Preparative and Structural Studies on the Carbonyl Cyanides of Iron, Manganese, and Ruthenium: Fundamentals Relevant to the Hydrogenases

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The reaction of cyanide, carbon monoxide, and ferrous derivatives led to the isolation of three products, trans- and cis-[Fe(CN)4(CO)2]− and [Fe(CN)5(CO)]3−, the first two of which were characterized by single-crystal X-ray diffraction. The new compounds show self-consistent IR, 13C NMR, and mass spectroscopic properties. The reaction of trans-[Fe(CN)5(CO)]3− with Et4NCN gives [Fe(CN)5(CO)]3− via a first-order (dissociative) pathway. The corresponding cyanation of cis-[Fe(CN)4(CO)2]2−, which is a minor product of the Fe(II)/CN−/CO reaction, does not proceed at measurable rates. Methylation of [Fe(CN)5(CO)]3− gave exclusively cis-[Fe(CN)4(CNMe)(CO)]2−, demonstrating the enhanced nucleophilicity of CN− trans to CN− vs CN− trans to CO. Methylation has an electronic effect similar to that of protonation as determined electrochemically. We also characterized [M(CN)2(CO)]3+ for Ru (n = 1) and Mn (n = 2) derivatives. The Ru complex, which is new, was prepared by cyanation of a [RuCl2(CO)3]2+ solution.

Introduction

While cyanide is often discussed in terms of its σ-acceptor properties, the most dominant characteristic of this ligand is its potency as a σ-donor.1 Because of its strong donor properties, cyanide stabilizes the binding of carbon monoxide to metals in intermediate oxidation states. In contrast, stoichiometrically related M−CO−halide derivatives tend to be less stable. The ability of cyanide to promote the complexation of σ-acceptor ligands is probably related to the catalytic properties of the cobalticyanides.2

The ability of cyanometalates to stabilize CO binding and to promote transformations of small molecules has come into focus because of the presence of cyanide at the active sites of the two major families of hydrogenases, the Fe-only and the Fe−Ni hydrogenases.3−9 The biosynthesis of such bioorganometalic centers is a fascinating and incompletely resolved issue, although recently Bock et al. have isolated a possible precursor to the CN− and CO ligands.10 Our interests in this theme stem from a desire to prepare active site analogues of the hydrogenases from preassembled Fe−CN−CO building blocks. For example, the Ni−Fe hydrogenases feature [Fe(CO)(CN)2]2[Ni(μ-SR)2(SR)2] sites that could in principle be assembled by the reaction of Fe(CO)(CN)2-containing precursors with a preformed nickel tetrathiolate. There are, however, no suitable sources of an Fe(CO)(CN)2 fragment (e.g., Fe(CN)2(CO)4). Prior to our efforts11 and those of Koch,12 the only known Fe−CN−CO compounds were [Fe(CN)(CO)4]−,13 [Fe2(μ-CN)(CO)6]−,14 and [Fe(CN)5(CO)]3−.15 Liaw has shown that [Fe(CN)(CO)4]− is a useful precursor to Fe−CN−CO−SR species.16 Because of the undeveloped state of Fe−CN−CO chemistry, we undertook the present exploratory project aimed at expanding the range of Fe(II)−CN−CO derivatives. This

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has resulted in the synthesis of trans-[Fe(CN)₄(CO)₂]²⁻ and cis-[Fe(CN)₄(CO)₂]²⁻ and a new route to [Fe(CN)₅(CO)]³⁻. In complementary work, we describe [Ru(CN)₃(CO)₃]⁻ and [Mn(CN)₃(CO)₃]²⁻; Jiang and Koch have recently described [Fe(CN)₅(CO)]³⁻. A list of known M–CO–CN derivatives is presented in Table 1.

### Results

Synthesis of trans- and cis-[Fe(CN)₄(CO)₂]²⁻ and [Fe(CN)₅(CO)]³⁻. Treatment of MeCN suspensions of FeCl₂ with CO followed by the addition of 4 equiv of Et₄NCN afforded yellow solutions containing three anions, trans-[Fe(CN)₄(CO)₂]²⁻ (1), cis-[Fe(CN)₄(CO)₂]²⁻ (2), and [Fe(CN)₅(CO)]³⁻ (3), Figure 1 and Scheme 1. Addition of PPh₄⁺ precipitated both 1 and 2, which were further purified by extraction into MeCN. The dominant product was the trans isomer. The trianion 3 does not form a water-insoluble PPh₄⁺ salt. Instead, 3 was precipitated using the more hydrophobic PPN⁺ (PPN⁺ = bis(triphenylphosphine)iminium cation) after removing the two dicarbonyl derivatives. We also examined the reaction of FeCl₂ with CO followed by the addition of 3 equiv of Et₄NCN in MeCN, which afforded a yellow suspension. The IR spectroscopy of the MeCN solution also indicated the formation of complexes 1, 2, and 3 in low yield. IR spectra for the crude reaction mixtures showed no evidence for tricarbonyl species.

