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Coordination Chemistry of $[HFe(CN)_2(CO)_3]^-$ and Its Derivatives: Toward a Model for the Iron Subsite of the [NiFe]-Hydrogenases

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The photoreaction of $Fe(CO)_5$ and cyanide salts in MeCN solution affords the dianion $[Fe(CN)_2(CO)_3]^{2-}$, conveniently isolated as $[K(18\text{-crown-}6)]_2[Fe(CN)_2(CO)_3]$. Solutions of $[Fe(CN)_2(CO)_3]^{2-}$ oxidize irreversibly at −600 mV (vs Ag/AgCl) to give primarily $[Fe(CN)_3(CO)_3]^-$. Protonation of the dianion affords the hydride $[K(18\text{-crown-}6)][HFe(CN)_2(CO)_3]$ with a $pK_a \approx 17$ (MeCN). The ferrous hydride exhibits enhanced electrophilicity vs its dianionic precursor, which resists substitution. Treatment of $[K(18\text{-crown-}6)][Fe(CN)_2(CO)_3]$ with tertiary phosphines and phosphites gives isomeric mixtures of $[HFe(CN)_2(CO)_2L]^-$ ($L = P(OPh)_3$ and PPh_3). Carbonyl substitution on $[\mathbf{1}H(CO)_2]^-$ by $P(OPh)_3$ is first-order in both the phosphite and iron ($k = 0.18\ M^{-1}\ s^{-1}$ at 22 °C) with $\Delta H^\ddagger = 51.6\ kJ\ mol^{-1}$ and $\Delta S^\ddagger = -83.0\ J\ K^{-1}\ mol^{-1}$. These ligands are displaced under an atmosphere of CO. With *cis*-$Ph_2PCH{=}CHPPh_2$ (dppv), we obtained the monocarbonyl, $[HFe(CN)_2(CO)(dppv)]^-$, a highly basic hydride ($pK_a > 23.3$) that rearranges in solution to a single isomer. Treatment of $[K(18\text{-crown-}6)][HFe(CN)_2(CO)_3]$ with Et_4NCN resulted in rapid deprotonation to give $[Fe(CN)_2(CO)_3]^{2-}$ and HCN. The tricyano hydride $[HFe(CN)_3(CO)_2]^{2-}$ is prepared by the reaction of $[HFe(CN)_2(CO)_2(PPh_3)]^-$ and $[K(18\text{-crown-}6)]CN$. Similar to the phosphine and phosphite derivatives, $[HFe(CN)_3(CO)_2]^{2-}$ exists as a mixture of all three possible isomers. Protonation of the hydrides $[HFe(CN)_2(CO)(dppv)]^-$ and $[HFe(CN)_3(CO)_2]^-$ in acetonitrile solutions releases H_2 and gives the corresponding acetonitrile complexes $[K(18\text{-crown-}6)][Fe(CN)_3(NCMe)(CO)_2]$ and $Fe(CN)_2(NCMe)(CO)(dppv)$. Alkylation of $[K(18\text{-crown-}6)]_2[Fe(CN)_2(CO)_3]$ with MeOTf gives the thermally unstable $[MeFe(CN)_2(CO)_3]^-$, which was characterized spectroscopically at −40 °C. Reaction of dppv with $[MeFe(CN)_2(CO)_3]^-$ gives the acetyl complex, $[Fe(CN)_2(COMe)(CO)(dppv)]^-$. Whereas $[Fe(CN)_2(CO)_3]^{2-}$ undergoes protonation and methylation at Fe, acid chlorides give the iron(0) *N*-acylisocyanides $[Fe(CN)(CO)_3(CNCOR)]^-$ ($R = Ph, CH_3$). The solid state structures of $[K(18\text{-crown-}6)][HFe(CN)_2(CO)(dppv)]$, $Fe(CN)_2(NCMe)(CO)(dppv)$, and $[K(18\text{-crown-}6)]_2[HFe(CN)_3(CO)_2]$ were confirmed crystallographically. In all three cases, the cyanide ligands are cis to the hydride or acetonitrile ligands.

Introduction

Ferrous carbonyl cyanide complexes have aroused recent interest because of their presence in [FeFe]- and [NiFe]-hydrogenases—metalloenzymes that are responsible for the interconversion of dihydrogen to protons and electrons with high catalytic efficiency.[1] The active site of the [FeFe] enzyme features Fe(CO)(CN) and $Fe(CO)_2(CN)$ sites, and the active site of the [NiFe] enzyme features a $Fe(CO)(CN)_2$ site. Additionally, mutants of the [NiFe]-hydrogenases are proposed to contain tricyano ($Fe(CO)(CN)_3$-containing) centers.[2]

The active site of [NiFe]-hydrogenase is composed of a Ni center coordinated by two terminal and two bridging cysteine thiolates in a highly distorted tetrahedral arrangement and an octahedral Fe atom coordinated by two bridging cysteine thiolates, two cyanides, and a terminal carbonyl.[3] No bridging ligand has been observed crystallographically in the catalytically relevant reduced forms of the active site; however, a bridging hydride has been detected by ENDOR and HYSCORE spectroscopies.[4]

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As indicated in the thorough review by Fehlhammer and Fritz, metal cyanides are reactive toward a broad range of electrophiles (e.g., HX, RX, RCOX), which attack almost exclusively at cyanide.[5] Such reactivity studies have emphasized midvalent metal cyanides, which are more widely available, or low valent polycarbonyl cyanides wherein the metal is only weakly basic. It seems likely that *low-valent* metal cyanides could display metal-centered reactivity, competitive with the N-centered reactions. Indeed, complexes of the type $Rh^I(chel)CN$ (where chel = $N(CH_2CH_2PPh_2)_3$ and $P(CH_2CH_2PPh_2)_3$) protonate at Rh.[6] Similarly, protonation of $[Fe^I_2(SR)_2(CN)_2(CO)_4]^{2-}$ and $[Fe^I_2(SR)_2(CN)(CO)_4(PMe_3)]^-$ occurs at the iron,[7] not at FeC*N*, although in these cases, the kinetic site of protonation may be FeC*N*.[8] The alkylation of Ni(0) carbonyl cyanides implicates the direct alkylation at nickel, not the cyanide ligands.[9] In view of this background, it is not surprising that $[Fe(CN)_2(CO)_3]^{2-}$ undergoes protonation at iron, not FeC*N*, to give $[HFe(CN)_2(CO)_3]^-$, [**1**H$(CO)_2]^-$.[10] In the present paper, we examine the regiochemistry of reactions of $[Fe(CN)_2(CO)_3]^{2-}$ with other electrophiles, including alkylating and acylating agents.

The hydride, [**1**H$(CO)_2]^-$, features the $HFe(CN)_2(CO)$ center that is found at the active site for certain states of [NiFe]-hydrogenases.[3] Numerous structural and functional models for the [NiFe]-hydrogenase active site have been reported featuring ferrous cyanide complexes,[11,12] but few studies have aimed at the *hydride-containing* Ni−C and Ni−R states. With this background in mind, the present paper describes the substitution chemistry of [**1**H$(CO)_2]^-$ as a prelude to the construction of bimetallic models.

