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Borane-Protected Cyanides as Surrogates of H-Bonded Cyanides in [FeFe]-Hydrogenase Active Site Models

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Abstract

Triarylborane Lewis acids bind [Fe₂(pdt)(CO)₄(CN)₂]²⁻ (pdt²⁻ = 1,3-propanedithiolate) and [Fe₂(adt)(CO)₄(CN)₂]²⁻ [**3**]²⁻ (adt²⁻ = 1,3-azadithiolate, HN(CH₂S⁻)₂) to give the 2:1 adducts [Fe₂(xdt)(CO)₄(CNBAr₃)₂]²⁻. Attempts to prepare the 1:1 adducts [**1**(BAr₃)]²⁻ (Ar = Ph, C₆F₅) were unsuccessful, but related 1:1 adducts were obtained using the bulky borane B(C₆F₄-*o*-C₆F₅)₃ (BAr^F₃). By virtue of the N-protection by the borane, salts of [Fe₂(pdt)(CO)₄(CNBAr₃)₂]²⁻ sustain protonation to give hydrides that are stable (in contrast to [**H1**]⁻). The hydrides [**H1**(BAr₃)₂]⁻ are 2.5–5 pK_a units more acidic than the parent [**H1**]⁻. The adducts [**1**(BAr₃)]²⁻ oxidize quasi-reversibly around -0.3 V versus Fc^{0/+} in contrast to ca. -0.8 V observed for the [**1**]^{2-/−} couple. A simplified synthesis of [**1**]²⁻, [**3**]²⁻, and [Fe₂(pdt)(CO)₅(CN)]⁻ ([**2**]⁻) was developed, entailing reaction of the diiron hexacarbonyl complexes with KCN in MeCN.

Introduction

A highlight in the history of bioorganometallic chemistry is the discovery of cyanide ligands as cofactors in the [FeFe] and [NiFe] hydrogenases (H₂ases).¹ The role of cyanide in H₂ases remains underdetermined since few models incorporating this cofactor are available for testing, and those models that do exist exhibit reactions highly complicated by the behavior of the cyanide ligands.² Hydrogen bonding between the protein backbone and cyanide is known to anchor the active sites, which are otherwise lightly tethered to the protein.³ Cyanide is a powerful σ -donor ligand that in part serves to stabilize the ferrous state, as

illustrated by the redox inactivity of the $\text{Fe}(\text{CN})_2(\text{CO})$ center in the $[\text{NiFe}] \text{H}_2\text{ases}$.⁴ The situation is different in the $[\text{FeFe}] \text{H}_2\text{ases}$ since each Fe center carries one cyanide and at least one of the Fe centers undergoes redox.⁵

In synthetic analogues, cyanide interferes with the two key attributes of functional models: acid/base and redox reactions. Thus, even though salts of $[\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{CN})_2]^{2-}$ ($\text{pdt}^{2-} = 1,3\text{-propanedithiolate}$), $[\mathbf{1}]^{2-}$, were described in 1999,^{6,7} little work has been reported since their initial discovery in part because the products of protonation and oxidation of $[\mathbf{1}]^{2-}$ are unstable. Protonation of $(\text{Et}_4\text{N})_2[\mathbf{1}]$ occurs initially at the basic $\text{Fe}-\text{CN}$ followed by formation of the μ -hydrido derivative $\text{Et}_4\text{N}[(\mu\text{-H})\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{CN})_2]$ ($\text{Et}_4\text{N}[\mathbf{H1}]$), which exists as two major isomers.^{8,9} The salt $\text{Et}_4\text{N}[\mathbf{H1}]$ is labile, with a half-life of minutes in solution. Both chemical and electrochemical studies indicate that oxidized derivatives of $[\mathbf{1}]^{2-}$ are unstable.¹⁰ As a consequence of the problems associated with cyanide-centered reactions, most functional models feature phosphine ligands as surrogates.^{11,12}

Although cyanide is not compatible with many modeling schemes owing to its ambidentate reactivity, nature prevents such problems by encapsulating the active site in globular proteins. The crystal structures of the $[\text{FeFe}] \text{H}_2\text{ases}$ demonstrate the significance of hydrogen bonding to cyanide as observed in the 1.39 Å structure for the CpI enzyme from *Clostridium pasteurianum* (Figure 1).¹³ The distal $\text{Fe}-\text{CN}$ is strongly hydrogen-bonded to the ammonium center of Lys358 ($\text{N}\cdots\text{N}$ distance = 2.74 Å).¹⁴ The lysine group is highly conserved, and this specific hydrogen-bonding interaction has been shown to be critical for activity.^{13,15} The proximal cyanide is also weakly hydrogen bonded to Ser232 ($\text{N}\cdots\text{O}$ distance = 2.92 Å).