The three products were identified by IR and ¹³C NMR spectroscopy; additionally each compound gave well-resolved ESI-mass spectra with molecular ions. The IR spectrum of trans-[Fe(CN)₄(CO)₂]²⁻ (1) exhibits one ν̅CO band at 1999 cm⁻¹ whereas the cis isomer 2 had two ν̅CO bands at 2042 and 1944 cm⁻¹. The νCN bands at 2103, 2119, and 2108 cm⁻¹ were also diagnostic for the trans and cis isomers, respectively. The structure of the isomers was further confirmed by ¹³C NMR measurements in the CO/CN region, which showed the correct multiplicity.

Characterization of pentacyanide 3 was also straightforward, except that its properties are somewhat dependent on its solvation. Other cyanometalates are known to be solvatochromic (vide infra), but this behavior had not been observed with the carbonyl cyanide series. Freshly isolated (PPN)₃[Fe(CN)₅(CO)] is white, but upon drying in vacuo it becomes deep yellow. The IR spectrum of the yellow form of (PPN)₃[Fe(CN)₅(CO)] exhibits νCN at 2090 and 2075 cm⁻¹ and one ν̅CO at 1932 cm⁻¹. The corresponding white (PPN)₃⁻[Fe(CN)₅(CO)] showed νCN bands at 2094 (shoulder) and 2077 cm⁻¹ and one ν̅CO band at 1946 cm⁻¹ in MeCN solution.

Addition of 1 equiv of H₂O to a MeCN solution of (PPN)₃[Fe(CN)₅(CO)] shifted the ν̅CO band to higher energy.

![Figure 1](image.png)

**Table 1.** Known M–CO–CN Derivatives a

<table>
<thead>
<tr>
<th>Group VIA M = Cr, Mo, W</th>
<th>Group VIA M = Mn, Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(CN)₅(CO)₅]⁻</td>
<td>[Fe(CN)₃(CO)₃]⁺</td>
</tr>
<tr>
<td>[Mo(CN)₅(CO)₅]⁻</td>
<td>[Ru(CN)₃(CO)₃]⁺</td>
</tr>
<tr>
<td>[W(CN)₅(CO)₅]⁻</td>
<td>[Os(CN)₃(CO)₃]⁺</td>
</tr>
<tr>
<td>[Co(CN)₅(CO)₅]⁻</td>
<td>[Ni(CN)₃(CO)₃]⁺</td>
</tr>
<tr>
<td>[Co(CN)₅(CO)₅]⁻</td>
<td>[Rh(CN)₃(CO)₃]⁺</td>
</tr>
<tr>
<td>[Rh(CN)₅(CO)₅]⁻</td>
<td>[Pd(CN)₃(CO)₃]⁺</td>
</tr>
<tr>
<td>[Ir(CN)₅(CO)₅]⁻</td>
<td>[Pt(CN)₃(CO)₃]⁺</td>
</tr>
<tr>
<td>[Os(CN)₃(CO)₅]⁻</td>
<td>[MC(CN)₃(CO)₃]⁺</td>
</tr>
<tr>
<td>[MC(CN)₃(CO)₃]⁻</td>
<td>[MC(CN)₃(CO)₃]⁺</td>
</tr>
</tbody>
</table>

a Entries are from ref 21 except [Fe(CN)₅(CO)]³⁻, [Fe(CN)₄(CO)₂]²⁻, [Ru(CN)₃(CO)₃]⁻, [Ni(CN)₃(CO)₃]⁻, ¹¹Ru(CN)₃(CO)₁₀, and Ru(CN)₅(CO)₁₂.²⁴

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(22) Joo, F.; Alper, H. Organometallics 1985, 4, 1775–1778.
from 1932 to 1968 cm\(^{-1}\). Collectively, our data are consistent with the colorless form of 3 being subject to hydrogen bonding. The dicarbonyls 1 and 2 are not visibly solvatochromic, probably because their absorption maxima are shifted more deeply into the UV.