Results and Discussion

Synthesis and Protonation of $[Fe(CN)_2(CO)_3]^{2-}$. The dianion $[Fe(CN)_2(CO)_3]^{2-}$ arises in good yields by the photoreaction of solutions of either preformed $[Fe(CN)(CO)_4]^-$ or $Fe(CO)_5$ and cyanide salts in MeCN solution. The conversion from $Fe(CO)_5$ to $[Fe(CN)_2(CO)_3]^{2-}$ can be effected in a one-pot process, although the second step is slow apparently because of self-extinction. An intense absorption band for $[Fe(CN)_2(CO)_3]^{2-}$ occurs at 230 nm ($\varepsilon = 2 \times 10^5$ cm^{-1} M^{-1}) and overlaps with the absorption band of the precursor $[Fe(CN)(CO)_4]^-$ at 210 nm ($\varepsilon = 8 \times 10^3$ cm^{-1} M^{-1}). Salts of $[Fe(CN)_2(CO)_3]^{2-}$ can also be synthesized in water, but the conversion was slower and the purification less efficient. Usually $[Fe(CN)_2(CO)_3]^{2-}$ was isolated as the [K(18-crown-6)]$^+$ salt because the product is easily separated from [K(18-crown-6)][$Fe(CN)(CO)_4$] and [K(18-crown-6)]CN by a single reprecipitation. Other salts were more difficult to purify.

The reaction of $Fe(bda)(CO)_3$ and Et_4NCN also gave $Et_4N[Fe(CN)(CO)_4]$ and $(Et_4N)_2[Fe(CN)_2(CO)_3]$ by displacement of bda (benzylideneacetone); however, the conversion proceeds to completion only upon addition of 3 equiv of Et_4NCN because of the competing reaction between liberated bda and unreacted cyanide, and the organic side-products complicate workup.

Tetraethylammonium and [K(18-crown-6)]$^+$ salts of $[Fe(CN)_2(CO)_3]^{2-}$ readily dissolve in deoxygenated water. The ν_{CO} band of $[Fe(CN)_2(CO)_3]^{2-}$ occurs 46 cm^{-1} higher in energy in aqueous solution (1890 cm^{-1}) as opposed to MeCN solution (1844 cm^{-1}). This type of solvent dependent shift, which has been observed in other cyanocarbonyl complexes of iron,[13,14] reflects the tendency of the cyanide ligands to engage in strong hydrogen bonds with protic solvents.

The electron-rich character of $[Fe(CN)_2(CO)_3]^{2-}$ is indicated by the ease with which it can be oxidized. The cyclic voltammogram of [K(18-crown-6)]$_2$[$Fe(CN)_2(CO)_3$] was found to consist of a single irreversible oxidation at −600 mV (vs Ag/AgCl, MeCN solution). Treatment of a MeCN solution of $[Fe(CN)_2(CO)_3]^{2-}$ with 2 equiv of $FcPF_6$ ($E_{1/2}$ = 517 mV vs Ag/AgCl) resulted in a color change to bright yellow, and IR analysis of the resulting solution showed numerous peaks in the range from 1800−2200 cm^{-1}. The only product identifiable by ESI-MS was $[Fe(CN)_3(CO)_3]^-$.[13] Aerobic oxidation of $[Fe(CN)_2(CO)_3]^{2-}$ is also complex, but IR spectra show the formation of both $[Fe(CN)_5(CO)]^{3-}$ and *trans*-$[Fe(CN)_4(CO)_2]^{2-}$.[10]

Protonation of $[Fe(CN)_2(CO)_3]^{2-}$. Addition of 1 equiv of strong acids to solutions of [K(18-crown-6)]$_2$[$Fe(CN)_2(CO)_3$] resulted in immediate and quantitative protonation of the iron complex. The resulting hydride $[HFe(CN)_2(CO)_3]^-$ ([**1**H$(CO)_2]^-$), which is extremely air-sensitive in solution, was isolated as the salt [K(18-crown-6)][**1**H$(CO)_2$]. Colorless CH_2Cl_2 or MeCN solutions of this complex become bright yellow immediately upon exposure to air; however, the products could not be identified by IR spectroscopy or ESI-MS. Isolation of the hydride complex as an analytically pure solid was complicated by the formation of salts (e.g., [K(18-crown-6)]Cl from HCl, [K(18-crown-6)]OTs from

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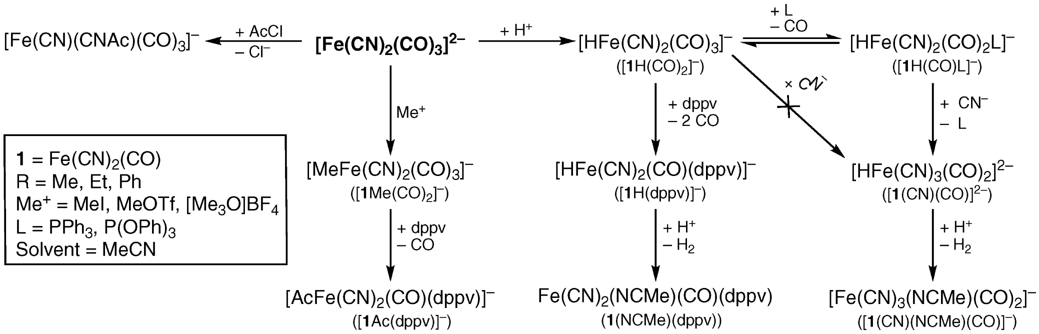
Scheme 1. Main reactions described in this paper



toluenesulfonic acid) with solubilities similar to that of the complex, but this problem was solved by using $[H(OEt_2)_2][BAr^F_4]$ ($BAr^F_4 = B[C_6H_2\text{-}3,5\text{-}CF_3)_2]_4^-$), which allowed for the removal of the co-formed salts, which are soluble in ether.

The basicity of $[\mathbf{1}H(CO)_2]^-$ in MeCN solution was semi-quantified by monitoring changes in its IR spectrum. Protonation is fully effected using NH_4PF_6 ($pK_a = 16.46$), and $[\mathbf{1}H(CO)_2]^-$ can be fully deprotonated by 1 equiv of 2-aminoethanol ($pK_a = 17.53$), indicating a $pK_a \sim 17$. All pK_a values are for compounds dissolved in MeCN unless otherwise specified. Solutions of $[\mathbf{1}H(CO)_2]^-$ in CD_2Cl_2 undergo rapid H/D exchange with D_2O to give the corresponding deuteride complex, $[DFe(CN)_2(CO)_3]^-$, while such solutions of $[\mathbf{1}H(CO)_2]^-$ do not undergo H/D exchange with D_2 (Scheme 1).

Derivatives of $[HFe(CN)_2(CO)_3]^-$. The ferrous hydride $[\mathbf{1}H(CO)_2]^-$ exhibits enhanced electrophilicity relative to its dianionic precursor, which resists substitution reactions. Treatment of [K(18-crown-6)]$[\mathbf{1}H(CO)_2]$ with tertiary phosphines or phosphites in MeCN solution resulted in rapid evolution of CO and formation of [K(18-crown-6)]$[HFe(CN)_2(CO)_2L]$ (L = $P(OPh)_3$ and PPh_3), [K(18-crown-6)]$[\mathbf{1}H(CO)L]$. These complexes exhibit two ν_{CO} bands, consistent with cis carbonyl ligands. ^{1}H- and ^{31}P NMR spectra show multiple stable isomers as also observed for $[\mathbf{1}H(CO)_2]^-$. The reaction of $[\mathbf{1}H(CO)_2]^-$ with phosphorus donor ligands is an equilibrium process. Upon placing a MeCN solution of [K(18-crown-6)]$[\mathbf{1}H(CO)(PPh_3)]$ under an atmosphere of CO, a mixture of $[\mathbf{1}H(CO)_2]^-$, $[\mathbf{1}H(CO)(PPh_3)]^-$, and PPh_3 was observed by ^{1}H- and ^{31}P NMR spectroscopy. Purging these solutions with N_2 gave $[\mathbf{1}H(CO)(PPh_3)]^-$. The $P(OPh)_3$ complex formed analogously. Treatment of $[\mathbf{1}H(CO)\{P(OPh)_3\}]^-$ with 1 equiv of PPh_3 gave $[\mathbf{1}H(CO)(PPh_3)]^-$. The phosphine ligand in PPN$[HFe(CO)_3(PPh_3)]$ is known to be reversibly displaceable by CO.[15]

The introduction of the phosphorus ligand significantly affects the acidity of the hydride. Whereas the pK_a of $[\mathbf{1}H(CO)_2]^-$ is ~17 in MeCN, $[\mathbf{1}H(CO)L]^-$ (L = PPh_3, $P(OPh)_3$) resisted deprotonation by tetramethylguanidine ($pK_a = 23.3$ in MeCN). Such decreases in acidity are precedented in the case of $HCo(CO)_{4-x}(PPh_3)_x$ ($x = 1, 0$) where the K_a of the phosphine adduct was 10^7 greater for the tetracarbonyl.[16] The $P(OPh)_3$- and PPh_3-substituted complexes do not undergo further substitution by these phosphorus ligands even in refluxing solvent.

