

The Influence of Cyanide on the Carbonylation of Iron(II): Synthesis of Fe–SR–CN–CO Centers Related to the Hydrogenase Active Sites

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Received April 4, 2001

Revised Manuscript Received May 30, 2001

Recently iron sulfides have been proposed as being central to the emergence of life.¹ For example, Huber and Wächtershäuser showed that iron sulfides catalyze carbonylation reactions leading to the formation of peptides and thioesters.² The two best characterized Fe–S–CO enzymes (the hydrogenases) also feature cyanide, and it is likely that cyanide has a decisive stabilizing effect on the CO binding. Cyanide has been previously considered in the prebiotic context,³ but the influence of cyanide on the carbonyl chemistry of iron has received scant attention. In this report, we show that cyanide has a major effect on the carbonylation of ferrous salts, especially in the presence of sulfur ligands.

CO-saturated MeCN slurries of FeCl₂ were treated sequentially with NaSAr and Et₄NCN to give good yields of (Et₄N)₂[Fe(SAr)₂(CN)₂(CO)₂] (**1a**, Ar = Ph; **1b**, Ar = *p*-tol) (Scheme 1). These same species also form in low yield upon treatment of Fe₃(SPh)₆(CO)₆ with CN⁻.⁴ NMR and IR⁵ spectroscopic studies established that **1a** and **1b** exist in solution as both the *trans,cis*- and *cis,cis*-isomers. The molecular structure of *trans,cis*-**1a** was determined crystallographically (Figure 1). In solution **1** is configurationally stable under a CO atmosphere, although in the absence of CO it suffers ligand redistribution to give (Et₄N)₂[Fe(SPh)₄] and *trans*-[Fe(CN)₄(CO)₂]²⁻ (**2**) (vide infra). Markó had previously demonstrated the carbonylation of Fe(II) thiolate solutions in the presence of chelating donor ligands, e.g. bipyridine, ethylenediamine, and Ph₂PCH₂CH₂PPh₂.⁶

Carbonylation of nonaqueous Fe(II)/EtS⁻ solutions (as described for the preparation of **1**) in the presence of CN⁻ afforded **2**, not analogues of **1**. IR spectra of fresh reaction solutions indicate that [Fe(SEt)₂(CN)₂(CO)₂]²⁻ is in fact formed, but that this species redistributes readily to the tetracyanide.

In the absence of CN⁻, carbonylation of Fe(II)/PhS⁻ solutions gives the ferrous derivatives Fe₃(SPh)₆(CO)₆ and [Fe(SPh)₃(CO)₃]⁻.^{4,6,7} The carbonylation of Fe(II)/NaSEt solutions affords the *subferrous* species Fe₂(SEt)₂(CO)₆ as first reported by Reihlen.⁸ The yields are low (3–6%), and pyrophoric iron metal is also formed in substantial amounts, but the formation of low

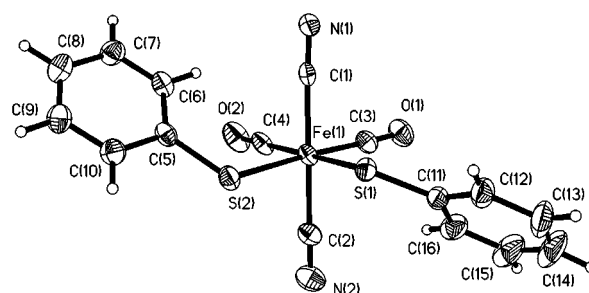
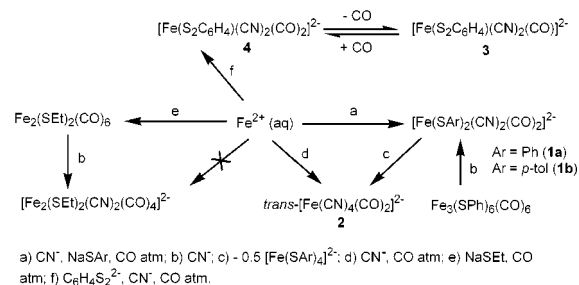


Figure 1. Structure of the dianion in (Et₄N)₂[Fe(SAr)₂(CN)₂(CO)₂] (**1a**) with thermal ellipsoids set at the 50% probability level. Selected distances (Å) and angles (deg): Fe–C1, 1.935(4); Fe–C2, 1.928(4); Fe–C3, 1.782(4); Fe–C4, 1.805(4); Fe–S1, 2.3479(10); Fe–S2, 2.3489(10); S(1)–Fe(1)–S(2), 82.43(3).

Scheme 1



valent iron may be significant in view of the likely role of subferrous species in the iron-only hydrogenases.⁹ Interestingly, the reductive nature of this carbonylation is quenched by the presence of cyanide. We showed that Fe₂(SEt)₂(CO)₆ reacts with CN⁻ to give [Fe₂(SEt)₂(CN)₂(CO)₄]²⁻, but such subferrous species are *not* observed when the Fe(II)/NaSEt solutions are carbonylated in the presence of CN⁻ (Scheme 1),¹⁰ i.e., our studies do not support the spontaneous assembly of hydrogenase-like subferrous species from Fe(II)/CN⁻ solutions.