The present work is premised on the idea that hydrogen bonding to $\text{Fe}-\text{CN}$ centers can be simulated by $\text{FeCN}-\text{BR}_3$ interactions. The ability of triarylboranes to bind to cyanide ligands is well-established as exemplified by *trans*- $\text{RuH}(\text{CNBPh}_3)(\text{diphos})_2$, $\text{Ni}(\text{diphos})(\pi\text{-allyl})(\text{CNBPh}_3)$, $[\text{M}(\text{CNBAR}^{\text{F}}_3)_4]^{2-}$ ($\text{M} = \text{Ni}, \text{Pd}$; $\text{BAR}^{\text{F}}_3 = \text{B}(\text{C}_6\text{F}_5)_3$), and $\text{FeCp}(\text{CNBAR}^{\text{F}}_3)(\text{CO})_2$ ($\text{diphos} = \text{diphosphine}$).^{16–18} Motivated by interest in frustrated Lewis pairs (FLPs)¹⁹ and the role of boranes in alkene-polymerization,²⁰ the chemistry of boranes has rapidly developed,²¹ as have methods to evaluate their Lewis acidities.²² Recently, BAR^{F}_3 was used to convert the unreactive species $(\text{CO})_2(\text{CN})_2\text{Fe}(\text{pdt})\text{Ni}(\text{dxpe})$ ($\text{dxpe} = \text{dppe}, \text{dcpe}$) into hydride-containing model catalysts capable of catalytic oxidation of H_2 .²³ In parallel with these results, borane Lewis acids were examined with $[\text{FeFe}]\text{-H}_2\text{ase}$ active site models, as described below.

Results

Synthesis of $[\text{Fe}_2(\text{pdt})(\text{CO})_5(\text{CN})]^-$ and $[\text{Fe}_2(\text{xdt})-(\text{CO})_4(\text{CN})_2]^{2-}$ ($\text{xdt} = \text{adt}, \text{pdt}$)

A new synthesis was developed for cyanide-containing $[\text{FeFe}]\text{-H}_2\text{ase}$ models using KCN as a cyanide source (Scheme 1). Quaternary ammonium salts (R_4N^+ , $\text{R} = \text{Et}, \text{Bu}$) salts of cyanide had previously been used to generate the same anions.^{6,7} The salt $\text{K}_2[\mathbf{1}]$ formed in good yields upon treating $\text{Fe}_2(\text{pdt})(\text{CO})_6$ with an excess of KCN in refluxing MeCN. The salt $\text{K}_2[\text{Fe}_2(\text{adt})(\text{CO})_4(\text{CN})_2]$ ($\text{adt}^{2-} = 1,3\text{-azadithiolate}$, $\text{HN}(\text{CH}_2\text{S}^-)_2$) ($\text{K}_2[\mathbf{3}]$) was prepared analogously, also in good yield. The potassium salts are soluble in MeCN and even dissolve

in tetrahydrofuran (THF) and Et₂O in the presence of small amounts of MeCN. As we show below, the K⁺ in these salts usefully modifies the basicity of the Fe–CN centers, allowing the synthesis of complexes unattainable as their Et₄N⁺ salts. The monocyanides K–[Fe₂(pdt)(CO)₅(CN)] (K[**2**]) and K[Fe₂(adt)(CO)₅(CN)] were observed as respective intermediates in the formation of K₂[**1**] and K₂[**3**]. Using a slight deficiency of KCN, K[**2**] could be prepared in excellent yield from the hexacarbonyl. Like Et₄N[**2**], K[**2**] exhibits good solubility in MeCN and THF.