In contrast to the situation for monophosphines and phosphites, 1 equiv of the chelating diphosphine *cis*-$Ph_2PCH{=}CHPPh_2$ (dppv) was found to displace two CO ligands from $[\mathbf{1}H(CO)_2]^-$, rapidly generating $[HFe(CN)_2(CO)(dppv)]^-$ ($[\mathbf{1}H(dppv)]^-$). The solution IR spectrum of [K(18-crown-6)]$[\mathbf{1}H(dppv)]$ in MeCN consisted of a single ν_{CO} band at 1936 cm^{-1} and two ν_{CN} bands at 2087 and 2080 cm^{-1}. The IR spectrum of $[\mathbf{1}H(dppv)]^-$ closely resembles that of $[CpFe(CN)_2(CO)]^-$.[17] Unlike the aforementioned cases of $[\mathbf{1}H(CO)(PR_3)]$ (R = Ph, OPh), solutions of $[\mathbf{1}H(dppv)]^-$ were unaffected by CO. Upon standing in solution, $[\mathbf{1}H\text{-}(dppv)]^-$ was found to convert to a mixture containing >90% of a single isomer over the course of hours at room temperature, although the IR spectra of the isomers were apparently indistinguishable. Thus, seconds after adding dppv to a CD_3CN solution of $[\mathbf{1}H(CO)_2]^-$, the ^{1}H NMR spectrum exhibited a triplet and two doublets of doublets (see Supporting Information). Within minutes, these signals diminished, concomitant with the appearance of a new triplet (δ −8.64; $^2J_{P-H} = 58$ Hz). A singlet (δ 103.7) in the ^{31}P NMR spectrum indicated of the unique C_s-symmetrical isomer. This thermodynamic product can be described as having the cyanides and dppv in the equatorial plane with the hydride and CO along the axis.

We also attemped the substitution of CO by sulfur ligands, since the coordination sphere about Fe in the [NiFe]-hydrogenases is $FeH(CN)_2(CO)(SR)_2$. The hydride $[\mathbf{1}H(CO)_2]^-$ was deprotonated by NaSPh. We observed no reaction between $[\mathbf{1}H(CO)L]^-$ (L = PPh_3, $P(OPh)_3$) and Me_2S, NaS_2CNEt_2, NaSPh, and $MeSCH_2CH_2SMe$. No reaction was also observed between $[\mathbf{1}H(CO)_2]^-$ and olefins such as styrene or norbornene.

Kinetics of Carbonyl Substitution. The rate of substitution of CO in $[\mathbf{1}H(CO)_2]^-$ by $P(OPh)_3$ was examined under conditions of excess phosphite (Figure 1). Upon varying the amount of $P(OPh)_3$ from 10 to 40 equiv, the rate increased by a factor of 4, indicating a first-order dependence upon the incoming ligand; the rate was also first-order in $[\mathbf{1}H(CO)_2]^-$, consistent with a second-order rate law. Rates were evaluated over a temperature range of 22 to −29 °C (see Supporting Information) to give the following activation

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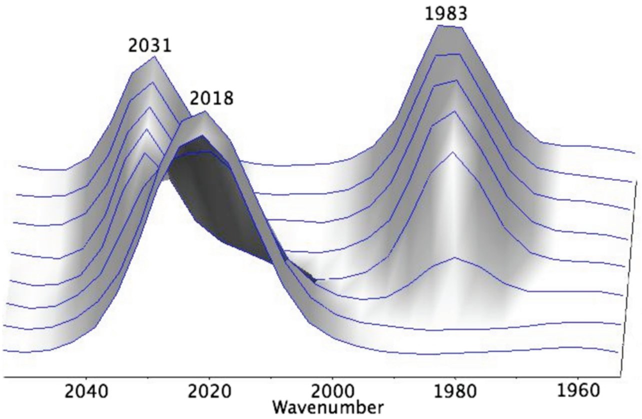

Figure 1. IR spectra (ν_{CO} region only) for the reaction of [K(18-crown-6)][$\mathbf{1}$H(CO)$_2$] with 10 equiv of $P(OPh)_3$ in MeCN solution at 20 °C.

parameters: $\Delta H^{\ddagger} = 51.6$ kJ mol^{-1} and $\Delta S^{\ddagger} = -83$ J K^{-1} mol^{-1}.

$[HFe(CN)_3(CO)_2]^{2-}$. Substitution of CO in [$\mathbf{1}$H(CO)$_2$]$^-$ is limited by the Brønsted basicity of the attacking ligand since highly basic reagents deprotonate the complex. Consistent with this pattern, treatment of [K(18-crown-6)][$\mathbf{1}$H(CO)$_2$] with Et_4NCN resulted in rapid deprotonation of the hydride to cleanly regenerate $[Fe(CN)_2(CO)_3]^{2-}$, as indicated by *in situ* IR spectroscopy. The facility of the deprotonation is consistent with the low acidity of HCN, with a pK_a = 18.1.[18] An indirect route to the tricyanide was therefore undertaken, bearing in mind the decreased acidity and convenient lability of [$\mathbf{1}$H(CO)(PPh$_3$)]$^-$ and the lability of PPh$_3$. Treatment of a MeCN solution of [$\mathbf{1}$H(CO)(PPh$_3$)]$^-$ with 1 equiv Et_4NCN was found to rapidly generate the targeted hydrido tricyanide complex $[HFe(CN)_3(CO)_2]^{2-}$ ([$\mathbf{1}$H(CN)(CO)]$^{2-}$) concomitant with displacement of PPh$_3$. The analogous phosphite complex [$\mathbf{1}$H(CO){P(OPh)$_3$}]$^-$ was found to react similarly. Excess cyanide does not result in further substitution. The IR spectrum of [$\mathbf{1}$H(CN)(CO)]$^{2-}$ showed the expected two-band ν_{CO} pattern at approximately 20 cm^{-1} lower energy than for [$\mathbf{1}$H(CO)(PPh$_3$)]$^-$. The ^{1}H NMR spectrum showed the presence of three hydride signals, reflecting the presence of the three possible isomers in a ratio of ~10:6:0.5. The isomer ratio in CD_3CN solution was found to be unchanged upon sitting for days at room temperature.

