488 J. Am. Chem. Soc. 2000, 122, 488−494

Dinuclear and Mononuclear Iron(II)−Thiolate Complexes with Mixed CO/CN$^-$ Ligands: Synthetic Advances for Iron Sites of [Fe]-Only Hydrogenases

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Received July 5, 1999

Abstract: The pentacoordinate, 16-electron Fe^{II} complex [PPN][Fe(CO)$_2$(CN)(S,NH-C$_6$H$_4$)] (**1**), stabilized by strong S, N π-donation of chelating [S,NH-C$_6$H$_4$]$^{2-}$ ligand, was prepared by the reaction of 2-aminophenyl disulfide and [PPN][Fe(CO)$_4$(CN)]. Protonation of complex **1** by electrophiles (2-mercaptopyrimidine and 2-aminophenylthiol) yielded hexacoordinate iron(II)−thiolate cyanocarbonyl complexes [PPN][Fe(CO)(CN)(S-C$_4$H$_3$N$_2$)$_2$] (**5**) and [PPN][Fe(CO)$_2$(CN)(S-C$_6$H$_4$NH$_2$)(S,NH$_2$-C$_6$H$_4$)] (**3**), respectively. The IR spectrum of complex **5** in the aprotic solvent CH$_3$CN displayed a weak ν(CN) band at 2090 cm^{-1} and a strong ν(CO) band at 1945 cm^{-1}. Chemical oxidation of complex **5** in CH$_3$CN at − 20 °C with [Cp$_2$Fe][PF$_6$] displayed absorption bands at 2096 and 1962 cm^{-1} which were assigned to the ν(CN) and ν(CO) vibrational frequencies respectively of the thermally unstable neutral Fe^{III}(CO)(CN)(S-C$_4$H$_3$N$_2$)$_2$. Complex **5** was reobtained upon addition of [PPN][BH$_4$] to Fe^{III}(CO)(CN)(S-C$_4$H$_3$N$_2$)$_2$ in CH$_3$CN at −20 °C. The first dinuclear Fe(II)−thiolate cyanocarbonyl compound [PPN]$_2$[(CN)(CO)$_2$Fe(μ-S,S-C$_6$H$_4$)]$_2$ (**4**), the promising structural and functional model compound of the dinuclear iron active sites of [Fe]-only hydrogenases isolated from *D. desulfuricans* and *C. pasteurianum*, was prepared by reacting 1,2-benzenedithiol with complex **1** in THF at −10 °C. The X-ray structural analysis shows that complex **4** possesses crystallographically imposed centrosymmetry. Two six-coordinate Fe(II) centers are connected via two thiolate bridges, and both CN$^-$ ligands point into the antiparallel direction. The IR spectrum of complex **4** in the aprotic solvent CH$_2$Cl$_2$ revealed a weak absorption band for the CN$^-$ ligands at 2101 cm^{-1}, and two strong absorption bands for the CO groups at 2013 and 1960 cm^{-1}. When the CH$_2$Cl$_2$ solution of complex **4** was exposed to ^{13}CO at 0 °C, absorbances at 1968 and 1915 cm^{-1} appeared within 10 min. Reappearance of the 2013 and 1960 cm^{-1} bands on the removal of the ^{13}CO and replacement with ^{12}CO atmosphere demonstrated reversibility of the CO ligand lability of complex **4**. The vibrational spectroscopies of the Fe(CO)$_2$(CN) and Fe(CO)(CN) fragments (ν(CN) ranges from 2094 to 2105 cm^{-1}, ν(CO) ranges from 1928 to 2013 cm^{-1}) found in complexes **1**, **3**, **4**, and **5** may be regarded as spectroscopic references of [Fe] hydrogenases in the various enzymatic states.

Introduction

The impressive synergism that has developed in the past few years between biophysical and synthetic inorganic chemists with regard to understanding the spectroscopic signals and functions of the [Fe(CO)$_x$(CN)$_y$] active sites in [Fe] hydrogenases and [NiFe] hydrogenases has highlighted the chemistry of iron−thiolate cyanocarbonyl complexes.[1−7] The recent report of high-quality X-ray crystal structure of [Fe]-only hydrogenase from *Desulfovibrio desulfuricans* revealed that the active site contains a dinuclear iron(II)−propanedithiolate with mixed CO and CN$^-$ ligands bound to a [4Fe-4S] cluster via cysteinate bridge, and also suggested that the unsaturated Fe center present in the H-cluster of the enzyme can act as a binding site for the soft

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10.1021/ja992300q CCC: $19.00 © 2000 American Chemical Society
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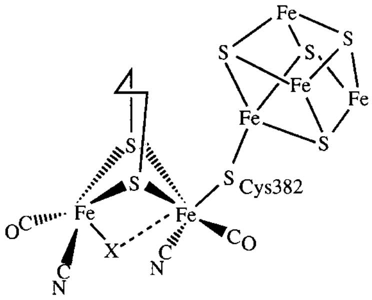
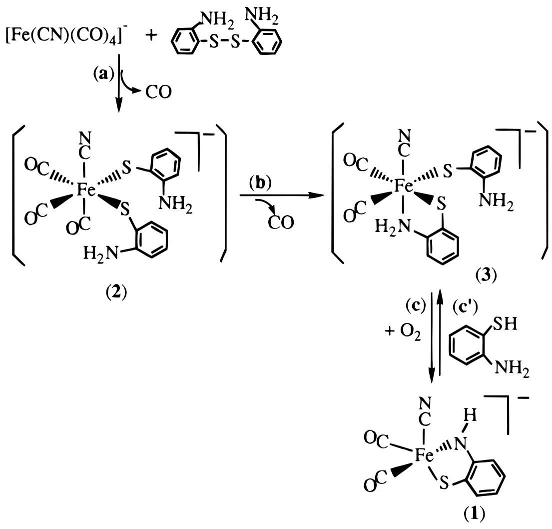


