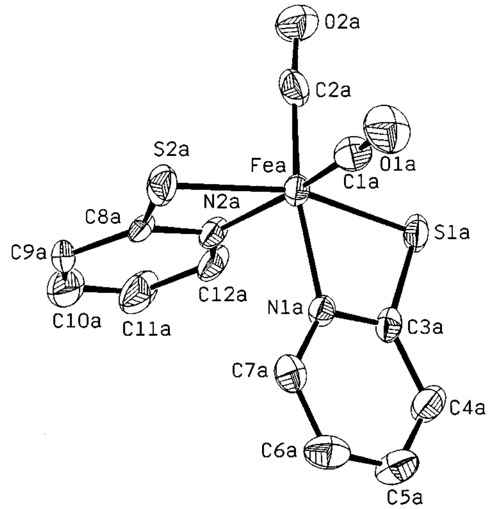


Figure 1. ORTEP drawing of one of two crystallographically independent molecules in *cis*-$[Fe(CO)_2(SC_5H_4N)_2]$.

The X-ray crystal structure of *cis*-$[Fe(CO)_2(SC_5H_4N)_2]$ (Figure 1) consists of two crystallographically independent molecules. The average Fe−S distance of 2.325(3) Å is significantly shorter than that in high-spin d^6 Fe(II) $[Fe(SC_5H_4N)_3]^-$ (average distance 2.575(1) Å).[1a] The bond angles at the Fe center are considerably distorted from the idealized octahedral limits due to the presence of two four-membered N,S-chelate rings, a characteristic most apparent in the internal chelate angles, S−Fe−N, of 71.1(2) and 71.0(2)°. This angle is larger than the S−Fe(II)−N bond angle (average 66.0(2)°) observed in $[Fe(SC_5H_4N)_3]^-$.[1a] The two carbonyl groups are disposed in a cis arrangement and are trans to the nitrogen atoms.

In summary, the complexes $[Fe^0(CO)_4(SC_5H_4N)]^-$, *cis*-$[Fe^{II}(CO)_2(SC_5H_4N)_2]$, and $[Fe^{II}(SC_5H_4N)_3]^-$ are chemically interconvertible. The Fe(0) complex contains a monodentate $[SC_5H_4N]^-$ ligand, which binds as an S,N-bidentate ligand in the Fe(II) complexes.

Experimental Section

Manipulations, transfers, and reactions of samples were conducted under nitrogen according to standard Schlenk techniques or in a glovebox (Ar gas). Solvents were distilled under nitrogen from appropriate drying agents (diethyl ether from CaH_2; acetonitrile from CaH_2/P_2O_5; hexane and THF from Na/benzophenone) and stored in dried, N_2-filled flasks over 4 Å molecular sieves. A nitrogen purge was used on these solvents before use, and transfers to reaction vessels were via stainless steel cannula under N_2 at a positive pressure. The reagents bis(2-pyridyl) disulfide, iron pentacarbonyl, bis(triphenylphosphoranylidene)ammonium chloride ([PPN][Cl]), and tetraethylammonium hydroxide (Aldrich) were used as received. Infrared spectra were recorded on a spectrometer (Bio-Rad FTS-185 FTIR) with sealed solution cells (0.1 mm) and KBr windows. ^{1}H and ^{13}C chemical shifts are relative to tetramethylsilane. UV−visible spectra were recorded on a GBC 918 spectrophotometer. Analyses of carbon, hydrogen, and nitrogen were obtained with a CHN analyzer (Heraeus).

Preparation of [PPN][$Fe(CO)_4(SC_5H_4N)$]. [PPN][$HFe(CO)_4$] (1 mmol, 0.708 g) dissolved in THF (3 mL) was stirred under N_2,[9] and a solution of bis(2-pyridyl) disulfide (1 mmol, 0.220 g) in THF (7 mL) was added dropwise by cannula under positive N_2 gas at room temperature. After an additional 5

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min of stirring, the volume of the solution was reduced to 3 mL and the orange oily product precipitated by addition of hexane (15 mL). The thermally unstable product was isolated by removing the solvent (since decomposition occurred after prolonged vacuum, the percent yield of the oily [PPN][Fe(CO)$_4$(SC$_5$H$_4$N)] was difficult to determine.). IR (ν_{CO}) (THF): 2017 w, 1912 vs cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 8.19 (br), 7.33 (m), 7.16 (br) ppm (SC$_5$H$_4$N). ^{13}C NMR (CD$_3$CN): δ 218.94 (s) ppm (CO), 171.16, 148.56, 135.56, 125.51, 116.56 ppm (SC$_5$H$_4$N).

Preparation of *cis*-[Fe(CO)$_2$(SC$_5$H$_4$N)$_2$]. [PPN][HFe(CO)$_4$] (1 mmol, 0.708 g) was added to bis(2-pyridyl) disulfide (2 mmol, 0.440 g) in THF (10 mL) at ambient temperature. After 12 h of stirring at room temperature, the solvent was removed at reduced pressure. The residue was redissolved in 20 mL of THF/hexane, and the red solution was filtered to remove [PPN][SC$_5$H$_4$N]. The filtrate was stored at − 15 °C for 4 weeks to induce precipitation of dark red crystals of *cis*-[Fe(CO)$_2$(SC$_5$H$_4$N)$_2$]. The yield was 0.221 g (66.6%). IR (ν_{CO}): 2040 vs, 1989 s cm^{-1} (THF); 2047 s, 2000 s cm^{-1} (hexane). ^{1}H NMR (CD$_3$COCD$_3$): δ 6.83 (m), 6.97 (m), 7.60 (m), 8.28 (m) ppm (SC$_5$H$_4$N). ^{13}C NMR (CD$_3$COCD$_3$): δ 213.8 (CO), 119.2, 126.1, 138.4, 147.2, 179.9. Absorption spectrum (THF) [$\lambda_{\max}$, nm (ϵ, M^{-1} cm^{-1})]: 517 (166), 346 (3922), 306 (13 885). Anal. Calcd for C$_{12}$H$_8$O$_2$N$_2$S$_2$Fe: N, 8.43; C, 43.39; H, 2.43. Found: N, 8.51; C, 43.58; H, 2.50.