Protonation of Ferrous Hydride Complexes. The basicity of the new iron hydrides is highly dependent upon the coligands, as expected.[19] Treatment of a MeCN solution of [$\mathbf{1}$H(dppv)]$^-$ with 1 equiv of $[H(OEt_2)_2]BAr^F_4$ resulted in the slow crystallization of a yellow product along with the evolution of H_2 (^{1}H NMR spectrum: δ4.56). The IR spectrum of the precipitated yellow solid exhibited a ν_{CO} band 1993 cm^{-1} (vs 1934 cm^{-1} for [$\mathbf{1}$H(dppv)]$^-$). Elemental analysis and NMR measurements indicated that this reaction produced Fe(CN)$_2$(NCMe)(CO)(dppv), $\mathbf{1}$(NCMe)(dppv). This species is formed as a single isomer as evidenced by a singlet at δ 83.7 in the ^{31}P NMR spectrum. Protonation of CH_2Cl_2 solutions of [$\mathbf{1}$H(dppv)]$^-$ with [H(OEt$_2$)][BArF$_4$] resulted in the release of H_2. The IR spectrum of this solution showed one ν_{CO} peak at 2003 cm^{-1} and a broadened ν_{CN} band. The ^{31}P NMR spectrum showed a singlet. Upon dissolving this product into MeCN, the ν_{CO} band shifted to 1993 cm^{-1}, and the ν_{CN} sharpened. We hypothesize that protonation generates a labile H_2 ligand that is displaced by FeC*N* on another molecule of Fe(CN)$_2$(CO)(dppv) to give the polymer [Fe(CN)$_2$(CO)(dppv)]$_n$. In MeCN solution, this species depolymerizes to give $\mathbf{1}$(NCMe)(dppv).

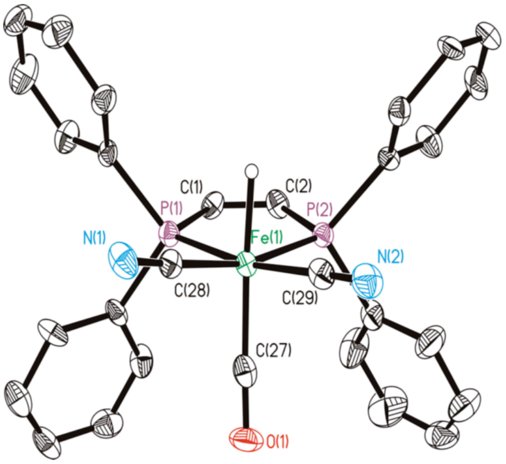

Figure 2. Molecular structure of the anion [HFe(CN)$_2$(dppv)(CO)]$^-$ with thermal ellipsoids set at the 35% probability level. Cation, solvates, and nonhydride hydrogen atoms were omitted for clarity.

Similarly, protonation of the tricyanide [K(18-crown-6)]$_2$[$\mathbf{1}$H(CN)(CO)] with an MeCN solution of HCl resulted in the immediate release of H_2 and the formation of [K(18-crown-6)][Fe(CN)$_3$(NCMe)(CO)$_2$]. The formation of [Fe(CN)$_3$(NCMe)(CO)$_2$]$^-$ is evidenced by an approximately 60 cm^{-1} shift to higher energy for ν_{CO}, similar to the shift seen upon formation of $\mathbf{1}$(NCMe)(dppv) from [K(18-crown-6)][$\mathbf{1}$H(dppv)]. Liaw and co-workers had previously obtained [Fe(CN)$_3$(NCMe)(CO)$_2$]$^-$ in low yield from the reactions of PPN[FeBr(CN)$_2$(CO)$_3$] as well as (PPN)$_2$[FeBr(CN)$_3$(CO)$_2$].[20] No reaction between [$\mathbf{1}$(CN)(NCMe)(CO)]$^-$ and cyanide was observed.

Structural Studies of Ferrous Cyanide Complexes. The structure of [K(18-crown-6)][$\mathbf{1}$H(dppv)], determined by single-crystal X-ray diffraction (Figure 2), is consistent with the IR and NMR data. The hydride was located in the difference map with a Fe−H distance of 1.51(6) Å. The cyanide and carbonyl ligands were distinguished by their Fe−C bond lengths (Table 1). The [K(18-crown-6)]$^+$ cation lies in close proximity to the *cis*-cyanide ligands; the resulting interaction is such that the potassium ion is removed from the center of the crown ether toward the cyanides.

The complex $\mathbf{1}$(NCMe)(dppv) was also characterized by single crystal X-ray diffraction (see Supporting Information). The molecular structure is consistent with retention of stereochemistry of the precursor [$\mathbf{1}$H(dppv)]$^-$ upon protonolysis.

Crystallographic analysis of the tricyanide [K(18-crown-6)]$_2$[$\mathbf{1}$H(CN)(CO)] (Figure 3) failed to locate the hydride ligand; however, an unoccupied coordination site is indicated

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Table 1. Bond Lengths (Å) for [K(18-crown-6)][**1**H(dppv)] and **1**(NCMe)(dppv)

[**1**H(dppv)]$^-$		**1**(NCMe)(dppv)	
Fe(1)−P(1)	2.169(2)	Fe(1)−P(1)	2.2563(9)
Fe(1)−P(2)	2.169(2)	Fe(1)−P(1A)	2.2563(9)
Fe(1)−C(27)	1.770(10)	Fe(1)−C(2)	1.748(4)
Fe(1)−C(28)	1.915(8)	Fe(1)−C(3)	1.938(3)
Fe(1)−C(29)	1.914(9)	Fe(1)−C(3A)	1.938(3)
Fe(1)−H(1A)	1.51(6)	Fe(1)−N(2)	1.980(4)
C(27)−O(1)	1.154(9)	C(2)−O(1)	1.156(5)
C(28)−N(1)	1.162(8)	C(3)−N(1)	1.153(4)
C(29)−N(2)	1.161(9)	C(3A)−N(1A)	1.153(4)

in an otherwise five-coordinate square pyramidal complex. The presence of a pair of [K(18-crown-6)]$^+$ counter-cations and a non-coordinating acetonitrile solvate imply the presence of a hydride ligand. The three cyanide ligands reside in the equatorial plane with one carbonyl: the hydride and the remaining carbonyl occupy axial positions. The potassium atoms in the [K(18-crown-6)]$^+$ cations are located within close proximity to the trans cyanide ligands.

Alkylation and Acylation of [Fe(CN)$_2$(CO)$_3$]$^{2-}$. To test the scope of its nucleophilic reactivity, [Fe(CN)$_2$(CO)$_3$]$^{2-}$ was treated with a selection of organic electrophiles. Combining a MeCN solution of [K(18-crown-6)]$_2$[Fe(CN)$_2$(CO)$_3$] with 1 equiv of MeOTf resulted in a rapid reaction, as indicated by changes in the IR spectra. The IR spectrum of the resulting solution resembled that for [K(18-crown-6)][**1**H(CO)$_2$]. Figure 4, consistent with alkylation at Fe, that is, the formation of [K(18-crown-6)][MeFe(CN)$_2$(CO)$_3$], [K(18-crown-6)][**1**Me(CO)$_2$]. The formula was confirmed by ESI-MS of the reaction mixture. At −40 °C, solutions of this alkylated derivative are stable for hours. The same IR spectra were obtained when the reaction was performed using MeI or [Me$_3$O]BF$_4$ as the methylating agents; in each case, however, the product decomposed upon attempted isolation.