Figure 1. Schematic drawing of the H cluster according to the crystal structure *D. desulfuricans* [Fe]-hydrogenase.[3,4]

ligand H_2.[3] A more CO/CN^--rich environment was found for iron in the recently reported X-ray structure of [Fe] hydrogenases from *Clostridium pasteurianum* (CpI), which indicated that the active-site cluster consists of a [4Fe-4S] cubane subcluster covalently bridged by a cysteinate to a dinuclear iron subcluster with iron atoms coordinated by nonbiological CO and CN^- groups.[4] A schematic drawing of the active centers of [Fe] hydrogenases as deduced from the crystallographic studies is shown in Figure 1. Moreover, the infrared spectra of [Fe] hydrogenase from *Desulfovibrio vulgaris* concluded that the weak absorption bands for the CN^- ligand range from 2079 to 2106 cm^{-1}, and the broad strong absorption bands (ranging from 2016 to 1894 cm^{-1}) are assigned to the carbonyl stretching frequencies under various manipulations of the protein.[5a,b] Very recently, a Mössbauer study of the H cluster in [Fe] hydrogenase isolated from *C. pasteurianum* (CpII) showed that the binuclear Fe subcluster contains two low-spin Fe^{II} sites in the reduced state (H_{red}), while the dinuclear Fe subcluster is in mixed-valent $Fe^{III}Fe^{II}$ site in the oxidized states (H_{ox} and H_{ox}-CO).[5c] Also, the iron site in the [NiFe] hydrogenases active site from *Desulfovibrio gigas* has been established as a pyramidal $[Fe(CN)_2(CO)]$ unit with the opposite face coordinated to two S-cysteines bridged to a nickel.[1b−d,f]

Model compounds with donor ligands as close as possible to the biological coordination are needed to serve as spectroscopic references, explore biological pathways of reversible activation of H_2, and elucidate the electronic structure of active centers of the binuclear iron subcluster. Recently two iron cyanocarbonyl model complexes have been reported by Darensbourg et al.[6] and Koch et al.,[7] respectively. In one interesting model compound iron is sandwiched between a cyclopentadienyl ring and two cyanides, one carbon monoxide. The infrared and structural properties of the potassium salt of this complex match well to those of the $Fe(CO)(CN)_2$ site in [NiFe] hydrogenases isolated from *D. gigas*.[6] The other model compound is a low-spin six-coordinate iron(II)−thiolate cyanocarbonyl complex, the first example of the mononuclear iron(II)−thiolate complexes with mixed CO and CN^- ligands.[7] To our knowledge, there is no example of the dinuclear iron(II)−thiolate complexes with mixed CO and CN^- ligands characterized by X-ray crystallography.[8] Reported herein are the syntheses and structural characterizations of the mononuclear iron(II,III)−thiolate and the first dinuclear iron(II)−thiolate compounds with mixed diatomic ligands (CO and CN^- ligands) bound to the Fe serving as the promising structural and functional model compounds of the dinuclear iron active sites of [Fe]-only hydrogenases.[3,4]

Scheme 1



Results and Discussion

When di(2-aminophenyl) disulfide (0.4 mmol) was reacted directly with $[PPN][Fe(CO)_4(CN)]$ (0.4 mmol) in THF at room temperature,[9] substantial amounts of air-stable, pentacoordinate, 16-electron Fe^{II} complex $[PPN][Fe(CO)_2(CN)(S,NH-C_6H_4)]$ (**1**) were isolated as a dark brown solid after recrystallization from THF−hexane (Scheme 1). 2-Aminophenyl disulfide and H_2O were also obtained as byproducts identified by NMR. The IR spectrum of complex **1** in the aprotic solvent CH_3CN reveals a weak absorption band for the CN^- ligand at 2099 cm^{-1} while the two strong absorption bands (1997 s, 1933 s cm^{-1}) are assigned to the carbonyl stretching frequencies. The ^1H NMR spectrum shows the expected signals for the chelate $[S,NH-C_6H_4]^{2-}$ ligand in a diamagnetic d^6 Fe(II) species. When a THF solution of complex **1** is purged with ^{13}CO, the IR ν_{CO} peaks at 1992 and 1929 cm^{-1} immediately shift to 1946 and 1885 cm^{-1} while the IR ν_{CN} stretching frequency remains unchanged. The magnitude ~45 cm^{-1} of the isotopic shift ($\Delta\nu_{CO}$) is consistent with the calculated position, based only on the difference in masses between ^{12}CO and ^{13}CO.

Figure 2 presents the structure of complex **1** as an ORTEP; significant bond distances and angles are given in Table 2. The geometry around the iron(II) center is intermediate between trigonal bipyramidal and square pyramidal, with the bite angle of the chelating 2-thiolatophenylamido being 84.65(12)°. The five-membered chelate ring $[FeSNC_2]$ is almost planar with a deviation of 0.03 Å. The average Fe−CO and Fe−CN bond lengths of 1.763(6) and 1.926(6) Å, respectively, closely compare with those found in Fe(II) complexes $[Fe^{II}(PS3)(CO)(CN)]^{2-}$ (PS3 = tris(2-phenylthiolate)phosphine) (1.710(8) and 1.950(8) Å)[7] and $[CpFe(CN)_2(CO)]^-$ (1.73(2) and 1.906(9) Å).[6] The significantly shorter Fe−S bond of length 2.226(2) Å and Fe−N bond of length 1.855(4) Å in complex **1**, as comparing with the reported Fe(II)−S bond of length 2.3452(8) Å in the $[Fe(dsdm)(bmes)Fe(CO)_2]$ (H_2dsdm = *N*,*N*′-dimethyl-*N*,*N*′-bis-(2-sulfanylethyl)ethylenediamine; H_2bmes = 2-bis(sulfanylethyl)sulfide),[10] were attributed to the strong π-donating ability of

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[8] (a) Recently, the complexes $[(\mu\text{-S-(CH}_2)_3\text{-S)Fe}^{I}_2(CO)_6]$ (Fe(I)···Fe(I) distance 2.510(1) Å), $[(\mu\text{-S-(CH}_2)_3\text{-S)Fe}^{I}_2(CN)(CO)_5]^-$, and $[(\mu\text{-S-(CH}_2)_3\text{-S)Fe}^{I}_2(CN)_2(CO)_4]^{2-}$ were synthesized by M. Y. Darensbourg and coworkers (personal communication). (b) Very recently, the crystal structure of the dinuclear Fe(I)−thiolate cyanocarbonyl complex was reported by Rauchfuss and co-workers. Schmidt, M.; Contakes, S. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 9736.