We previously studied the compounds \([\text{Fe(CO)}_2(\text{CN})_2]^{-}\) and \([\text{Fe}(\text{S}_2\text{C}_6\text{H}_4)(\text{CO})(\text{CN})_2]^{2-}\). We found that in solution both species decompose to give a mixture of trans-1 and 3 species, as determined by IR measurements. We demonstrated that a coproduct of this decomposition is \([\text{Fe(SR)}_4]^{2-}\) demonstrated by crystallographic characterization of (Et\(_4\)N\(_2\))[Fe(SR)_4].

\[
\text{[Fe(SPh)}_2(\text{CN})_2(\text{CO})_2]^{2-} \overset{\text{MeCN}}{\underset{\text{trans-}[\text{Fe(CN)}_3(\text{CO})_2]^{2-} + 1}{\text{MeCN}}} \text{[Fe(CN)}_3(\text{CO})_2]^{2-} + [\text{Fe(SPh)}_2]^{2-} \quad (1)
\]

\[
[\text{Fe}(\text{S}_2\text{C}_6\text{H}_4)(\text{CN})_2(\text{CO})]^{2-} \overset{\Delta}{\underset{\text{MeCN}}{\text{[Fe(CN)}_3(\text{CO})_2]^{2-} + 3}} \text{[Fe}(\text{S}_2\text{C}_6\text{H}_4)]^{2-} \quad (2)
\]

**Product Distribution and Mechanistic Considerations.**

The distribution of 1–3 from the carbonylation of ferrous cyanide solutions was relatively unaffected when 5 equiv of Et\(_4\)NMeCN was used in place of 4 equiv. When the synthesis was conducted using aqueous KCN, however, the pentacyanide 3 became the dominant product. High temperatures also favor 3 (see Table 2). We propose that some 3 arises via decarbonylation of \(\text{trans-[Fe(CN)}_3(\text{CO})_2]^{2-}\) under these conditions. Indeed upon heating, a solution of \(\text{trans-[PPh}_2]^{2-}\) \([\text{Fe}(\text{CN})_3(\text{CO})_2]^{2-}\) gave a 42% isolated yield of the pentacyanide 3. On the other hand, the thermolysis also produced 3% cis-isomer 2 and a yellow insoluble product 4, which is proposed to be a polymer. The yellow polymer 4 reacts with CN\(^{-}\) to give 3.

We examined the preparation of iron cyanides where CN\(^{-}/\)Fe < 6 in the absence of CO with the goal of identifying possible reaction intermediates. The reaction of 4 equiv of Et\(_4\)NMeCN with a MeCN suspension of FeCl\(_2\) gave a deep red-orange solution. If after 1 h this solution is treated with CO, the dominant product is 3. On the other hand, treatment of this red solution with 9,10-phenanthroline gave \([\text{Fe(CN)}_3(\text{phen})]^{2-}\), isolated as its bis(PPh\(_3\)\(^{+}\)) salt. This blue salt is highly solvatochromic, giving red solutions in water. Solvatochromism is a well-known characteristic for iron cyanides.

We also examined the reaction of the cis isomer with 4 equiv of Et\(_4\)NCN in refluxing MeCN solution. No reaction was detected by IR spectroscopy, i.e., the cis isomer is less labile than the trans isomer.

**Structure of \(\text{trans-}[\text{Fe(CN)}_3(\text{CO})_2]^{2-}\).**

The structures of cis- and \(\text{trans-[Fe(CN)}_3(\text{CO})_2]^{2-}\) are presented in Figures 3 and 4, respectively. Both are octahedral.

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**Table 2.** Yield Data for Reactions Leading to Fe-CN-CO Derivatives

<table>
<thead>
<tr>
<th>reactants</th>
<th>(T ) (°C)</th>
<th>solvent</th>
<th>products (% yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>FeCl(_2), Et(_4)NMeCN (4 equiv), 1 atm of CO</td>
<td>25</td>
<td>MeCN</td>
<td>39%</td>
</tr>
<tr>
<td>FeCl(_2), Et(_4)NMeCN (5 equiv), 1 atm of CO</td>
<td>25</td>
<td>MeCN</td>
<td>38%</td>
</tr>
<tr>
<td>FeCl(_2), Et(_4)NMeCN (4 equiv), 1 atm of CO, (\Delta)</td>
<td>82</td>
<td>MeCN</td>
<td>not detected</td>
</tr>
<tr>
<td>FeCl(_2), Et(_4)NMeCN (5 equiv), 1 atm of CO, (\Delta)</td>
<td>82</td>
<td>MeCN</td>
<td>not detected</td>
</tr>
<tr>
<td>FeCl(_2), KCN (4 equiv), 1 atm of CO</td>
<td>25</td>
<td>H(_2)O</td>
<td>9%</td>
</tr>
</tbody>
</table>

\*: The reaction also produced a yellow insoluble product 4.