In the IR spectra of K₂[**1**] and K₂[**3**], the ν_{CO} and ν_{CN} bands occur at slightly higher energy than the analogous Et₄N⁺ compounds (Table 1).^{10,24} This shift may be attributed to the coordination of K⁺ to the cyanide ligands as observed previously for K[CpFe(CO)(CN)₂].²⁵ The salt K₂[**1**] was found to undergo anion exchange with PPNCl and Et₄NCl in MeCN, shifting ν_{CN} and ν_{CO} to lower energy, matching the previously reported IR spectrum.^{6,26}

2:1 Borane Adducts of [Fe₂(pdt)(CO)₄(CN)₂]^{2–}

The Lewis acid BAr^F₃ binds to the nitrogen centers of [**1**]^{2–} to give stable adducts (eq 1)

In addition to BAr^F₃, the weaker Lewis acids BPh₃ and B(2,4,6-C₆H₂F₃)₃ (BAr^{F#}₃) also formed related adducts. Treatment of a CH₂Cl₂ solution of (Et₄N)₂[**1**] with 2 equiv of these Lewis acids resulted in lightening of the solution color from red to orange. Upon binding of the borane, IR bands in the ν_{CO} and ν_{CN} regions shift to higher frequencies (Table 2). On the basis of the ν_{CO} bands for the adducts, the relative Lewis acidities of the boranes were BAr^F₃ > BAr^{F#}₃ > BPh₃, as established by Child's methods,^{22,27,28} computational methods, and other studies.^{29,30} The coordination of Lewis acids greatly increased the solubility of the complexes. Whereas the uncapped compound (Et₄N)₂[**1**] is soluble in MeCN and CH₂Cl₂, the adducts [**1**(BAr₃)₂]^{2–} are soluble in THF and, in the case of [**1**(BAr^F₃)₂]^{2–}, even in Et₂O.

Rapid turnstile rotation of Fe(CO)₂(CNBAr₃) centers was indicated by observation of a single BAr₃ environment in the ¹H NMR spectra of [**1**(BPh₃)₂]^{2–} and [**1**(BAr^{F#}₃)₂]^{2–}. Similarly, the ¹⁹F NMR spectra of [**1**(BAr^{F#}₃)₂]^{2–} and [**1**(BAr^F₃)₂]^{2–} showed only a single averaged environment. The Fe–CNBAr₃ linkage was confirmed by ¹¹B NMR spectra. The ¹¹B NMR spectrum of [**1**(BAr^F₃)₂]^{2–} adducts feature a broadened signal at δ –14. For the alternative linkage isomer Fe–NC–BAr₃, a sharp signal is expected near δ –20¹⁸. Similarly, the ¹¹B NMR spectrum of [**1**(BPh₃)₂]^{2–} exhibits a broad signal at δ –4.5, consistent with a M–CNBPh₃[–] linkage.¹⁷ The ¹¹B NMR spectrum of [**1**(BAr^{F#}₃)₂]^{2–} exhibits a broad signal at δ –15.

The structure of (Et₄N)₂[**1**(BAr^F₃)₂] was confirmed by X-ray crystallography (Figure 2). Reassuring for our modeling efforts, no obvious structural differences exist between (Et₄N)₂[**1**(BAr^F₃)₂] and the previously reported structure of (Et₄N)₂[**1**]¹⁰ (Supporting Information, Table S3). For example, the Fe–Fe, C≡N, Fe–CO, and C≡O distances differ

by less than 0.02 Å. Slight shortening of the Fe–CN bond is observed upon coordination of BAr^{F}_3 , with the Fe–CN bond 0.06 Å shorter for $(\text{Et}_4\text{N})_2[\mathbf{1}(\text{BAr}^{\text{F}}_3)_2]$ than for $(\text{Et}_4\text{N})_2[\mathbf{1}]$.

2:1 Borane Adducts of $[\text{Fe}_2(\text{adt})(\text{CO})_4(\text{CN})_2]^{2-}$

Given the basicity of the NH center in $[\mathbf{3}]^{2-}$, adducts of this complex with boranes were anticipated to be more complex than they were for $[\mathbf{1}]^{2-}$. IR measurements indicated that addition of 2 equiv of BAr^{F}_3 to $(\text{Et}_4\text{N})_2[\mathbf{3}]$ resulted in an unstable complex. The less Lewis-acidic BPh_3 afforded the desired 2:1 adduct $(\text{Et}_4\text{N})_2[\text{Fe}_2(\text{adt})(\text{CO})_4(\text{CNBPh}_3)_2]$, $(\text{Et}_4\text{N})_2[\mathbf{3}(\text{BPh}_3)_2]$. The IR spectrum of this salt is very similar to that for $(\text{Et}_4\text{N})_2[\mathbf{1}(\text{BPh}_3)_2]$ (Table 2). Its ^1H NMR spectrum displayed a single BPh_3 environment, consistent with both BPh_3 groups being bound to Fe–CN centers and rapid rotation of the $\text{Fe}(\text{CO})_2(\text{CNBPh}_3)$ subunits.