In analogy to the preparation of **1**, we examined the carbonylation of Fe(II) solutions in the presence of benzenedithiolate dianion (bdt²⁻ = C₆H₄S₂²⁻). This reaction afforded complexes (Et₄N)₂[Fe(bdt)(CN)₂(CO)] (**3**) and (Et₄N)₂[Fe(bdt)(CN)₂(CO)₂] (**4**). Initially complex **4** is observed spectroscopically; however, purging N₂ through the reaction solution gave **3**, which was characterized crystallographically as being pentacoordinate (Figure 2). The Fe–CN and Fe–CO distances differ by 0.2 Å, consistent with the strong π-bonding role of the CO vs the primary σ-interaction for the CN⁻ ligand. Several related 16 e⁻ pentacoordinate Fe(II) dithiolenes are known, e.g., Fe(bdt)(PMe₃)₃ and Fe-[S₂C₂(SMe)₂](CO)(PR₃)₂,¹¹ but **3** is distinctive because it very closely simulates the Fe site in the [NiFe]-hydrogenases, which also feature (SR)₂(CN)₂(CO) coordination.¹²

Previously the best models for this site included the octahedral complex [Fe(SR)₃(PR₃)(CN)(CO)]²⁻, the Fe unit in {[Fe(NS₃)-

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(5) Selected IR spectra in MeCN for **1–5** (cm⁻¹). **1a**: ν_{CN} 2103(w), 2094(w), 2075(vw); ν_{CO} 2007(s), 1976(sh) 1953(s). **2**: ν_{CN} 2103 (s); ν_{CO} 1999 (s). **3**: ν_{CN} 2080(w), 2075(vw); ν_{CO} 1897(s). **4**: ν_{CN} 2104(vw), 2096(w); ν_{CO} 2006(s), 1949(s). **5**: ν_{CN} 2196(s), 2159(s); ν_{CO} 2005(s), 1949(s).

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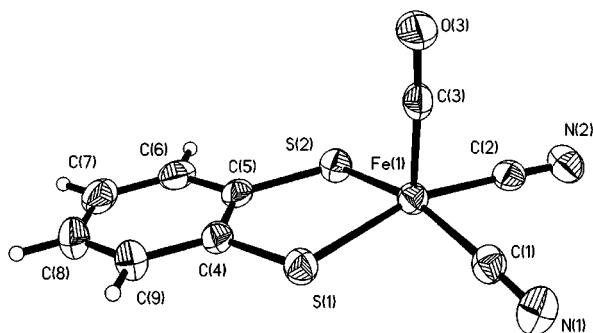


Figure 2. Structure of the dianion in $(\text{Et}_4\text{N})_2[\text{Fe}(\text{S}_2\text{C}_6\text{H}_4)(\text{CN})_2(\text{CO})]$ (**3**) with thermal ellipsoids set at the 50% probability level. Selected bond distances (Å) and angles (deg): Fe–S1, 2.1987(6); Fe–S2, 2.2081(6); Fe–C1, 1.922(2); Fe–C2, 1.926(2); Fe–C3, 1.694(2); C1–Fe–C2, 88.24(8); C1–Fe–C3, 95.93(9); C2–Fe–C3, 93.85(9); S1–Fe–S2, 89.49(2).

$(\text{CO})_2\text{NiCl}(\text{dppe})$ ($\text{NS}_3 = \text{N}(\text{CH}_2\text{CH}_2\text{S})_3$), and the cyclopentadienyl derivative $[\text{CpFe}(\text{CN})_2(\text{CO})]^-$.^{13,14} In **3**, the complete $\text{Fe}(\text{SR})_2(\text{CN})_2(\text{CO})$ microenvironment of the enzyme is replicated. The IR spectrum for **3** exhibits ν_{CO} and ν_{CN} which are lower than those reported for the Fe center in *D. gigas* (2093, 2083, 1947 cm^{-1}).¹² Coordination of a $\text{Ni}(\text{SR})_2$ unit to the sulfur atoms in **3** would, however, decrease electron density at Fe with a corresponding increase in ν_{CO} and ν_{CN} to values more similar to those in the $\text{Fe}(\text{CN})_2(\text{CO})$ unit in the enzyme. Such a shift in ν_{CO} was observed^{13b} in the conversion of $[\text{Fe}(\text{NS})_3(\text{CO})]^-$ ($\nu_{\text{CO}} = 1885 \text{ cm}^{-1}$) into $\{\text{Fe}(\text{NS}_3)(\text{CO})_2\}\text{NiCl}(\text{dppe})$ ($\nu_{\text{CO}} = 1944, 2000 \text{ cm}^{-1}$). Thus **3** is an obvious precursor to bimetallic NiFe derivatives.