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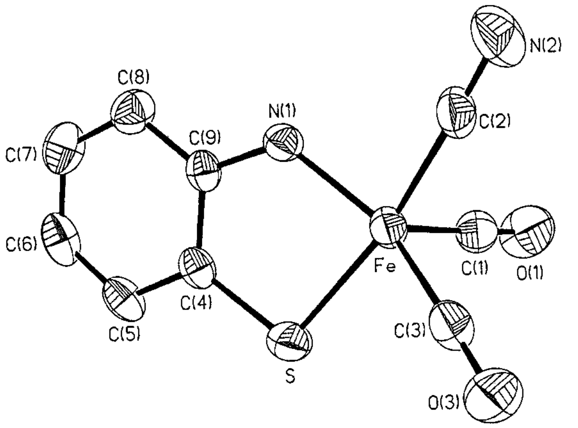

Figure 2. ORTEP drawing and labeling scheme of the $[Fe(CO)_2(CN)(S,NH\text{-}C_6H_4)]^-$ anion.

Table 1. Crystallographic Data of Complexes (a) **1**, (b) **4**$\cdot C_6H_{12}\cdot(CH_2Cl_2)_2$, and (c) **5**$\cdot$THF

	1	**4**$\cdot C_6H_{12}\cdot(CH_2Cl_2)_2$	**5**$\cdot$THF
chem formula	$C_{45}H_{34}N_3O_2$-P_2SFe	$C_{98}H_{86}N_4O_4$-$P_4S_4Cl_4Fe_2$	$C_{50}H_{45}N_6O_2$-P_2S_2Fe
fw	799.61	1889.33	943.83
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$C2/c$
λ, Å (Mo Kα)	0.7107	0.7107	0.7107
a, Å	9.8985(1)	10.887(2)	24.4494(3)
b, Å	14.1558(2)	17.574(2)	12.2321(2)
c, Å	14.4381(2)	24.673(4)	31.6646(3)
α, deg	90.094(1)	90	90
β, deg	99.168(1)	92.059(12)	96.737(1)
γ, deg	92.304(1)	90	90
V, Å^3	1995.56(4)	4717.8(11)	9404.5(2)
Z	2	2	8
d_{calcd}, g cm^{-3}	1.331	1.330	1.333
μ, mm^{-1}	0.552	0.629	0.524
T, K	295(2)	295(2)	295(2)
R	0.0859[a]	0.0698[a]	0.0578[a]
$R_{WF}2$	0.1237[b]	0.2192[b]	0.1323[b]
GOF	1.225	1.096	1.063

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

the bidentate $[S,NH\text{-}C_6H_4]^{2-}$ ligand which stabilized the unsaturated Fe(II) complex **1**.[11−13]

A reasonable reaction sequence accounting for the formation of complex **1** is shown in Scheme 1a−c, based on the IR ν_{CO} monitor of the reaction in THF at room temperature. An oxidative addition/decarbonylation reaction yielded an unstable intermediate *fac*-$[Fe^{II}(CO)_3(CN)(S\text{-}C_6H_4NH_2)_2]^-$ (**2**) (IR: 2111w (ν_{CN}), 2029 s, 1975 s (ν_{CO}) cm^{-1} (THF)) with two anionic $[S\text{-}C_6H_4NH_2]^-$ ligands bound to the Fe(II) metal in a monodentate (S-bonded) manner (Scheme 1a).[14] Chelation of one of the $[S\text{-}C_6H_4NH_2]^-$ ligands and concomitant dissociation of CO resulted in the formation of unstable, oily $[Fe^{II}(CO)_2(CN)(S,\text{-}NH_2\text{-}C_6H_4)(S\text{-}C_6H_4NH_2)]^-$ (**3**) (IR: 2104 w (ν_{CN}), 2013 s, 195 s (ν_{CO}) cm^{-1} (THF)) (Scheme 1b).[15] Upon contact with dry O_2, the color of complex **3** in THF solution immediately turned from brown to dark brown. The IR and ^1H NMR spectra indicated the formation of complex **1** accompanied by byproducts, H_2O and di(2-aminophenyl) disulfide (Scheme 1c). In this oxidative reaction, the Fe(II) was not observed to undergo oxidation, and consequently, the oxidation process was best assigned to the terminal thiolate ligand $[S\text{-}C_6H_4NH_2]^-$ to yield di(2-aminophenyl) disulfide via radical ($[S\text{-}C_6H_4NH_2]^\bullet$) recombination, and the concomitant deprotonation of the amine proton of anion **3** (the coordination of N atom presumably increases the acidity of amine protons to accelerate the deprotonation of NH_2) led to the formation of water.[16]

Table 2. Selected Bond Distances (Å) and Angles (deg) for (a) Complex **1** (b) Complex **4**

Complex 1			
Fe−C(1)	1.743(6)	Fe−C(3)	1.782(6)
Fe−C(2)	1.926(6)	Fe−N(1)	1.855(8)
Fe−S	2.226(2)	C(2)−N(2)	1.137(6)
C(1)−O(1)	1.141(6)	C(3)−O(3)	1.147(6)
S−C(4)	1.726(5)	N(1)−C(9)	1.364(5)
C(1)−Fe−C(3)	94.6(2)	C(1)−Fe−N(1)	115.1(2)
C(3)−Fe−N(1)	150.3(2)	C(1)−Fe−C(2)	94.2(2)
C(3)−Fe−C(2)	91.8(2)	N(1)−Fe−C(2)	87.7(2)
C(1)−Fe−S	98.0(2)	C(3)−Fe−S	90.0(2)
N(1)−Fe−S	84.65(12)	C(2)−Fe−S	167.6(2)
C(4)−S−Fe	99.5(2)	C(9)−N(1)−Fe	124.4(3)
N(2)−C(2)−Fe	178.4(5)		
Complex 4			
Fe(1)−C(1)	1.784(6)	Fe(1)−C(2)	1.771(6)
Fe(1)−C(3)	1.941(6)	Fe(1)−S(1)	2.290(2)
Fe(1)−S(2)	2.288(2)	Fe(1)−S(1A)	2.373(2)
Fe(1A)−S(1)	2.373(2)	C(3)−N(1)	1.138(7)
S(1)−C(4)	1.767(6)	S(2)−C(9)	1.747(6)
C(1)−Fe(1)−C(2)	91.0(3)	C(1)−Fe(1)−C(3)	91.1(3)
C(1)−Fe(1)−S(1)	94.2(2)	C(1)−Fe(1)−S(1A)	94.2(2)
C(1)−Fe(1)−S(2)	174.8(2)	S(1)−Fe(1)−S(2)	88.27(6)
S(1)−Fe(1)−S(1A)	83.80(6)	S(2)−Fe(1)−S(1A)	90.60(6)
Fe(1)−S(1)−Fe(1A)	96.20(6)	C(3)−Fe(1)−S(1A)	86.8(2)