**Table 3.** Rate Constants for the Reaction of 0.0156 M \(\text{FeCl}_2\) and 0.156 M Et\(_4\)NMeCN in MeCN and EtCN (369 K)

<table>
<thead>
<tr>
<th>temp (K)</th>
<th>((10^6 k)), s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>324</td>
<td>6.5</td>
</tr>
<tr>
<td>336</td>
<td>66.6</td>
</tr>
<tr>
<td>355</td>
<td>628.9</td>
</tr>
<tr>
<td>369</td>
<td>2033.6</td>
</tr>
</tbody>
</table>

\*: The fit indicates \(\Delta H^\ddagger = 29.3 (2.8)\) kcal/mol and \(\Delta S^\ddagger = 9.0 (7.8)\) cal/(K mol) (numbers in parentheses indicate standard deviation).

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Carbonyl Cyanides of Iron, Manganese, and Ruthenium

complexes. The cis isomer 2 has two crystallographically imposed symmetry planes, one containing C1—O1, C1A—O1A, C3—N3, C3A—N3A; the other plane bisects the angle C1—Fe—C1A and C3—Fe—C3A and contains C2—N1, Fe, C2A—N1A. The trans isomer 1 is centrosymmetric crystallographically.

The Fe—CO distances of 1.81 Å for trans isomer 1 and 1.85 Å for cis isomer 2 are considerably shorter than those observed for the isoelectronic homoleptic carbonyl complex [Fe(CO)$_6$]$_2^+$ (1.911 Å)$^{30}$ and are indicative of extensive back-bonding. In contrast, the Fe—CN distances of 1.93—1.96 Å (Table 4) are consistent with the predominantly σ character of the Fe—CN bond.

Alkylation of [Fe(CN)$_3$(CO)]$^3$—. We examined the methylation of 3 using MeOTf in order to understand the charge distribution in this complex. The cis cyanide ligands in [Fe(CN)$_3$NO]$^{2—}$ exhibit enhanced nucleophilicity toward metal electrophiles.$^{31—34}$ The reaction of 3 with 1 equiv of MeOTf produced cis-[Fe(CN)$_3$(CNMe)(CO)]$^{2—}$ (5) as the exclusive product. Analytically pure samples of this yellow salt were obtained by mechanical separation of the yellow crystals from the PPNOTf coproduct. One CNMe singlet was observed in the $^1$H NMR spectrum, and the $^{13}$C NMR spectrum showed four signals in the C region consistent with the low symmetry of this complex compared with 3 (see above). Spectroscopic studies show that dimethylation of 3 gave fac-[Fe(CN)$_3$(CNMe)$_2$(CO)]$^−$ (6). The stereochemistry of this salt was established by the observation of two $v_{CN}$ bands at 2223 and 2198 cm$^{-1}$ and two $v_{CO}$ bands at 2113 and 2103 cm$^{-1}$, in addition to the $v_{CO}$ band at 2009 cm$^{-1}$. The $^1$H NMR spectrum of [Fe(CN)$_3$(CNMe)$_2$(CO)]$^−$ also shows only one Me signal consistent with the facial structure.

The structure of [Fe(CN)$_3$(CNMe)(CO)]$^{2—}$ (5) was confirmed by single-crystal X-ray diffraction (Figure 5). The anion is octahedral with the CNMe ligand cis to CO. A crystallographic (mirror) plane contains C1, C2, C4, and C5. The Fe—CO distance of 1.78 Å in 5 is shorter by 0.07 Å than that in cis-[Fe(CN)$_3$(CO)]$^{2—}$ (Table 4), consistent with the strong σ-donor role of the CNMe vs CO ligand. Two research groups$^{35,36}$ have recently reported the crystallographic characterization of [Fe(CN)$_3$(CO)]$^{3—}$; they found Fe—CO distances of 1.75—9 Å, consistent with our results. In contrast, the Fe—CNMe distance of 1.86 Å is also shorter.