1:1 Borane Adducts of $[\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{CN})_2]^{2-}$

Attempts were made to generate the 1:1 borane adducts of $[\mathbf{1}]^{2-}$. As indicated by IR spectroscopy, treatment of $(\text{Et}_4\text{N})_2[\mathbf{1}]$ with 1 equiv of BAr^{F}_3 or BPh_3 gave a mixture of $(\text{Et}_4\text{N})_2[\mathbf{1}(\text{BAr}_3)_2]$, starting material, and insoluble solids (that do not redissolve in the presence of boranes). In an effort to stabilize 1:1 adducts, the bulky borane $\text{B}(\text{C}_6\text{F}_4\text{-}o\text{-}\text{C}_6\text{F}_5)_3$ ($\text{BAr}^{\text{F}*}_3$) was examined. The reaction of $(\text{Et}_4\text{N})_2[\mathbf{1}]$ with 1 equiv of $\text{BAr}^{\text{F}*}_3$ precipitated intractable solids, even when the addition was conducted slowly and on dilute solutions. When 2 equiv of $\text{BAr}^{\text{F}*}_3$ were added quickly, the 2:1 adduct $(\text{Et}_4\text{N})_2[\mathbf{1}(\text{BAr}^{\text{F}*}_3)_2]$ formed in good yield.

The formation of 1:1 adducts required starting with $\text{K}_2[\mathbf{1}]$ instead of the Et_4N^+ salt. Treatment of $\text{K}_2[\mathbf{1}]$ with 1 equiv of $\text{BAr}^{\text{F}*}_3$ gave $\text{K}_2[\mathbf{1}(\text{BAr}^{\text{F}*}_3)]$ (eq 2).

The IR spectrum of this adduct shows ν_{CN} bands at disparate energies (2126, 2058 cm^{-1}), consistent with the coordination of $\text{BAr}^{\text{F}*}_3$ to a single cyanide ligand (see Figure 3).

The salt $\text{K}_2[\mathbf{1}(\text{BAr}^{\text{F}*}_3)_2]$ was produced in good yield. This pale red solid exhibits good solubility in ether and THF, as found for $(\text{Et}_4\text{N})_2[\mathbf{1}(\text{BAr}^{\text{F}}_3)_2]$. The IR spectra of $\text{K}_2[\mathbf{1}(\text{BAr}^{\text{F}*}_3)]$ and $\text{K}_2[\mathbf{1}(\text{BAr}^{\text{F}*}_3)_2]$ were found to vary with solvent (CH_2Cl_2 vs MeCN). The solvent effect is reversible. In contrast, the IR spectrum for $(\text{Et}_4\text{N})_2[\mathbf{1}(\text{BAr}^{\text{F}*}_3)_2]$ was unchanged in these solvents (Table 3).

Hydride Derivatives $[(\mu\text{-H})\text{Fe}_2(\text{xdt})(\text{CO})_4(\text{CNBAr}_3)_2]^-$ (xdt = adt, pdt)

In contrast to the complications reported for the protonation of $[\mathbf{1}]^{2-}$,⁹ protonation of the borane adducts $[\mathbf{1}(\text{BAr}_3)_2]^{2-}$ proceeded straightforwardly (eq 3).

Exploiting their distinctive solubility, the borane complexes $(\text{Et}_4\text{N})_2[\mathbf{1}(\text{BAR}_3)_2]$ were protonated as an ether or THF solution with excess $\text{HCl}\cdot\text{Et}_2\text{O}$. Protonation is accompanied by a lightening in the solution color and precipitation of Et_4NCl . Protonation causes a shift of both ν_{CO} and ν_{CN} to higher energies, consistent with oxidation of the diiron centers (Table 4).