For reference, we examined the methylation of K[Fe(CN)(CO)$_4$] with MeOTf in MeCN solution. The exclusive product, identified by IR spectroscopy, was Fe(CO)$_4$(CNMe).[21] We had earlier reported that the protonation of the monocyanide [Fe(CN)(CO)$_4$]$^-$ reacts with HCl to give a mixture of Fe(CO)$_4$(CNH) (major) and HFe(CN)(CO)$_4$ (minor).[10] The methylation result suggests that protonation may also occur at FeC*N*, the likely kinetic site, followed by slower rearrangement to the hydride tautomer. We have observed this pattern of *N*- followed by *Fe*-protonation in studies of [Fe$_2$(S$_2$C$_2$H$_4$)(CN)$_2$(CO)$_4$]$^{2-}$.[8]

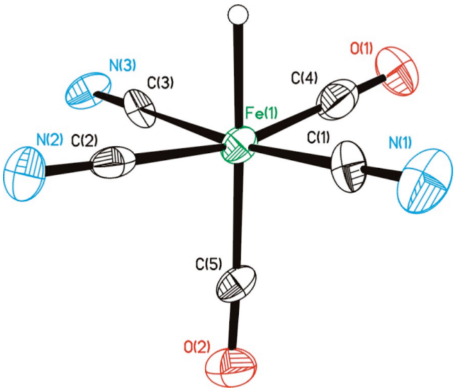

Figure 3. Molecular structure of the anion [HFe(CN)$_3$(CO)$_2$] with thermal ellipsoids set at the 35% probability level. [K(18-crown-6)]$^+$ cations and acetonitrile solvate was omitted for clarity.

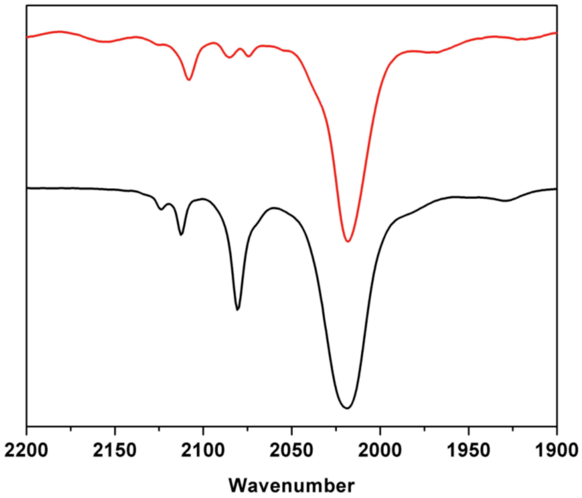

Figure 4. Solution (MeCN) IR spectra of [K(18-crown-6)][HFe(CN)$_2$(CO)$_3$] (bottom) and [K(18-crown-6)][MeFe(CN)$_2$(CO)$_3$] (top).

MeCN solutions of [**1**Me(CO)$_2$]$^-$, which are unstable, were found to react with dppv to give a robust derivative. Upon addition of dppv to the complex, gas evolution was observed. In the IR spectrum, a band at 1937 cm^{-1} appeared as seen for the hydride [K(18-crown-6)][**1**H(dppv)] and a band of medium intensity was observed at 1592 cm^{-1}, consistent with $\nu_{C=O}$ of an acetyl complex. The ^{1}H NMR spectrum exhibited a singlet for an acetyl group at δ 2.60, and the ESI-mass spectrum confirmed that the complex was indeed the acetyl, [**1**Ac(dppv)]$^-$. Cardaci and co-workers observed similar spectral features in Fe(COMe)(CN)(CO)$_2$(PMe$_3$)$_2$, which they prepared from cyanation of [Fe(Me)(CO)$_3$(PMe$_3$)$_2$]$^+$.[22] Acetyl complex [**1**Ac(dppv)]$^-$ exhibited no tendency to decarbonylate—even in refluxing MeCN.

Whereas [Fe(CN)$_2$(CO)$_3$]$^{2-}$ was found to protonate and alkylate at the metal, acid chlorides (MeCOCl, PhCOCl) gave *N*-acyl isocyanide complexes [Fe(CN)(CO)$_3$(CNCOR)]$^-$ (R = Me, Ph), which were readily obtained in analytical purity. As expected,[23] the IR spectra in the ν_{CO} region are similar for [Fe(CN)(CO)$_3$(CNCOR)]$^-$ and [Fe(CN)(CO)$_4$]$^-$ (see Supporting Information). The acyl derivatives were characterized by a new ν_{CO} band at ~1660 cm^{-1} for the RC(O)NC ligand.

Summary

In this work, we have developed the H-CN-CO-Fe system. Two members of the series are now well characterized, [HFe(CN)$_3$(CO)$_2$]$^{2-}$ and [HFe(CN)$_2$(CO)$_3$]$^-$. The species [HFe(CN)$_5$]$^{4-}$ and [HFe(CN)$_4$(CO)]$^{3-}$ remain unknown,

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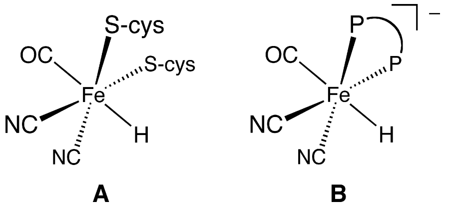

Figure 5. Fe site of the Ni−R and Ni−C states in the [NiFe]-hydrogenases (A) and $[\mathbf{1}H(dppv)]^-$ (B).

although related hydridocyanocobaltates are known.[24] This series of complexes complements the ferrous cyanide carbonyl complexes of the type $[Fe(CN)_x(CO)_{6-x}]^{2-x}$ ($x = 3, 4, 5$).[13,14,25]

The compound [K(18-crown-6)][**1**H(dppv)] is a rare example of a hydrido iron carbonyl cyanide. Another example is the bimetallic species $Fe_2(S_2C_3H_6)(\mu\text{-}H)(CN)(CO)_4(PMe_3)$.[26] Morris has reported $HFe(CN)(R_2PCH_2CH_2PR_2)_2$ (R = Et, Ph, *p*-tol), wherein the regiochemistry of protonation (hydride vs. cyanide) depends upon the basicity of the diphosphine ligand.[26b] Spectroscopically and structurally, $[\mathbf{1}H(dppv)]^-$ is a reasonable structural model for the Fe site of the [NiFe]-hydrogenases (Figure 5). The similarity extends to the IR spectra in the ν_{CO} and ν_{CN} regions.[27]

Whereas $[Fe(CN)_2(CO)_3]^{2-}$ resists substitution, its protonated derivative $[\mathbf{1}H(CO)_2]^-$ is readily monosubstituted by soft ligands such as phosphines and phosphites. Substitution by $P(OPh)_3$ was examined in some detail, and the negative activation entropy and bimolecular rate law point to an associative mechanism. For the related reaction of a variety of metal hydride complexes (e.g., $[HFe(CO)_4(PPh_3)]^+$, $HCo(CO)_4$), Pearson has suggested that the nucleophile induces migration of the hydride to a carbonyl ligand followed by rapid deinsertion with loss of CO (Scheme 2).[28] A similar mechanism is expected for the substitution of chelating diphosphines. Thus, a stable acetyl species forms upon addition of dppv to $[\mathbf{1}Me(CO)_2]^-$, whereas the corresponding formyl species is apparently less stable, resulting in decarbonylation to give the hydride complex.