Table 4. Selected Bond Distances (Å) for trans-[Fe(CN)$_3$(CO)]$^{2—}$ (1), cis-[Fe(CN)$_3$(CO)]$^{2—}$ (2), and cis-[Fe(CN)$_3$(CNMe)(CO)]$^{2—}$ (5)

<table>
<thead>
<tr>
<th>parameter</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe—CO</td>
<td>1.81(3)</td>
<td>1.84(7)</td>
<td>1.78(1)</td>
</tr>
<tr>
<td>Fe—CN</td>
<td>1.93(7)</td>
<td>1.94(0)</td>
<td>1.92(0)</td>
</tr>
<tr>
<td>C—N</td>
<td>1.14(3)</td>
<td>1.15(9)</td>
<td>1.16(0)</td>
</tr>
<tr>
<td>C—NCNMe</td>
<td>1.16(3)</td>
<td>1.16(6)</td>
<td>1.16(6)</td>
</tr>
<tr>
<td>CN—Me</td>
<td>1.16(6)</td>
<td>1.17(6)</td>
<td>1.17(6)</td>
</tr>
</tbody>
</table>

that for \([\text{Fe(CN)}_6]^{4-}\), with a reversible couple occurring at a potential of 1 V (Table 5). We also found that the addition of 1 equiv of HOTf to a solution resulted in a shift in \(E_{1/2}\) to 629 mV; these results are consistent with the effect of water on the IR spectrum and the color of 3 (see above).

Encouraged by the CV results, we generated \([\text{Fe(CN)}_5-(\text{CO})_2]^{2-}\) using ferrocenium as the oxidant. This reaction afforded a red-brown solution. The IR spectrum of 3 exhibits \(\nu\text{CO}\) bands at 2127 and 2096 cm\(^{-1}\). The \(\nu\text{CO}\) band at 1980 cm\(^{-1}\) is shifted by 48 cm\(^{-1}\) to a higher energy relative to \([\text{Fe(CN)}_5-(\text{CO})_2]^{2-}\) (see above). Under \(\text{N}_2\), \((\text{PPN})_2[\text{Fe(CN)}_5-(\text{CO})_2]\) was stable in MeCN solution for hours at room temperature.

\section*{Synthesis and Structure of \([\text{M(CN)}_3(\text{CO})_3]\) Salts (M = Mn, n = 2; M = Ru, n = 1)}

The Ru and Mn derivatives were examined as analogues of \([\text{Fe(CN)}_3(\text{CO})_3]\). The synthesis of the Mn derivative was previously described by Behrens,\(^{44}\) but we streamlined the procedure: Addition of PPh\(_4\)Cl to an aqueous extract of the high-temperature reaction residue of Mn(CO)\(_4\)Cl and KCN gave a 55% yield of PPh\(_4\)Mn(CN)\(_3\)(CO)\(_3\). Crystallographic analysis of this salt revealed two similar molecules of \(\text{fac-}[\text{Mn(CN)}_3(\text{CO})_3]^{2-}\) in the asymmetric unit, one of which is shown in Figure 6. The \(\text{Mn}-\text{CO}\) vs \(\text{M}-\text{CN}\) linkages of both molecules were assigned on the basis of Mn–C distances, because the former are typically 0.1–0.2 Å shorter (Table 6). The IR spectrum of small amounts of water or phenol lowered the oxidation potential of 3. For example, the addition of 1 equiv of H\(_2\)O to a MeCN solution of 3 resulted in a shift in \(E_{1/2}\) of 443 to 629 mV; these results are consistent with the effect of water on the IR spectrum and the color of 3 (see above).

\begin{table}[h]
\centering
\caption{Redox Couples for \([\text{Fe(CN)}_6]^{4-}\) Complexes}
\begin{tabular}{ll}
\hline
compound & \(E_{1/2}\) (mV) vs NHE \\
\hline
[\text{Fe(CN)}_6]^{3-} & -609 \\
[\text{Fe(CN)}_6]^{2-} & -443 \\
trans-[\text{Fe(CN)}_6(\text{CO})_2]^{3-} & 1417 \\
cis-[\text{Fe(CN)}_6(\text{CO})_2]^{3-} & 1607 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Selected Bond Distances (Å) and Angles (deg) for Two Molecules in the Asymmetric Unit of the Anion in \((\text{PPH}_4)_2[\text{fac-}[\text{Mn(CN)}_3(\text{CO})_3]^{2-}\)]}
\begin{tabular}{lccc}
\hline
parameter & molecule 1 & molecule 2 \\
\hline
\text{Mn–CO} & 1.751(17) & 1.758(17) \\
 & 1.784(16) & 1.804(18) \\
 & 1.792(19) & 1.835(19) \\
\text{Mn–CN} & 1.993(17) & 1.970(16) \\
 & 2.013(16) & 1.984(18) \\
 & 2.019(15) & 2.055(17) \\
\text{C–O(av)} & 1.172 & 1.145 \\
\text{C–N(av)} & 1.156 & 1.145 \\
\text{OC–Mn–CO(av)} & 92.3 & 93.1 \\
\text{NC–Mn–CN(av)} & 88.1 & 87.3 \\
\hline
\end{tabular}
\end{table}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig5}
\caption{Molecular structure of the anion \(\text{cis-[Fe(CN)}_3(\text{CNMe})(\text{CO})_2]^{2-}\) with thermal ellipsoids drawn at the 50% level.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig6}
\caption{Molecular structure of the anion \(\text{fac-[Mn(CN)}_3(\text{CO})_3]^{2-}\) with thermal ellipsoids drawn at the 50% level.}
\end{figure}