The hydrido complexes exhibit characteristic high-field ^1H NMR signals. ^1H NMR spectra of $[\mathbf{H1}(\text{BAR}_3)_2]^-$ in CD_2Cl_2 solution display two or three hydride signals, depending on the borane. Ignoring the conformation of the Fe_2pdt center, four isomers are possible for $[\mathbf{H1}(\text{BAR}_3)_2]^-$, three of which are symmetrical with equivalent CNBAR_3^- ligands (Figure 4). All four isomers are observed for the $[(\mu\text{-H})\text{Fe}_2(\text{pdt})\text{-(CO)}_4(\text{CN}^t\text{Bu})_2]^+$ system.³²

Freshly generated solutions of $[\mathbf{H1}(\text{BAR}^{\text{F}_3})_2]^-$ consist of three isomeric hydrides, indicated by ^1H NMR signals at δ -13.7, -16.4, and -19.0 in a ratio of 1:1:5. Over the course of 2 d, the isomer ratio shifted to 1:36:32. The structures of these isomers can be partially inferred from the ^{19}F NMR spectra, since the *p*-F signals are well-resolved. On the basis of these data, the ^1H NMR signal at δ -16, which corresponds to the kinetically favored species, is assigned to the unsymmetrical apical/basal (a/b) isomer. The other two hydride signals arise from symmetrical complexes (single ^{19}F NMR signals), probably the b/b and a/a isomers.

The ^1H NMR spectrum of $[\mathbf{H1}(\text{BAR}^{\text{F}_3})_2]^-$ consisted of only two high-field signals, at δ -16.4 and -19.2, in a 3:1 ratio. After equilibration over the course of 3 d, this ratio shifted to 1:1.5. In the ^{19}F NMR spectrum of $[\mathbf{H1}(\text{BAR}^{\text{F}_3})_2]^-$, the ratio of the *o*-F and *p*-F signals compared to the ratio of the hydride signals are consistent with one symmetric and one asymmetric isomer (Supporting Information). The species with the ^1H NMR signal at δ -16.4 is assigned to the a/b isomer on the basis of the relative intensities of ^1H and ^{19}F NMR signals.

Freshly generated solutions of $[\mathbf{H1}(\text{BPh}_3)_2]^-$ consisted of three isomers, indicated by ^1H NMR signals at δ -13.3, -16.1, and -19.2 in a ratio of 1.6:4.3:1. This mixture isomerizes over the course of 2 d to a 1:11:11 ratio. The ^1H NMR spectrum of $[\mathbf{H1}(\text{BPh}_3)_2]^-$ features four signals assigned to the 2,6-protons on BPh_3 , the ratio of which are consistent with two symmetric isomers and one asymmetric isomer. On the basis of the integrations of the hydride signals and *ortho*-aryl signals of $[\mathbf{H1}(\text{BPh}_3)_2]^-$, the high-field signal at δ -16.14 could be assigned as the a/b isomer. The ^1H NMR signals for the symmetrical isomers of $[\mathbf{H1}(\text{BAR}_3)_2]^-$ are assigned in analogy to the assignments for $[(\mu\text{-H})\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{CN}^t\text{Bu})_2]^+$.³² The most downfield hydride signal (δ -13.5) is assigned to one of the b/b isomers, presumably *trans* for electrostatic reasons, and the most upfield hydride signal (δ -19.0) is assigned to the a/a isomer.

The boranes noticeably affect the basicity of the diiron unit. The $\text{p}K_{\text{a}}^{\text{MeCN}}$ of $[\mathbf{H1}]^-$ is estimated to be 16 as it is fully deprotonated by 1 equiv of benzylamine ($\text{p}K_{\text{a}}^{\text{MeCN}} = 16.91$).³³ Protonation of $[\mathbf{1}]^{2-}$ to give $[\mathbf{H1}]^-$ occurs with one equiv 2,4,6-trimethylpyridinium ($\text{p}K_{\text{a}}^{\text{MeCN}} = 14.98$).³³ As observed with $[\mathbf{H1}]^-$, both $[\mathbf{H1}(\text{BAR}^{\text{F}_3})_2]^-$ and $[\mathbf{H1}(\text{BAR}^{\text{F}_3})_2]^-$ can also be reversibly deprotonated. By ^{19}F NMR spectroscopy using anilinium ($\text{p}K_{\text{a}}^{\text{MeCN}} = 10.62$) as the acid,³³ the $\text{p}K_{\text{a}}^{\text{MeCN}}$ of $[\mathbf{H1}(\text{BAR}^{\text{F}_3})_2]^-$ was calculated to