The influence of the coligands on the basicity of the Fe versus the C*N* centers is relevant to understanding the regiochemistry of protonation reactions. Angelici has assessed the basicity of series of $Fe(CO)_3(phosphine)_2$ and $Fe(CO)_3(diphosphine)$ complexes and has shown that the enthalpies of protonation correlates with pK_a.[29] For example, $Fe(CO)_3(PMe_3)_2$, has a heat of protonation ($-\Delta H_{HM}$) of 23.3 kcal/mol. We estimate that $[Fe(CO)_3(PMe_3)_2]^+$ has a pK_a(MeCN) of 16.6 (see Supporting Information). For comparison, $[\mathbf{1}H(CO)_2]^-$ has pK_a(MeCN) of about 17. Similar comparability of pK_a values has been observed in dinuclear complexes, as well, with $[Fe_2(S_2C_3H_6)(\mu\text{-}H)(CO)_4(PMe_3)_2]^+$ and $[Fe_2(S_2C_3H_6)(\mu\text{-}H)(CN)_2(CO)_4]^-$, both having pK_a values between 10.4 and 11.3.[8,26]

Neutral complexes of the type $Fe(CO)_3L_2$ (L = $P(OPh)_3$, PPh_3, PPh_2Me, $P(NMe_2)_3$) undergo reversible one-electron oxidation in a range from 0.73 to 0.19 V versus Ag/AgCl, and the diphosphine complex $Fe(CO)_3(dppe)$ oxidizes at 0.15 V versus Ag/AgCl. The products in these cases are the corresponding five-coordinate (17e) derivatives.[30] These neutral $Fe(CO)_3L_2$ complexes are all much more difficult to oxidize than $[Fe(CN)_2(CO)_3]^{2-}$ (−600 mV, irreversible).

Protonation of metal cyanides most often occurs at cyanide to give complexes containing the CNH ligand.[5] Depending on their degree of substitution, the cyanocarbonyls of Fe(0) protonate either mainly at cyanide or at Fe to give a hydride complex. The regiochemistry of protonation in such complexes depends on the basicity of the respective sites. For example, the low temperature (−30 °C) protonation of $[Fe(CN)(CO)_4]^-$ results in the formation of a mixture of mainly $Fe(CO)_4(CNH)$ as well as $HFe(CN)(CO)_4$ prior to decomposition by loss of HCN.[10] Consistent with this result, methylation on the monocyanide gives $Fe(CO)_4(CNMe)$. The dicyanide, $[Fe(CN)_2(CO)_3]^{2-}$, is significantly more basic at Fe, and no CNH and CNMe species are observed. The substitution of CO for CN^-, in this case, has the effect of elevating the nucleophilicity of the Fe(0) center above that of the FeC*N* centers.

Whereas the coligands slightly affect the acidity of the MCN*H* center,[31] the acidity of the M*H* is highly sensitive to the nature of the ligand set. This effect can be seen when comparing the difference in heats of protonation ($\Delta\Delta H_{H+}$) of complexes of the type $CpRu(PR_3)_2(CN)$ to those of $Fe(CO)_3(PR_3)_2$. In the first case, only protonation at cyanide occurs, and $\Delta\Delta H_{H+}$ increases by only 1.9 kcal mol^{-1} upon substituting PPh_3 for PMe_3.[32] In the latter case, protonation at Fe occurs, and $\Delta\Delta H_{H+}$ increases by 9.2 kcal mol^{-1} upon substituting PPh_3 for PMe_3.[33]

Protonation of the dicyanoferrous hydrides described in this work did not afford isolable complexes of H_2. Protonation of the hydride in $[\mathbf{1}H(CO)L]^-$ would generate charge-neutral products, whereas most stable H_2 complexes are cations.[34] Consisting of six potentially anionic ligands—four thiolates and two cyanides, the active site of the [NiFe]-hydrogenases (and the H_2 adducts) would also be expected to be anionic. The instability of such adducts may be consistent with the high efficiency of [NiFe]-hydrogenase

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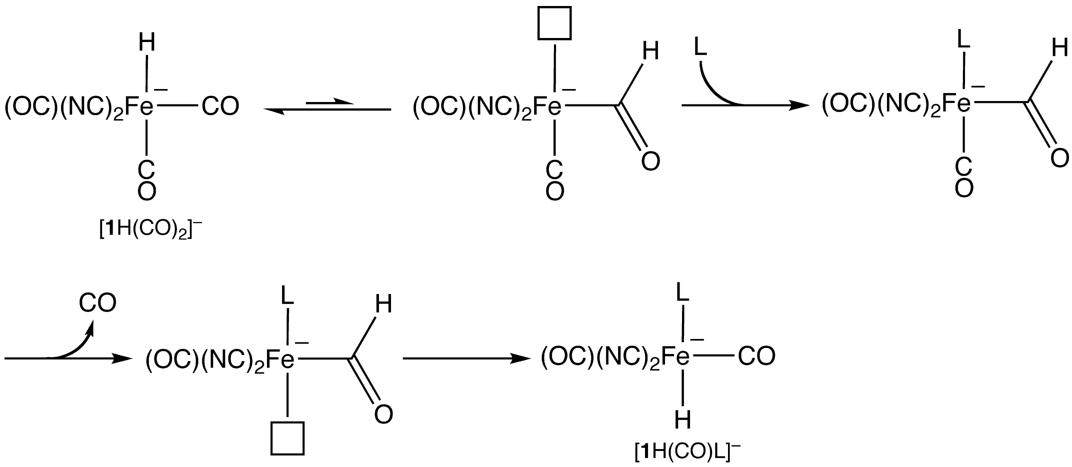
Scheme 2



(H_2 uptake: 1500 μmol H_2 min^{-1} mg protein^{-1}).[35] It is known that H_2 formation by membrane-bound [NiFe]-hydrogenases in *Ralstonia* species is inhibited by H_2.[36]

Experimental Section

Reactions were conducted as previously described using standard Schlenk techniques or in an inert atmosphere glovebox under dinitrogen. Solvents were dried via filtration through two 1 m columns of alumina. CD_3CN and CD_2Cl_2 were purchased from Cambridge Isotopes and were dried with and distilled from CaH_2. $[H(OEt_2)_2]BAr^F_4$ was prepared by literature methods.[37] Other reagents were purchased and used as received.

$[K(18\text{-crown-6})]_2[Fe(CN)_2(CO)_3]$. A slurry of 0.25 g (3.8 mmol) of KCN in MeCN was treated with 1.10 g (4.16 mmol) of 18-crown-6 and stirred until the solids dissolved. $Fe(CO)_5$ (0.25 mL, 1.9 mmol) was added to the solution, and the pale yellow reaction mixture was photolyzed. Photolysis was continued until no more significant changes were observed in the IR spectrum and no more gas evolution was observed. The reaction mixture was filtered to give a clear, very pale yellow solution. The product was precipitated by concentrating the reaction solution to a volume of about 10 mL and adding about 60 mL of EtOAc. The solid was isolated by filtration and washed with 20 mL of Et_2O. Yield: 0.835 g (55%). Note: After 5 h of photolysis, an approximate 50:50 ratio of $[Fe(CN)_2(CO)_3]^{2-}/[Fe(CN)(CO)_4]^-$ was observed. Continuing the photolysis for another 17 h resulted in a negligible increase in that ratio. Using MeOH as the reaction solvent resulted in the formation of only $[Fe(CN)(CO)_4]^-$; no dicyanide was observed, possibly because of overlap of the absorption bands of $[Fe(CN)(CO)_4]^-$ and the solvent (~205 nm).