NMR measurements revealed one C–O singlet at 2117 and 2097 cm⁻¹ and one C–N singlet at 2110 and 2097 cm⁻¹, respectively. The Ru(II) analogue of the Mn(I) compound, \([\text{Ru} (\text{CN})_3 (\text{CO})_3]^{2-}\), is a new anion. This colorless species was prepared by the addition of cyanide to a carbonylated solution of ruthenium trichloride under CO followed by precipitation using PPh₄⁺ (eq 3). The IR spectrum of PPh₄[Ru(CN)₃(CO)₃]⁻ exhibits ν(CN) bands at 2163 and 2144 cm⁻¹ and ν(CO) bands at 2117 and 2075 cm⁻¹, consistent with the facial isomer. ¹³C NMR measurements revealed one CO singlet at 111.7 and one CN singlet at 122.99. Only one cyano carbonyl of Ru is known, a derivative of \([\text{Ru}_3 (\text{CO})_{12}]\)⁻. Crystallographic analysis of Na[DMF][Ru(CN)₃(CO)₃] confirmed the expected structure for the anionic metal center. The anion is linked to a polymeric framework wherein all CN ligands are coordinated via N–Na⁺ linkages (Figure 7). Each Na⁺ center is additionally coordinated to two DMF ligands, which also bridge to another Na⁺ atom. The Ru–CO distances are shorter than Ru–CN distances by ~0.1 Å (Table 7), as also observed for Fe–CO–CN complexes discussed above. The NC–Ru–CN bond angles are 87.8°, the slight deviation from 90° being attributable to complexation to the Na–DMF network.

Conclusions

The goal of this study was to explore fundamental aspects of Fe(II)–CO–CN chemistry. This class of complexes is also potentially related to prebiotic processes and biosynthesis of the hydrogenase enzymes.³⁵ Stable Fe–CN–CO complexes form under very mild conditions by treatment of ferrous salts with CO and cyanide. Depending on the reaction conditions, either trans-[Fe(CN)₃(CO)₂]²⁻ (1) or [Fe(CN)₃(CO)]⁻ (2) is the dominant product. The trans dicarbonyl 1 converts to the pentacyanide 3 via a first-order (dissociative) pathway, as expected. The inefficient formation of cis-[Fe(CN)₃(CO)]⁻ (2) is curious in light of the apparent thermodynamic stability of this species. The nonobservation of [Fe(CN)₅(CO)]⁻ and Fe(CN)₅(CO)₄ is attributed their high reactivity toward CN⁻, leading to trans-[Fe(CN)₃(CO)]⁻ (1). We were able to prepare fac-[Ru(CN)₃(CO)₃]⁻–[PPh₄]+ with a preformed tricarbonyl complex, as well as confirm the structure of fac-[Mn(CN)₃(CO)]⁻.

Whereas the alkylation of cyanide ligands has been exhaustively examined,⁴⁶ the methylation of [Fe(CN)₅(CO)]⁻ (3) represents a rare study on the regiochemistry of methylation of a polycyano complex. The results support the view that CN trans to CN is more basic than CN trans to CO.