The ability of complex **1** to bind the second thiolate ligand to form six-coordinate iron(II)−thiolate cyanocarbonyl complex was also demonstrated by the facile reaction with 2-aminophenylthiol. When a solution of complex **1** in THF was treated with 2-aminophenyl thiol, an immediate color change from dark brown to brown was observed. The absorption bands at 2101 w (ν_{CN}), 1992 s, and 1929 s (ν_{CO}) cm^{-1} disappeared, with concomitant formation of a spectrum (2104 w (ν_{CN}), 2013 vs, and 1958 s (ν_{CO}) cm^{-1} (THF)) assigned to formation of hexacoordinate complex **3** (Scheme 1c′). Apparently, the anionic pentacoordinate **1** and hexacoordinate **3** complexes are chemically interconvertible at ambient temperature. This result supports that the reactions of complex **1** with electrophiles (2-aminophenylthiol, etc.) occur at the more electron-rich amide site to yield charge-controlled, collision complexes.

The first dinuclear Fe(II)−thiolate cyanocarbonyl compound $[PPN]_2[(CN)(CO)_2Fe(\mu\text{-}S,S\text{-}C_6H_4)]_2$ (**4**) was prepared in a one-step synthesis by treating 1,2-benzenedithiol with complex **1** in THF under N_2 atmosphere at −10 °C (Scheme 2a). Complex **4** was isolated as an air-stable brown solid at −10 °C. The thermally unstable complex **4** is soluble in CH_2Cl_2 and CH_3-

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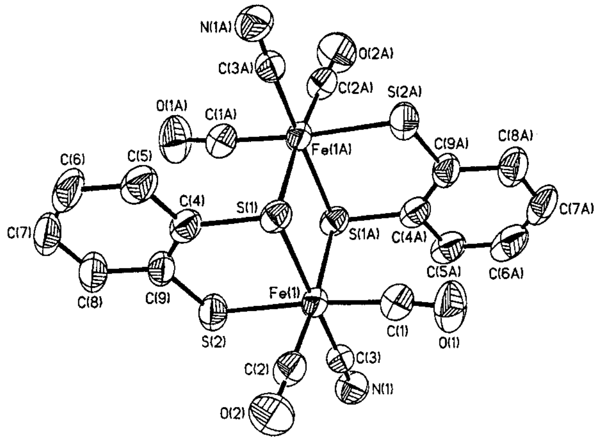
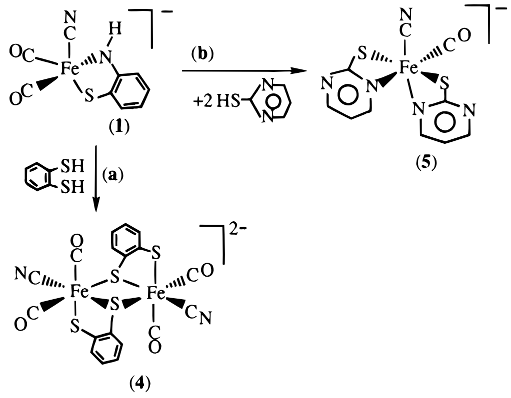


Figure 3. ORTEP drawing and labeling scheme of the $[(CN)(CO)_2Fe(\mu\text{-}S,S\text{-}C_6H_4)]_2{}^{2-}$ anion with thermal ellipsoids drawn at the 50% probability.

Scheme 2



CN and partially soluble in THF. The structure of complex **4** is depicted in Figure 3. Selected bond distances and angles are given in Table 2. Complex **4** consists of discrete PPN^+ cations and $[(CN)(CO)_2Fe(\mu\text{-}S,S\text{-}C_6H_4)]_2{}^{2-}$ anions. The dinuclear $[(CN)(CO)_2Fe(\mu\text{-}S,S\text{-}C_6H_4)]_2{}^{2-}$ is electronically dianionic and therefore both irons should be divalent. Complex **4** possesses crystallographically imposed centrosymmetry. Two six-coordinate Fe(II) atoms are connected via two thiolate bridges, and both CN^- ligands (C(3)N(1) and C(3A)N(1A) ligands) point into the antiparallel direction. As can be seen from Figure 3, two pairs of CO groups (C(2)O(2), C(2A)O(2A) and C(1)O(1), C(1A)O(1A)) are also bonded to iron(II) atoms in a parallel direction, respectively. Each iron atom is surrounded pseudooctahedrally by two bridging thiolates, one terminal thiolate, two terminal carbonyl groups, and one cyanide ligand, with the bite angle of the chelating 1,2-benzenedithiolate being 88.27(6)° and the obtuse angle (S(1)−Fe(1)−S(1A)) being 83.80(6)°.

The nearly identical Fe(1)−S(1) and Fe(1)−S(2) bond lengths of 2.290(2) and 2.288(2) Å, respectively, well within the range (2.3 Å) observed for [Fe] hydrogenases from *D. desulfuricans*,[3] are considerably longer than the Fe(1A)−S(1) bond distance of 2.373(2) Å in complex **4** (Figure 3). These differences probably originate from the additional π-donating interactions of the S(1) and S(2) with Fe(1) metal center. The Fe(1)−S(1) and Fe(1)−S(2) bond distances of 2.289(2) Å (average) in complex **4** are longer than those in $[Fe(S,S\text{-}C_6H_4)(PMe_3)_3]$ (2.205(3) Å)[17] and in complex **1** (2.226(2) Å) stabilized by incorporation of π-donating chelating $[S,NH\text{-}C_6H_4]^{2-}$ ligand, but shorter than that observed for *cis*-$[Fe(CO)_2(S\text{-}C_5H_4N)_2]$ (average Fe(II)−S = 2.325(3) Å).[15] The average Fe−CO and Fe−CN bond lengths are 1.778(6) and 1.941(6) Å, respectively. The Fe(II)···Fe(II) distance of 3.472 Å in the model complex **4** is longer than those reported for the diiron subcluster active-site (2.6 and 2.62 Å) of [Fe] hydrogenases,[3,4] and excludes any direct metal−metal interactions. Formation of complex **4** can also be interpreted as coordinative association of two anionic mononuclear $[(CO)_2(CN)Fe(S,S\text{-}C_6H_4)]^-$. It may be attributed to the avoidance of electron deficiency at the iron(II) centers as well as to the availability of the nonbonding electron pairs of the sulfur atoms in $[(CO)_2(CN)Fe(S,S\text{-}C_6H_4)]^-$.[18] Notably, both the electronic and steric reasons are responsible for the formation of complex **4**.