Carbonylation of an MeCN solution of **3** gave *cis,cis*- $[\text{Fe}(\text{bdt})(\text{CN})_2(\text{CO})_2]^{2-}$ (**4**), while a nitrogen purge reverses this reaction. The reversible carbonylation of **3** is relevant to the proposed binding of H_2 at Fe in the $[\text{NiFe}]$ -hydrogenases. NMR measurements show that **3** reacts with Et_4NCN to give $[\text{Fe}(\text{bdt})(\text{CN})_3(\text{CO})]^{3-}$, although under CO, the tricyanide reverts to **4**, demonstrating that CN^- , which is normally considered a potent ligand, is displaceable by CO under mild conditions.

Analogous to the preparation of **3**, the reaction of *t*-BuNC, FeCl_2 , Na_2bdt , and CO gave $\text{Fe}(\text{bdt})(\text{CO})_2(\text{CN}-t\text{-Bu})_2$ (**5**). It is interesting that neutral **5** is relatively stable in the 18 e^- form, i.e., it does not decarbonylate. In contrast dianion **4** readily loses CO to give the 16 e^- derivative. This finding suggests that negative charge significantly enhances S-to-Fe π donation in **3**, an issue that will be subjected to further computational analysis.

Compound **3** also forms in excellent yield (based on bdt^{2-}) from the reaction of $\text{Fe}_2(\text{bdt})(\text{CO})_6$ (**6**) with 2 equiv of Et_4NCN . This transformation is unexpected based on previous studies on the reaction of CN^- with $\text{Fe}_2(\text{SR})_2(\text{CO})_6$ ($\text{R} = \text{alkyl}, \text{C}_6\text{H}_5$).^{10,15,16} This disproportionative transformation occurs via the intermediacy of $[\text{Fe}(\text{bdt})(\text{CN})(\text{CO})_2]^{2-}$,¹⁷ which formed when **6** was treated with 1 equiv of Et_4NCN (eqs 1 and 2).

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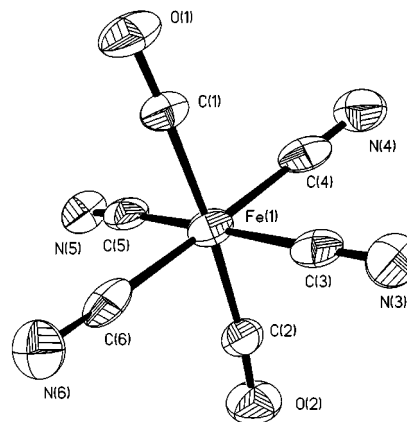
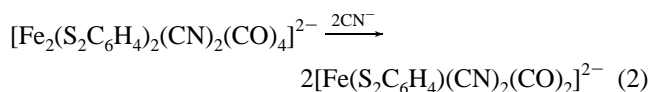
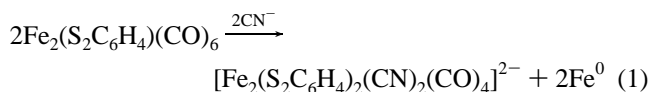


Figure 3. Molecular structure of the dianion of *trans*- $(\text{PPh}_4)_2[\text{Fe}(\text{CN})_4(\text{CO})_2]$ (**2**) with thermal ellipsoids drawn at the 50% level. Selected bond distances (Å) and angles (deg): Fe(1)–C(1), 1.811(7); Fe(1)–C(2), 1.816(8); Fe(1)–C(3), 1.948(8); Fe(1)–C(4), 1.952(8); Fe(1)–C(5), 1.934(8); Fe(1)–C(6), 1.951(8); C–O(avg), 1.145; C–N(avg), 1.168; C(1)–Fe(1)–C(2), 175.1(3); Fe(1)–C–O(avg), 176; Fe(1)–C–N(avg), 176; NC–Fe–CN (avg), 90; NC–Fe–CO(avg), 90.



Finally, the above reactions prompted an investigation on the influence of cyanide on the carbonylation of iron salts in the absence of thiolates. The addition of Et_4NCN to a MeCN solution of FeCl_2 under an atmosphere of CO rapidly gave rise to a series of CO adducts, which are under further study. Using four equiv of cyanide, we obtained ~50% yield of *trans*- $[\text{Fe}(\text{CN})_4(\text{CO})_2]^{2-}$ (**2**), isolated as its Et_4N^+ salt. Complex **2** was crystallographically characterized as the PPh_4^+ salt (Figure 3).¹⁸ The only previously characterized $\text{Fe}^{\text{II}}\text{—CN—CO}$ complex is $[\text{Fe}(\text{CN})_5(\text{CO})]^{3-}$, which is synthesized indirectly from preformed $[\text{Fe}(\text{CN})_5\text{L}]^{3-}$ derivatives.¹⁹

The key role of cyanide is attributable to its stabilization of low-spin Fe(II), which then enables the binding of CO, which then opens the door to reactivity of biosynthetic significance.

Acknowledgment. This research was supported by the National Institutes of Health and the Department of Energy.

Supporting Information Available: Tables of atomic coordinates, selected bond distances and angles, thermal parameters, selected spectroscopic, and preparative details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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