Experimental Section

General Considerations. Unless otherwise indicated, reactions were conducted using standard Schlenk techniques (N₂) at room temperature with stirring and solvents were dried via filtration through activated alumina. Elemental analyses were conducted by the University of Illinois Microanalytical Laboratory. ¹H NMR spectra were acquired on a Unity Varian 500 spectrometer. ¹³C NMR (CDCl₃) measurements on PPh₄⁺ salts gave signals at δ 118.90 (d), 131.35 (d), 135.69 (d), 136.41 (d), while for PPN⁺ the aryl signals were observed at δ 128.20 (dd), 130.39 (m), 133.23 (m), 134.64 (s). ¹H NMR (CD₃CN) for PPN⁺: 7.65 (s), 7.55 (m), 7.45 (m). IR spectra were collected on a Mattson Infinity Gold FTIR spectrometer. ESI-MS were collected on a Quattro quadrapole (QHQ) mass spectrometer. Cyclic voltammograms were measured at a scan rate of 200 mV/s on 10⁻³ M MeCN solutions using 0.01 M Bu₄NPF₆ as supporting electrolyte and referenced to Fe⁺⁺. A platinum wire counter electrode, a glassy carbon working electrode, and an Ag/AgPF₆(MeCN) reference electrode were used.

Table 7. Selected Bond Distances (Å) and Angles (deg) for \([\text{Na}^{+}(\text{DMF})]\text{[Ru(CN)₃(CO)₃]}\)⁻

<table>
<thead>
<tr>
<th>Bond/Distance</th>
<th>(\text{Na}^{+}(\text{DMF}))</th>
<th>([\text{Ru(CN)₃(CO)₃]})⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Rul–C1})</td>
<td>2.078(4)</td>
<td>1.12</td>
</tr>
<tr>
<td>(\text{Rul–C2})</td>
<td>2.064(4)</td>
<td>1.15</td>
</tr>
<tr>
<td>(\text{Rul–C3})</td>
<td>2.056(4)</td>
<td>93.7</td>
</tr>
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<td>(\text{Rul–C4})</td>
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<td>(\text{C7–N4})</td>
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Reaction of FeCl₂ with Et₄NCN under CO. Under a CO atmosphere a solution of 0.127 g (1.00 mmol) of FeCl₂ in 10 mL of MeCN was treated with a solution of 0.624 g (4.00 mmol) of Et₄NCN in 10 mL of MeCN. After 8 h, the yellow solution was evaporated to dryness, and the residue was redissolved in 10 mL of H₂O. The aqueous extract was then slowly added to a solution of 0.75 g (2.0 mmol) of Ph₄PCl in 10 mL of H₂O. The white precipitate of trans-(PPN)₂[Fe(CN)₄(CO)₂] (1) and cis-(PPN)₂[Fe(CN)₄(CO)] (2) was filtered off and then extracted into 5 mL of MeCN. Addition of 50 mL of Et₂O to the MeCN extract induced precipitation of trans-(PPN)₂[Fe(CN)₄(CO)] (1). Yield: 0.345 g (39%). The aqueous filtrate from above was added to a solution of 1.15 g (2.5 mmol) of PPNCI in 300 mL of H₂O. The resulting white precipitate (PPN)_2[Fe(CN)₄(CO)] (3) was collected by filtration and washed with 10 mL of H₂O and 25 mL of Et₂O. Colorless powders of 3 became yellow upon drying. Yield: 0.66 g (36%).

trans-(PPN)₂[Fe(CN)₄(CO)₂] (1). IR (CH₃CN): ν_CO = 2103 (s); ν_CO = 1999 (s) cm⁻¹. ¹³C NMR (126 MHz, CDCl₃): δ 212.84 (s, Fe=C-O), 140.58 (s, Fe-CN). Anal. Calcd for C₅₄H₄₄FeN₄O₄P₂: C, 72.49 (72.60); H, 4.51 (4.35); N, 6.26 (6.60). Trans-(PPN)₂[Fe(CN)₄(CO)₂] was collected by filtration and washed with 10 mL of H₂O and 25 mL of Et₂O. Under a CO atmosphere a solution of 0.127 g (1.00 mmol) of FeCl₂ with Et₄NCN in 10 mL of MeCN was treated with 0.03 g of polymer and a red solution formed. After 1 h of stirring, 0.18 g (1.0 mmol) of 1,10-phenanthroline in 5 mL of MeCN was added to the red solution and the solution turned blue. The blue solution was stirred overnight and then evaporated to dryness, and the residue was redissolved in 10 mL of H₂O to get a pale yellow solution. The aqueous solution was added to a solution of 1.5 g (2.6 mmol) of PPNCl in 300 mL of H₂O to give a blue precipitate, which was collected by filtration and washed with 10 mL of H₂O and 25 mL of ether followed by drying in vacuo to produce a yellow solid of (PPN)_2[Fe(CN)₄(CO)] (3). Yield: 0.112 g (42%).