Complex **4** exhibits a diagnostic ^1H NMR spectrum with the 1,2-benzenedithiolate proton resonances at 6.60 (t), 6.79 (t), 7.22 (d), and 7.33 (d) ppm which are consistent with the Fe(II) having a low-spin d^6 electronic configuration in an octahedral ligand field. The IR spectrum of complex **4** in the aprotic solvent CH_2Cl_2 reveals a weak absorption band for the CN^- ligands at 2101 cm^{-1}, and two strong absorption bands for the CO groups at 1960 and 2013 cm^{-1}, as expected for the existence of centrosymmetry in complex **4** (vibrationally uncoupled CO groups and CN^- groups on adjacent iron(II) sites).[12b,19] When the CH_2Cl_2 solution of complex **4** was exposed to ^{13}CO at 0 °C, absorbances at 1968 and 1915 cm^{-1} appeared within 10 min. Reappearance of the 2013 and 1960 cm^{-1} bands on removal of the ^{13}CO and replacement with ^{12}CO atmosphere demonstrated reversibility of CO ligand lability of complex **4**.

In contrast, protonation of complex **1** by 2 equiv of 2-mercaptopyrimidine in THF under N_2 at ambient temperature yielded hexacoordinate iron(II)−thiolate cyanocarbonyl complex $[PPN][Fe(CO)(CN)(S\text{-}C_4H_3N_2)_2]$ (**5**) with two anionic $[S\text{-}C_4H_3N_2]^-$ ligands bound to the Fe(II) ion in a bidentate manner (S,N-bounded) (Scheme 2b). The IR spectrum of complex **5** in the aprotic solvent CH_3CN displayed a weak ν(CN) band at 2090 cm^{-1} and a broad strong ν(CO) band at 1945 cm^{-1}, well within the range observed for [Fe] hydrogenase isolated from *D. vulgaris*.[5] The reversibility of CO ligand lability of complex **5** was demonstrated by exposing the CH_2Cl_2 solution of complex **5** to ^{13}CO. The IR ν_{CO} peak at 1949 cm^{-1} shifted to a single absorbance at 1904 cm^{-1}. The formation of complex **5** is presumed to occur via protonation of amide (NH), subsequent elimination of 2-aminophenylthiol, and concomitant chelation of $[S\text{-}C_4H_3N_2]^-$ ligands. The electrochemistry of complex **5**, measured in CH_3CN with 0.1 M $[n\text{-}Bu_4N][PF_6]$ as supporting electrolyte (scan rate 1.5 V/s), reveals a reversible oxidation−reduction process at +0.12 V ($E_{1/2}$) (vs $Ag/AgNO_3$) (Figure 4). The infrared spectrum of solution obtained by the chemical oxidation of complex **5** in CH_3CN at − 20 °C with $[Cp_2Fe][PF_6]$ displays absorption bands at 2096 and 1962 cm^{-1} which are assigned to the ν(CN) and ν(CO) vibrational frequencies of the thermally unstable neutral $Fe^{III}(CO)(CN)(S\text{-}C_4H_3N_2)_2$, respectively. Complex **5** was reobtained upon addition of 1 equiv of $[PPN][BH_4]$ to $Fe^{III}(CO)(CN)(S\text{-}C_4H_3N_2)_2$ in CH_3CN at −20 °C.

Figure 5 displays an ORTEP plot of the anionic mononuclear complex **5**. The selected bond distances and angles are listed

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(17) Sellmann, D.; Kleine-Kleffmann, U.; Zapf, L.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1984**, *263*, 321.

(18) Liaw, W.-F.; Chiou, S.-J.; Lee, G.-H.; Peng, S.-M. *Inorg. Chem.* **1998**, *37*, 1131.

(19) (a) Liaw, W.-F.; Chen, C.-H.; Lee, C.-M.; Lin, G.-Y.; Ching, C.-Y.; Lee, G.-H.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **1998**, *353*. (b) Liaw, W.-F.; Lee, C.-M.; Horng, L.; Lee, G.-H.; Peng, S.-M. *Organometallics* **1999**, *18*, 782.

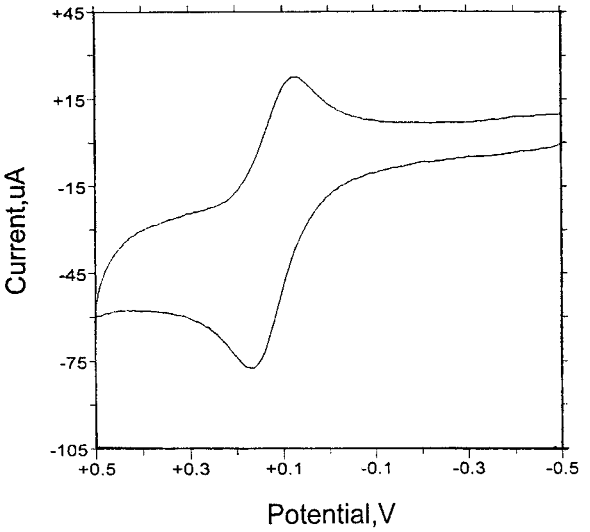


Figure 4. Cyclic voltammogram of a 2 mM solution of complex **5** in 0.1 M [n-Bu_4N][PF_6]/CH_3CN with glassy carbon working electrode at a scan rate of 1.5 V/s.