$[K(18\text{-crown-6})][HFe(CN)_2(CO)_3]$,$[K(18\text{-crown-6})][\mathbf{1}H(CO)_2]$. A solution of 0.050 g, (0.063 mmol) of $[K(18\text{-crown-6})]_2[Fe(CN)_2(CO)_3]$ in 5 mL of MeCN was treated with a solution of 0.064 g (0.063 mmol) of $[H(OEt_2)_2]BAr^F_4$ in 5 mL of MeCN, and the solution immediately became colorless. The product precipitated as a white powder upon addition of 40 mL of Et_2O. The powder was washed with 10 mL of Et_2O to remove $[K(18\text{-crown-6})]BAr^F_4$. IR and ^1H NMR spectra matched those previously reported.[10]

$[K(18\text{-crown-6})][HFe(CN)_2(CO)_2(PPh_3)]$,$[K(18\text{-crown-6})][\mathbf{1}H(CO)(PPh_3)]$. A solution of 0.387 g (0.485 mmol) of $[K(18\text{-crown-6})]_2[Fe(CN)_2(CO)_3]$ in 10 mL of MeCN was treated with 0.506 g (0.500 mmol) of $[H(OEt_2)_2]BAr^F_4$, resulting in an immediate change from pale yellow to colorless. Addition of a solution of 0.13 g (0.50 mmol) of PPh_3 in 5 mL of MeCN resulted in immediate gas evolution and a slight yellowing of the solution. Solvent was removed under vacuum to give a pale yellow powder. The powder was washed with 50 mL of Et_2O to extract the co-formed salt and was dried under vacuum. Yield: 0.200 g (56%). IR (MeCN): $\nu_{CN} = 2111$ (w), 2104 (w), 2092 (w); $\nu_{CO} = 2011$ (s), 1960 (s). ^1H NMR (500 MHz, CD_2Cl_2): δ 7.35−7.75 (m, 15 H, PPh_3), 3.61 (s, 24 H, 18-crown-6), −7.20 (d, 49 Hz), −9.90 (d, 52 Hz), −11.25 (d, 50 Hz). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 69.6 (s), 68.3 (s), 61.9 (s). ESI MS (MeCN): *m/z* 427 $(HFe(CN)_2(CO)_2(PPh_3)^-)$.

$[K(18\text{-crown-6})][HFe(CN)_2(CO)_2\{P(OPh)_3\}]\cdot[K(18\text{-crown-6})]Cl$, $[K(18\text{-crown-6})][\mathbf{1}H(CO)\{P(OPh)_3\}]\cdot[K(18\text{-crown-6})]Cl$. A solution of 0.066 g (0.083 mmol) of $[K(18\text{-crown-6})]_2[Fe(CN)_2(CO)_3]$ in 10 mL of MeCN was treated with 0.085 mL of 1 M HCl in Et_2O, resulting in an immediate change from pale yellow to colorless. Addition of a solution of 0.025 mL (0.095 mmol) of $P(OPh)_3$ in 5 mL of MeCN resulted in immediate gas evolution and a slight yellowing of the solution. Solvent was removed under vacuum to give a pale yellow powder and was dried under vacuum. Yield: 0.073 g (79%). IR (MeCN): $\nu_{CN} = 2118$ (w), 2112 (w), 2101 (vw), 2080 (vw), 2086 (vw); $\nu_{CO} = 2031$ (s), 1983 (s). ^1H NMR (500 MHz, CD_2Cl_2): δ 7.7−7.0 (m, 18 H, $P(O\mathit{Ph})_3$); 3.56 (s, 48 H, 18-crown-6); −8.13 (d, 70 Hz, Fe-*H*); −8.45 (d, 70 Hz, Fe-*H*); −12.60 (d, 70 Hz, Fe-*H*). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 172.3 (s); 165.5 (s); 130.1 (s).

$[K(18\text{-crown-6})][HFe(CN)_2(CO)(dppv)]$, $[K(18\text{-crown-6})][\mathbf{1}H(dppv)]$. A solution of $[K(18\text{-crown-6})]_2[Fe(CN)_2(CO)_3]$ (0.254 g, 0.318 mmol) in MeCN (10 mL) was treated with a solution of 0.329 g (0.325 mmol) of $[H(OEt_2)_2]BAr^F_4$ in 10 mL of MeCN, resulting in an immediate change from pale yellow to colorless. Addition of dppv (0.143 g, 0.362 mmol) resulted in immediate gas evolution and a color change to bright yellow. Solvent was removed under vacuum to give a pale yellow powder. Addition of 100 mL of Et_2O gave a cloudy yellow solution. Upon concentrating the clear yellow filtrate by half and storing in the freezer at −20 °C overnight, the product precipitated as pale yellow microcrystals. The solid was filtered and dried under vacuum. Yield: 0.218 g (82%). IR (MeCN): $\nu_{CN} = 2087$ (m), 2080 (m); $\nu_{CO} = 1936$ (s). ^1H NMR (500 MHz, CD_2Cl_2): δ 7.33−7.91 (m,

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20 H, Ph), 3.59 (s, 24, 18-crown-6), 1.69 (br s, 2 H, $Ph_2PCHCHPPh_2$), −8.64 (t, Fe-*H*, $J_{HP} = 58$ Hz), −14.02 (dd, Fe−*H*, $J_{HP} = 59$ Hz, $J_{HP} = 49$ Hz). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 108.2 (d), 103.7 (s), 97.2 (d). ESI MS (MeCN): *m/z* 533 ($HFe(CN)_2(CO)(dppv)^-$). Anal. Calcd for $C_{41}H_{47}FeKN_2O_7P_2$: C, 58.85; H, 5.66; N, 3.35. Found: C, 58.81; H, 5.27; N, 3.65.

Protonation of [K(18-crown-6)][1(dppv)]. In MeCN: A solution of [K(18-crown-6)][**1**H(dppv)] (0.102 g, 0.123 mmol) in 10 mL of MeCN was treated with HCl (1.0 M in Et_2O, 0.125 mL). Gas evolution and a peak for free H_2 at δ 4.56 in the ^1H NMR spectrum were observed. The product precipitated from solution as a yellow powder. The solid was isolated by filtration and recrystallized from 5 mL of CH_2Cl_2 upon addition of 50 mL of hexane. Yield: 0.078 g (76%). IR (MeCN): $\nu_{CN} = 2111$ (w), 2104 (w sh); $\nu_{CO} = 2004$ (s). ^1H NMR (500 MHz, CD_2Cl_2): δ 8.14 (s, 1H, C*H*); 8.03 (s, 1H, C*H*); 8.0−7.3 (m, 20 H, Ph), 2.16 (s, 3H, $NCCH_3$). ^{31}P NMR (202 MHz, $CDCl_3$): δ 84.1 (s̃) Anal. Calcd for $C_{31}H_{25}FeN_3OP_2$: C, 64.94; H, 4.39; N, 7.33. Found: C, 64.12; H, 4.19; N, 8.01.

In CH_2Cl_2: A solution of 0.050 g (0.060 mmol) of [K(18-crown-6)][**1**H(dppv)] in 10 mL of CH_2Cl_2 was treated with a solution of 0.067 g (0.066 mmol) of $[H(OEt_2)_2]BAr^F_4$ in 10 mL of CH_2Cl_2. Gas evolution was observed. IR (CH_2Cl_2): $\nu_{CN} = 2110$ (w, br); $\nu_{CO} = 2004$(s). Solvent was removed under vacuum to give a yellow powder. Upon dissolving the yellow powder in 10 mL of MeCN, the IR spectrum was indistinguishable from that of **1**(NCMe)(dppv).

$[K(18\text{-crown-}6)]_2[HFe(CN)_3(CO)_2]\cdot MeCN$, $[K(18\text{-crown-}6)]_2$[1H(CN)(CO)]·MeCN. A solution of $[K(18\text{-crown-}6)]_2[Fe(CN)_2(CO)_3]$ (0.0923 g, 0.116 mmol) in 5 mL of MeCN was treated with 60 μL (0.12 mmol) of a 2.0 M solution of HCl in Et_2O, giving a colorless solution of the hydride. This solution was treated with PPh_3 (0.0601 g, 0.229 mmol). When gas evolution ceased, a solution of 0.0083 g (0.13 mmol) KCN in ~5 mL of MeOH was added to the reaction mixture. After stirring for 30 min, the solvent was removed under vacuum to give a pale yellow powder. The product was extracted with 5 mL of MeCN, and the resulting pale yellow solution was layered with 25 mL of Et_2O. The pale yellow crystalline solid was isolated by filtration and washed with 60 mL of Et_2O to remove PPh_3. Yield: 0.045 g (49%). IR (MeCN): $\nu_{CN} = 2098$ (w), 2086 (w); $\nu_{CO} = 1992$ (s), 1935 (s). ^1H NMR (500 MHz, CD_2Cl_2): δ 3.58 (s, 48 H, 18-crown-6), 2.09 (s, 3 H, CH_3CN), −7.47 (s, Fe-*H*), −11.65 (s, Fe-*H*), −13.04 (s, Fe-*H*). Anal. Calcd for $C_{29}H_{49}FeK_2N_3O_{14}\cdot C_2H_3N$: C, 44.39; H, 6.25; N, 6.68. Found: C, 43.86; H, 5.96; N, 6.85.