Preparation of [PPN][Fe(SC$_5$H$_4$N)$_3$]. A solution containing *cis*-[Fe(CO)$_2$(SC$_5$H$_4$N)$_2$] (0.3 mmol, 0.099 g) and [PPN][SC$_5$H$_4$N] (0.3 mmol, 0.195 g) in 15 mL of CH$_3$CN was heated at 60 °C under nitrogen for 4 h. When the solution cooled to room temperature, the volume of the solution was reduced to 3 mL under vacuum and diethyl ether (20 mL) was added. The known orange [PPN][Fe(SC$_5$H$_4$N)$_3$] was isolated by removing the solvent and recrystallized from acetonitrile/diethyl ether.[1a] The yield was 0.190 g (68.6%). ^{1}H NMR (CD$_3$CN): δ 98.10 (br), 78.25 (s), 58.45 (s), 7.14 (s) ppm.[1a]

Reaction of [PPN][BH$_4$] with *cis*-[Fe(CO)$_2$(SC$_5$H$_4$N)$_2$] (and [Na][benzophenone] with [PPN][Fe(SC$_5$H$_4$N)$_3$]). A solution containing 0.167 g (0.5 mmol) of *cis*-[Fe(CO)$_2$(SC$_5$H$_4$N)$_2$] and 0.553 g (1 mmol) of [PPN][BH$_4$] in THF (15 mL) was stirred under CO atmosphere for 8 h at room temperature. The IR spectrum (ν_{CO} (THF): 1912 vs, 2017 w cm^{-1}) was identical to that of [PPN][Fe(CO)$_4$(SC$_5$H$_4$N)].

Crystallography. The crystal data are summarized in Table 1. Due to air sensitivity, the crystal of Fe(CO)$_2$(SC$_5$H$_4$N)$_2$ (ca. 0.20 × 0.40 × 0.40 mm) was mounted on a glass fiber and quickly coated in epoxy resin. The unit-cell parameters were obtained from 25 reflections with 2θ between 17.64 and 25.50°. Diffraction measurements were carried out on a Nonius CAD 4 diffractometer with graphite-monochromated Mo Kα radiation employing the $\theta/2\theta$ scan mode.[10] A φ scan absorption correction was made. Structural determinations were made using the NRCC-SDP-VAX package of programs.[11,12] Selected bond distances and angles are listed in Table 2.

Table 1. Crystallographic Data for *cis*-[Fe(CO)$_2$(SC$_5$H$_4$N)$_2$]

empirical	C$_{12}$H$_8$O$_2$N$_2$FeS$_2$
fw	332.17
cryst syst	monoclinic
space group	$P2_1/c$
λ(Mo Kα), Å	0.7107
a, Å	12.688(5)
b, Å	16.083(3)
c, Å	13.725(5)
β, deg	91.18(3)
V, Å^3	2800(2)
Z	8
ρ_{calcd}, g cm^{-3}	1.576
μ, cm^{-1}	13.586
F(000)	1349
no. of measd reflcs	3657
no. of obsd reflcs ($I > 2\sigma(I)$)	2190
no. of refined params	343 (2190 out of 3657 reflcs)
T, °C	25
R^a	0.053
$R_{\mathrm{w}}b$	0.055

^{a} $R = \sum|(F_o - F_c)|/\sum F_o$. ^{b} $R = [\sum_w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for *cis*-[Fe(CO)$_2$(SC$_5$H$_4$N)$_2$]

S(1a)−Fe(a)	2.322(3)	S(2a)−Fe(a)	2.328(3)
N(1a)−Fe(a)	2.004(7)	N(2a)−Fe(a)	1.986(7)
C(1a)−Fe(a)	1.761(9)	C(2a)−Fe(a)	1.764(10)
S(1a)−C(3a)	1.730(9)	S(2a)−C(8a)	1.711(9)
S(1a)−Fe(a)−S(2a)	163.06(11)	Fe(a)−S(1a)−C(3a)	78.5(3)
S(1a)−Fe(a)−N(1a)	71.14(19)	Fe(a)−S(2a)−C(8a)	78.3(7)
S(1a)−Fe(a)−N(2a)	96.19(20)	Fe(a)−N(1a)−C(3a)	100.2(5)
S(1a)−Fe(a)−C(1a)	94.1(11)	Fe(a)−N(1a)−C(7a)	139.9(6)
S(2a)−Fe(a)−N(2a)	70.96(20)	Fe(a)−N(2a)−C(8a)	100.4(5)
N(1a)−Fe(a)−C(2a)	166.3(3)	Fe(a)−N(2a)−C(12a)	138.3(6)
N(2a)−Fe(a)−C(1a)	168.3(4)	C(1a)−Fe(a)−C(2a)	91.6(4)

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Supporting Information Available: Tables of crystal data and experimental conditions for the X-ray studies, atomic coordinates and B_{eq} values, anisotropic thermal parameters, and bond lengths and angles for Fe(CO)$_2$(SC$_5$H$_4$N)$_2$ (5 pages). Ordering information is given on any current masthead page.

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