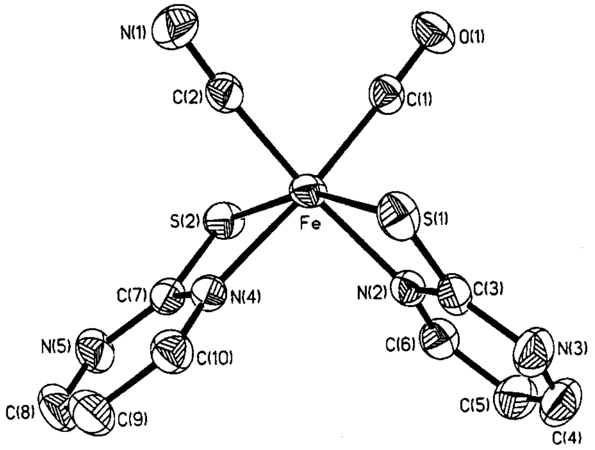


Figure 5. ORTEP drawing and labeling scheme of the [Fe(CO)(CN)-(S-$C_4H_3N_2$)$_2$]$^-$ anion.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **5**

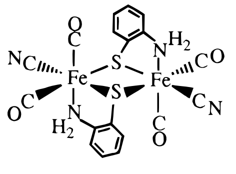
Fe−C(1)	1.823(3)	Fe−C(2)	1.845(4)
Fe−N(4)	1.999(3)	Fe−N(2)	2.001(3)
Fe−S(1)	2.3323(9)	Fe−S(2)	2.3550(9)
C(1)−O(1)	1.130(4)	C(2)−N(1)	1.135(4)
S(1)−C(3)	1.715(4)	S(2)−C(7)	1.735(4)
C(1)−Fe−C(2)	84.5(2)	C(1)−Fe−N(4)	173.17(12)
C(2)−Fe−N(4)	92.76(13)	C(1)−Fe−N(2)	92.83(13)
C(2)−Fe−N(2)	170.53(12)	N(4)−Fe−N(2)	90.80(10)
C(1)−Fe−S(1)	91.64(10)	C(2)−Fe−S(1)	100.06(11)
N(4)−Fe−S(1)	95.02(8)	N(2)−Fe−S(1)	70.88(8)
C(1)−Fe−S(2)	103.44(10)	N(4)−Fe−S(2)	70.38(8)
S(2)−Fe−S(1)	160.81(4)		

in Table 3. The constraint of the 2-mercaptopyrimidine ligand generates ca. 70.88(8)° S(1)−Fe−N(2) and 70.38(8)° S(2)−Fe−N(4) angles, enforcing a severe distortion from octahedron at the hexacoordinate iron(II) site. Because of disorder, the exact Fe−CN and Fe−CO bond distances are poorly determined in complex **5**. The hexacoordinate sphere as well as the long Fe^{II}−S and Fe^{II}−N bond distances (average 2.344(9) and 2.000(3) Å, respectively) of complex **5**, comparing with the pentacoordinate complex **1** (2.226(2) and 1.855(8) Å respectively), reflect the fact that bidentate [S-$C_4H_3N_2$]$^-$ may not serve as a strong π-donating ligand.

Table 4. Infrared Spectroscopic Data in ν(CO) and ν(CN) Regions

compd	ν(CN), cm^{-1}	ν(CO), cm^{-1}	references
1	(CH_3CN) 2099	1997, 1933	this work
	(THF) 2101	1992, 1928	
	(CH_2Cl_2) 2095	2000, 1936	
4	(CH_3CN) 2102	2011, 1961	this work
	(THF) 2106	2008, 1950	
	(CH_2Cl_2) 2100	2013, 1960	
5	(CH_3CN) 2090	1945	this work
	(THF) 2094	1942	
	(CH_2Cl_2) 2087	1948	
D. vulgaris	(air) 2106, 2087	2007.5, 1983, 1847.5	5a
[Fe] H_{2ase}	(H_2/Ar) 2095, 2079	2016, 1972, 1965, 1940	
	(H_2/CO) 2096, 2088	2016, 1971, 1964	
	(H_2) 2079, 2041	1965, 1941, 1916, 1894	
C. vinosum [NiFe]H_{2ase}	2093, 2083	1945	1d

In comparison, protonation of complex **1** by HBF_4 in CH_2Cl_2 under N_2 at −10 °C yielded, presumably, the neutral dinuclear iron(II)−thiolate cyanocarbonyl complex [(CN)-(CO)$_2$Fe(μ-S-C_6H_4-NH_2)]$_2$ (**A**), isostructural with complex **4**.[20]



(**A**)

The IR spectrum of the extremely unstable complex **A** in the aprotic solvent CH_2Cl_2 displayed a weak ν(CN) band at 2112 cm^{-1}, and two broad strong ν(CO) bands at 2056 and 2008 cm^{-1}. Attempts to recrystallize complex **A** have thus far been unsuccessful.

Conclusion and Comments

Applications of anionic iron(0)−cyanocarbonyl for preparation of iron(II)−thiolate cyanocarbonyl proved a successful approach in this direction. Isolation of the unsaturated complex **1** shows an access to the mononuclear iron(II)−thiolate cyanocarbonyl compound containing a vacant coordination site, a potential binding site for soft ligands.[3,6a] The bimetallic iron(II)−thiolate cyanocarbonyl complex **4** presented here is the first example of the binuclear iron(II)−thiolate compounds with mixed CO and CN$^-$ ligands serving as the promising structural and functional model compounds of the dinuclear iron active sites of [Fe] hydrogenases isolated from *D. desulfuricans* and *C. pasteurianum*.[3,4] We noticed that the thiolate-bridged binuclear Fe(II) complexes typically have an Fe···Fe distance of 3.2(2) Å (3.472 Å in complex **4**, 3.420(1) Å in [Fe(CO)(μ-"S_4")]$_2$ ("S_4"$^{2-}$ = 1, 2-bis(2-mercaptophenylthio)ethanato(2−)),[12b] and 3.0747(7) Å in [Fe(dsdm)(bmes)Fe(CO)$_2$]).[10] However, the Fe···Fe distances of 2.6 and 2.62 Å found in [Fe] hydrogenases respectively[3,4] are well within the range of those of dinuclear Fe(I) compounds.[8,21] The vibrational spectroscopies of the Fe(CO)$_2$(CN) and Fe(CO)(CN) fragments (ν(CN) ranges from 2094 to 2105 cm^{-1}, ν(CO) ranges from 1929 to 2013 cm^{-1}) found in complexes **1**, **3**, **4**, and **5** may be regarded as spectroscopic references of [Fe] hydrogenases in the various enzymatic states (Table 4). In comparison with IR ν_{CO} and ν_{CN}

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(20) The analogue [(CO)$_3$Mn(μ-S-C_6H_4-NH_2)$_2$Mn(CO)$_3$] was synthesized by reaction of [PPN][Mn(CO)$_3$(S,NH-C_6H_4)] with HBF_4 in THF, and was characterized by IR and X-ray structural analysis. To be submitted for publication.