Protonation of $[K(18\text{-crown-}6)][HFe(CN)_3(CO)_2]$. A solution of $[K(18\text{-crown-}6)]_2$[**1**H(CN)(CO)] (0.030 g, 0.038 mmol) in 5 mL of MeCN was treated with 0.040 mL of 1 M HCl in Et_2O. Gas evolution was observed, and the solution became darker yellow. Solvent was removed under vacuum to give a yellow solid. Yield: 0.028 g (84%). IR (MeCN): $\nu_{CN} = 2133$ (w), 2127 (w), 2118 (w); $\nu_{CO} = 2068$ (s), 2023 (s). These data match those previously reported by Liaw for $(PPN)_2[Fe(CN)_3(NCMe)(CO)_2]$.[12]

$[K(18\text{-crown-}6)][MeFe(CN)_2(CO)_3]$, $[K(18\text{-crown-}6)][1Me(CO)_2]$. A solution of 0.086 g (0.11 mmol) of $[K(18\text{-crown-}6)]_2[Fe(CN)_2(CO)_3]$ in 10 mL of CH_2Cl_2 was treated with 0.011 mL (0.10 mmol) of MeOTf resulting in a color change from pale yellow to colorless. IR (MeCN): $\nu_{CN} = 2109$ (w), 2083 (w), 2074 (w); $\nu_{CO} = 2016$ (s). ESI MS (MeCN): *m/z* 207 ($[MeFe(CN)_2(CO)_3]^-$).

$(Et_4N)[Fe(CN)_2(COMe)(CO)(dppv)]$, Et_4N[1Ac(dppv)]. A solution of 0.250 g (0.315 mmol) of $(Et_4N)_2[Fe(CN)_2(CO)_3]$ in 20 mL of CH_2Cl_2 was treated with 0.034 mL (0.31 mmol) of MeOTf. Addition of 0.134 g (0.337 mmol) of dppv resulted in a color change to light yellow-orange. The volume of the solution was reduced by half, and the product was precipitated from solution upon addition of 40 mL of Et_2O. The bright yellow solid was washed with 20 mL of benzene to remove a yellow impurity and dried under vacuum. The solid was dissolved in 5 mL of CH_2Cl_2, and an equal volume of water was added to extract Et_4NI. The clear, yellow CH_2Cl_2 layer was isolated and taken to dryness. Yield: 0.130 g (48%). IR (MeCN): $\nu_{CN} = 2077$ (m); $\nu_{CO} = 1936$ (s), 1592 (m). ^1H NMR (500 MHz, CD_3CN): δ 7.9−7.0 (m, 22 H, dppv), 2.59 (s, 3 H, CH_3). ^{31}P NMR (202 MHz, CD_3CN): δ 73.3 (br s), 72.1 (d, 3 Hz), 70.7 (br s), 69.9 (d, 3 Hz). ESI MS (MeCN): *m/z* 575 ($[Fe(CN)_2(COMe)(CO)(dppv)]^-$). Anal. Calcd for $C_{39}H_{45}FeN_3O_2P_2$: C, 66.39; H, 6.43; N, 5.96. Found: C, 65.41; H, 6.37; N, 5.79. A MeCN solution of the complex remained unchanged (no decarbonylation) after heating at reflux for 12 h.

$[K(18\text{-crown-}6)][Fe(CN)(CO)_3(CNCOPh)]$. A solution of $[K(18\text{-crown-}6)]_2[Fe(CN)_2(CO)_3]$ (0.097 g, 0.12 mmol) in 3 mL of MeCN was treated with PhCOCl (14 μL, 0.12 mmol), resulting in an immediate change from pale yellow to deep red. Solvent was removed under vacuum to give a dark red oil. The oil was extracted with 30 mL of Et_2O. The resulting solution was concentrated to approximately 2 mL, and the product was precipitated upon addition of 20 mL of hexane. The solid was isolated by filtration and dried under vacuum. Yield: 30 mg (42%). IR (MeCN): $\nu_{CN} = 2107$ (w), 2035 (m); $\nu_{CO} = 1947$ (s, sh), 1932 (vs), 1661 (m). ^1H NMR (500 MHz, CD_3CN): δ 8.18 (d, 2 H, *o*-Ph), 7.67 (t, 1 H, *p*-Ph), 7.54 (t, 2 H, *m*-Ph), 3.56 (s, 24 H, 18-crown-6). ESI MS (MeCN): *m/z* 297 ($[Fe(CN)(CNCOPh)(CO)_3]^-$). Anal. Calcd for $C_{24}H_{29}FeKN_2O_{10}$: C, 48.01; H, 4.87; N, 4.67. Found: C, 47.85; H, 4.90; N, 4.69. The corresponding acetyl derivative was prepared similarly using MeCOCl to give yellow solids with similar spectroscopic features.

Oxidation of $[K(18\text{-crown-}6)]_2[Fe(CN)_2(CO)_3]$. A solution of 0.048 g (0.060 mmol) of $[K(18\text{-crown-}6)]_2[Fe(CN)_2(CO)_3]$ in 10 mL of MeCN was treated with a solution of 0.040 g (0.12 mmol) of $FcPF_6$ in 10 mL of MeCN, giving a clear, yellow solution. The IR spectrum of the reaction mixture was difficult to interpret because of a large number of overlapping peaks; however, ESI-MS of the reaction mixture showed a significant signal for $[Fe(CN)_3(CO)_3]^-$.

Crystallography. Crystals were mounted to a thin glass fiber using Paratone-N oil (Exxon). Data, collected at 193 K on a Siemens CCD diffractometer, were filtered to remove statistical outliers. The integration software (SAINT) was used to test for crystal decay as a bilinear function of X-ray exposure time and sin(θ). The data were solved using SHELXTL (Table 2) by direct methods for $Fe(CN)_2(NCMe)(CO)(dppv)$ and $[K(18\text{-crown-}6)][HFe(CN)_3(CO)_2]\cdot MeCN$ and by dual methods for $[K(18\text{-crown-}6)][HFe(CN)_2(CO)(dppv)]\cdot MeCN\cdot Et_2O$; atomic positions were deduced from an *E* map or by an unweighted difference Fourier synthesis. Methyl hydrogen atom *U*'s were assigned as 1.5 U_{eq} of the carrier atom; remaining hydrogen atom *U*'s were assigned as 1.2 times carrier U_{eq}. Metal hydride hydrogen atoms were surfaced in a late Fourier difference map and were independently refined without restraints. Non-hydrogen atoms were refined anisotropically. Successful convergence of the full-matrix least-squares refinement of F^2 was indicated by the maximum shift/error for the final cycle.

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Supporting Information Available: Relevant spectra. Kinetic plots and details of kinetics experiments. Crystallographic information file (cif) for [K(18-crown-6)][**1**H(dppv)], **1**(NCMe)(dppv), and $[K(18\text{-crown-}6)]_2$[**1**H(CN)(CO)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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