Preparative Scale Reaction of trans-(PPN)₂[Fe(CN)₄(CO)₂] (1) and CN⁻. A solution of 0.06 g (0.067 mmol) of trans-(PPN)₂[Fe(CN)₄(CO)₂] (1) and 0.025 g (0.068 mmol) of Ph₄PCN in 10 mL of MeCN was warmed to reflux for 6 h. During this time the reaction was monitored by IR spectroscopy. The IR spectrum showed the formation of (PPN)₃[Fe(CN)₃(CO)] (3). The solution was filtered to remove a small quantity of an insoluble impurity. The filtrate was evaporated to dryness, and the residue was redissolved in 5 mL of H₂O. The aqueous solution was slowly added to a solution of 0.75 g of PPNCI in 100 mL of H₂O to precipitate white 3. Yield: 0.098 g (79%).

Thermolysis of trans-(PPN)₂[Fe(CN)₄(CO)₂] (1). A solution of 0.13 g of trans-(PPN)₂[Fe(CN)₄(CO)₂] (1) in 10 mL of MeCN was warmed to reflux for 12 h to give a yellow precipitate and a pale yellow solution. After removal of the yellow precipitate (0.01 g) by filtration, the colorless filtrate was evaporated to dryness. The residue was washed with 10 mL of H₂O to give a white suspension of cis-(PPN)₂[Fe(CN)₄(CO)] (2) (0.004 g), which was collected by filtration. The aqueous filtrate was added to a solution of 0.5 g of PPNCI in 100 mL of H₂O. The resulting white precipitate was collected by filtration and washed with 6 mL of H₂O and 25 mL of ether followed by drying in vacuo to produce a yellow solid of (PPN)_2[Fe(CN)₄(CO)] (3). Yield: 0.112 g (42%).

Preparative Scale Reaction of trans-(PPN)₂[Fe(CN)₄(CO)₂] (1) and CN⁻. A solution of 0.06 g (0.067 mmol) of trans-(PPN)₂[Fe(CN)₄(CO)₂] (1) in 10 mL of MeCN was warmed to reflux for 6 h. During this time the reaction was monitored by IR spectroscopy. The IR spectrum showed the formation of (PPN)₃[Fe(CN)₃(CO)] (3). The solution was filtered to remove a small quantity of an insoluble impurity. The filtrate was evaporated to dryness, and the residue was redissolved in 5 mL of H₂O. The aqueous solution was slowly added to a solution of 0.75 g of PPNCI in 100 mL of H₂O to precipitate white 3. Yield: 0.098 g (79%).
Table 8. Crystallographic Data for trans-(PPN)₂[Fe(CN)₄(CO)₂] (PPN-1), cis-(PPN)₂[Fe(CN)₆(CO)₂] (PPN-2), cis-(PPN)₂[Fe(CN)₆(CNMe)(CO)] (PPN-5), fac-(PPH₃)₂[Mn(N₂O₅)] and fac-(Na)(Ru(N₂O₅))

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a R = ||Fₒ|−|Fᵣ||Σ|Fᵣ|, b Rₑ = ([|w(Fₒ)−|Fᵣ|²]/Σ|w(Fᵣ)|²)⁰.⁵, c w = 1/σ²(Fᵣ).

<...>
[Ru(CN)₃(CO)₃] were mounted on a thin glass fiber by using oil (Paratone-N, Exxon) before being transferred to the diffractometer. Data were collected on a Siemens CCD automated diffractometer at low temperature. Data processing was performed with the integrated program package SHELXTL. All structures were solved using direct methods and refined using full-matrix least squares on $F^2$ using the program SHELXL-97. All hydrogen atoms were fixed in idealized positions with thermal parameters 1.5 times those of the attached carbon atoms. The data were corrected for absorption on the basis of $\gamma$ scans. Specific details for each crystal are given in Table 8. Full crystallographic data for each compound have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-170080 (PPN-1), 170081 (PPN-2), 170083 (PPN-5), 163659 (fac-(PPh₄)₂[Mn(CN)₃(CO)₃]), and 171511 (fac-Na(DMF)[Ru(CN)₃(CO)₃]).

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

Supporting Information Available: Eyring plot for cyanation of trans-[Fe(CN)₃(CO)₂]$^{2-}$ (1), molecular structure of the anion fac-Na(DMF)[Ru(CN)₃(CO)₃]$^{3-}$ with thermal ellipsoids drawn at the 50% level, and X-ray crystallographic files in CIF format and listings of positional and thermal parameters which do not appear in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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(49) Sheldrick, G. M. SHELXL-97; University of Göttingen: Göttingen, 1997.