(21) Dahl, L. F.; Wei, C. H. *Inorg. Chem.* **1963**, *2*, 328.

spectra of *D. vulgaris* [Fe] hydrogenase, the IR ν_{CO} and ν_{CN} spectra of the centrosymmetric model complex **4** (vibrationally uncoupled CO groups and CN^- groups on adjacent iron(II) sites; two CO stretching bands and one CN stretching band) suggests the lack of centrosymmetry in dinuclear iron subcluster active sites of [Fe] hydrogenases.[3−5] A ∼4 cm^{-1} shift in the ν(CN) value and ∼23 cm^{-1} shift in the ν(CO) value were observed in the case of changes in the coordination of the iron(II) center from pentacoordinate Fe(II)−thiolate **1** to hexacoordinate Fe(II)−thiolate cyanocarbonyl **3**. A ∼6 cm^{-1} shift in the ν(CN) value and a ∼17 cm^{-1} shift in the ν(CO) value were observed from Fe(II) complex **5** to the oxidized form $Fe^{III}(CO)(CN)(S\text{-}C_4H_3N_2)_2$. A ∼5 cm^{-1} shift in the ν(CN) value and a ∼20 cm^{-1} shift in the ν(CO) value were observed from anionic **1** to dianionic **4**. Notably, the response of ν(CN) to electron density changes (i.e. coordination, ancillary ligand, and oxidation state changes) around the Fe center shows less sensitivity as compared with that of ν(CO) in these iron(II,III)−thiolate complexes with mixed CO and CN^- ligands.[6,7]

Experimental Section

Manipulations, reactions, and transfers of samples were conducted under nitrogen according to standard Schlenk techniques or in a glovebox (argon gas). Solvents were distilled under nitrogen from appropriate drying agents (diethyl ether from CaH_2; acetonitrile from $CaH_2-P_2O_5$; methylene chloride from P_2O_5; hexane and tetrahydrofuran (THF) from sodium−benzophenone) and stored in dried, N_2-filled flasks over 4 Å molecular sieves. Nitrogen purge was used on these solvents before use and transfers to reaction vessels were via stainless steel cannula under positive pressure of N_2. The reagents iron pentacarbonyl, 2-aminophenyl disulfide, 1,2-benzenedithiol, hexamethyl disilazane sodium salt, 2-aminophenylthiol, 2-mercaptopyrimidine, ferrocenium hexafluorophosphate, bis(triphenylphosphoranylidene)ammonium chloride, and fluoroboric acid (Lancaster/Aldrich) were used as received. Complex $[PPN][Fe(CO)_4(CN)]$ was synthesized by published procedures.[9] Infrared spectra of the carbonyl ν(CO) and cyanide ν(CN) frequency region (2200−1700 cm^{-1}) were recorded on a Bio-Rad Model FTS-185 spectrophotometer with sealed solution cells (0.1 mm) and KBr windows. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Model AC 200 spectrometer. UV/vis spectra were recorded on a GBC 918 spectrophotometer. Cyclic voltammetric measurements were performed on a BAS-100B electrochemical analyzer, using glassy carbon as the working electrode. Cyclic voltammograms were obtained from 2 mM analyte concentration in CH_3CN using 0.1 M $[n\text{-}Bu_4N][PF_6]$ as supporting electrolyte. Analyses of carbon, hydrogen, and nitrogen were obtained with a CHN analyzer (Heraeus).

Preparation of $[PPN][Fe(CO)_2(CN)(S,NH\text{-}C_6H_4)]$ (1). The compounds $[PPN][Fe(CO)_4(CN)]$ (0.4 mmol, 0.293 g)[9] and 2-aminophenyl disulfide (0.4 mmol, 0.100 g) dissolved in 4 mL of THF were stirred at ambient temperature. A vigorous reaction occurred with evolution of CO gas. The reaction was monitored with FTIR. IR spectra [2111 w (ν_{CN}), 2029 s, 1975 s (ν_{Co}) cm^{-1} (THF), and 2104 w (ν_{CN}), 2013 s, 1958 s (ν_{Co}) cm^{-1} (THF)] were assigned to the formation of *fac*-$[PPN][Fe(CO)_3(CN)(S\text{-}C_6H_4NH_2)_2]$ (**2**) and $[PPN][Fe(CO)_2(CN)(S,NH_2\text{-}C_6H_4)(S\text{-}C_6H_4NH_2)]$ (**3**), respectively.[13,14] The reaction mixture was stirred overnight at room temperature, and a gentle stream of dry O_2 was bubbled through the brown solution. The brown solution completely converted into a dark brown solution accompanied by formation of byproducts, di(2-aminophenyl) disulfide and H_2O (identified by ^{1}H NMR in the separate NMR experiment). The dark brown solution was then filtered through Celite and hexane (15 mL) was added to precipitate the air-stable, dark brown solid $[PPN][Fe(CO)_2(CN)(S,NH\text{-}C_6H_4)]$ (**1**). The dark brown solid was washed with hexane and recrystallized from THF−hexane. The yield of dark brown product **1** was 0.48 g (75%). Diffusion of hexane into a solution of complex **1** in THF at −15 °C for 4 weeks led to dark brown crystals suitable for X-ray crystallogaphy. IR: 2099 w (ν_{CN}), 1997 s, 1933 s (ν_{Co}) cm^{-1} (CH_3CN); 2101 w, 1992 s, 1929 s cm^{-1} (THF); 2095 w, 2000 s, 1936 s cm^{-1} (CH_2Cl_2). ^{1}H NMR (C_4D_8O): δ 10.34 (br) (N−H), 7.25 (m), 6.77 (m) ppm ($S\text{-}C_6H_4$). Absorption spectrum (THF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 604 (3234), 525 (4318), 433 (6788), 327 (7270). Anal. Calcd for $C_{45}H_{35}O_2N_3SP_2Fe$: N, 5.26; C, 67.59; H, 4.42. Found: N, 5.49; C, 67.14; H, 4.75.

Preparation of $[PPN]_2[(CN)(CO)_2Fe(\mu\text{-}S,S\text{-}C_6H_4)]_2$ (4). Compound **1** (0.5 mmol, 0.4 g) was loaded into a 25 mL Schlenk tube, and 2 mL of dry THF was added by cannula under a positive pressure of N_2. 1,2-Benzenedithiol (60 μL, 0.5 mmol) was added to the dark brown solution of compound **1**. After being stirred at −10 °C for 20 min, the reaction solution was cooled to −15 °C and a brown precipitate was deposited gradually, collected by filtration, and washed several times with THF to give complex **4**. The brown solid was dried under vacuum. The yield of brown complex **4** was 0.154 g (37%). X-ray quality crystals were obtained by diffusion of hexane−diethyl ether into a CH_2Cl_2 solution of complex **4** at −15 °C. IR: 2100 w (ν_{CN}), 2013 s, 1960 s (ν_{Co}) cm^{-1} (CH_2Cl_2); 2102 w (ν_{CN}), 2011 s, 1961 s (ν_{Co}) cm^{-1} (CH_3CN). ^{1}H NMR (CD_2Cl_2): δ 6.60 (t), 6.79 (t), 7.22 (d), 7.33 (d) ppm ($S,S\text{-}C_6H_4$). Absorption spectrum (CH_2Cl_2) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 426 (4807), 562 (3510), 650 (1548). Anal. Calcd for $C_{90}H_{68}O_4N_4S_4P_4Fe_2$: N, 3.43; C, 66.10; H, 4.19. Found: N, 3.68; C, 65.89; H, 4.62.

Preparation of $[PPN][Fe(CO)(CN)(S\text{-}C_4H_3N_2)_2]$ (5). To a stirred solution of compound **1** (0.320 g, 0.4 mmol) in THF (5 mL) was added 2-mercaptopyrimidine (0.090 g, 0.8 mmol) under N_2 at room temperature. The reaction solution was stirred for 6 h, and then hexane was added to precipitate the brown solid. The reaction mixture was filtered, and the brown solid was dried under vacuum to afford the pure product in essentially quantitative yield (0.141 g, 37.5%). Recrystallization from saturated THF solution with hexane diffusion gave brown crystals of complex **5** at room temperature. IR: 2090 w (ν_{CN}), 1945 s (ν_{Co}) cm^{-1} (CH_3CN); 2094 w, 1942 s cm^{-1} (THF); 2087 w (ν_{CN}), 1948 s (ν_{Co}) cm^{-1} (CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ 6.51 (t), 6.81 (t), 7.96 (m), 8.14 (m), 8.33 (m), 8.89 (m) ppm ($SC_4H_3N_2$). Absorption spectrum (CH_2Cl_2) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 321 (9065), 385 (4320), 606 (104). Anal. Calcd for $C_{50}H_{44}O_2N_6S_2P_2Fe$: N, 8.91; C, 63.69; H, 4.70. Found: N, 8.81; C, 63.38; H, 4.75.

Reaction of $[PPN][Fe(CO)(CN)(S\text{-}C_4H_3N_2)_2]$ with $[Cp_2Fe][PF_6]$. A solution containing 0.189 g (0.2 mmol) of complex **5** and 0.067 g (0.2 mmol) of $[Cp_2Fe][PF_6]$ in CH_3CN (3 mL) was stirred at −20 °C. The reaction was monitored immediately by IR. The IR spectrum (2096 w (ν_{CN}), 1962 s (ν_{Co}) cm^{-1}) was assigned to the formation of neutral $Fe^{III}(CO)(CN)(S\text{-}C_4H_3N_2)_2$. In the same flask 0.2 mmol of $[PPN][BH_4]$ (0.112 g) in CH_3CN solution was added, followed by stirring at −20 °C for 5 min. The brown solid that was obtained upon removal of solvent from the resulting solution was extracted with 5 mL of degassed THF. Subsequent solvent removal produced complex **5** (identified by IR) ,which was washed with hexane and dried under vacuum.

Crystallography. Crystallographic data of complexes **1**, **4**, and **5** are summarized in Table 1, and in the Supporting Information. The crystals of **1**, **4,** and **5** are chunky. The crystals of **1**, **4**, and **5** chosen for X-ray diffraction studies measured 0.40 × 0.23 × 0.03 mm, 0.55 × 0.50 × 0.45 mm, and 0.40 × 0.30 × 0.25 mm**,** respectively. Each crystal was mounted on a glass fiber and quickly coated in epoxy resin. Unit-cell parameters for complex **4** were obtained by the least-squares refinement from 25 reflections with θ between 1.65 and 25.00°. Least-squares refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms and fixed hydrogen atoms contribution was based on F^2. Diffraction measurements were carried out on a Nonius CAD 4 diffractometer with graphite-monochromated Mo Kα radiation.[22] A φ scan absorption correction was made. The NRCC−SDP−VAX package of programs was employed,[23] and atomic scattering factors were from ref 24. Diffraction measurements for complexes **1** and **5** were carried out at 295(2) K on a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα radiation (λ 0.7107 Å) and θ between 1.43 and 25.03° for complex **1** and between 1.30 and 27.49° for complex **5**. Least-squares refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms and fixed

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(22) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(23) Gabe, E. J.; LePage, Y.; Chrarland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(24) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4, Table 2.2B.

hydrogen atoms contribution was based on F^2. A SADABS[25] absorption correction was made. The SHELXTL[26] structure refinement program was employed.

Acknowledgment. We gratefully acknowledge financial support from the National Science Council (Taiwan). We also thank Prof. Marcetta Y. Darensbourg for helpful suggestions.

Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters (PDF). An X-ray crystallographic file for the structure determinations of [PPN][Fe(CO)$_2$(CN)(S,NH-C$_6$H$_4$)], [PPN]$_2$[(CN)(CO)$_2$Fe(μ-S,S-C$_6$H$_4$)]$_2$, and [PPN][Fe(CO)(CN)(S-C$_4$H$_3$N$_2$)$_2$] (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA992300Q

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[25] Sheldrick, G. M. SADABS, Siemens Area Detector Absorption Correction Program, University of Göttingen, 1996.

[26] Sheldrick, G. M. SHELXTL, Program for Crystal Structure Determination, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1994.