be 10.8 ± 0.2 . Examination of mixtures of $[\mathbf{1}(\text{BAr}^{\text{F}\#}_3)_2]^{2-}$ and pyridinium ($\text{p}K_{\text{a}}^{\text{MeCN}} = 12.53$)³³ gave a $\text{p}K_{\text{a}}^{\text{MeCN}}$ of 13.5 ± 0.1 . Deprotonation of $[\mathbf{H1}(\text{BPh}_3)_2]^-$ with pyridine did not cleanly reform $[\mathbf{1}(\text{BPh}_3)_2]^{2-}$, probably because the adducts of this less-acidic borane are labile. The values for ν_{CO} are similar for $[\mathbf{H1}(\text{BAr}^{\text{F}\#}_3)_2]^-$ and $[\mathbf{H1}(\text{BPh}_3)_2]^-$, suggesting that their $\text{p}K_{\text{a}}$ values are probably comparable. The hydridic nature of $[\mathbf{H1}(\text{BAr}^{\text{F}\#}_3)_2]^-$ was investigated by treatment of a CD_2Cl_2 solution of $[\mathbf{H1}(\text{BAr}^{\text{F}}_3)_2]^-$ with Me_3NHBAr . ^1H NMR analysis failed to indicate any interaction.

The presence of adt^{2-} in $[\text{FeFe}]\text{-H}_2\text{ase}$ models has been shown to greatly affect the protonation pathway. The protonation of $(\text{Et}_4\text{N})_2[\mathbf{3}]$ has been previously reported as occurring at the amine, forming $[\text{Fe}_2(\text{Hadt})(\text{CO})_4(\text{CN})_2]^-$, $[\alpha\text{-H3}]^-$, followed by slow proton transfer over days to form the unstable bridging hydride $[(\mu\text{-H})\text{Fe}_2(\text{adt})(\text{CO})_4(\text{CN})_2]^-$, $[\mathbf{H3}]^-$.³⁴ Unlike the straightforward protonation of $[\mathbf{1}(\text{BAr}_3)_2]^{2-}$, protonation of $[\mathbf{3}(\text{BPh}_3)_2]^{2-}$ proved complicated and sensitive to solvent. Using $\text{H}(\text{Et}_2\text{O})_2\text{B}(\text{Ar}^{\text{F}6})_4$ protonation in MeCN solution resulted in N-protonation ($\nu_{\text{CN}} \approx 10\text{ cm}^{-1}$, $\nu_{\text{CO}} \approx 20\text{ cm}^{-1}$), whereas protonation in a CH_2Cl_2 solution produced some bridging hydrides ($\delta\text{-}15.3$ and $\delta\text{-}18.4$) ($\text{Ar}^{\text{F}6} = \text{C}_6\text{H}_3\text{-}3,5\text{-(CF}_3)_2$, Supporting Information).

Electrochemistry of $[\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{CNBAr}_3)_2]^{2-}$ and $[(\mu\text{-H})\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{CNBAr}_3)_2]^-$

According to its cyclic voltammogram, a freshly prepared CH_2Cl_2 solution of $(\text{Et}_4\text{N})_2[\mathbf{1}]$ irreversibly oxidizes at -0.79 V (Figure 5, all potentials vs $\text{Fc}^{0/+}$). The process is accompanied by the appearance of a deposit on the working electrode. In contrast, $(\text{Et}_4\text{N})_2[\mathbf{1}(\text{BAr}_3)_2]$ was found to oxidize quasi-reversibly without fouling the electrodes. The oxidation potentials vary between -0.23 and -0.36 V depending on the Lewis acid (Table 5).

The redox properties of $\text{Et}_4\text{N}[\mathbf{H1}]$ have not been evaluated because of the compound's instability. Borane-capping allowed for the observation of a quasi-reversible reduction for $\text{Et}_4\text{N}[\mathbf{H1}(\text{BAr}^{\text{F}}_3)_2]$ at -1.65 V vs $\text{Fc}^{0/+}$. The potentials of the $[\mathbf{1}(\text{BAr}_3)_2]^{2-/ -}$ and $[\mathbf{H1}(\text{BAr}_3)_2]^{-/2-}$ couples correlated with the Lewis acidity of the borane (Table 5). Reduction of $[\mathbf{H1}(\text{BPh}_3)_2]^-$ and $[\mathbf{H1}(\text{BAr}^{\text{F}\#}_3)_2]^-$ occurred near -1.74 V ; however, reversibility was only observed at scan rates above 0.5 V/s . Interestingly, BPh_3 and $\text{BAr}^{\text{F}\#}_3$ had similar effects on the redox potentials even though their Lewis acidities are quite different.^{28,29,35}

Discussion

A new synthesis of $[\mathbf{1}]^{2-}$ and $[\mathbf{3}]^{2-}$ was developed involving the use of KCN. The method offers advantages over the traditional route: not only is KCN cheaper and safer to use than Et_4NCN , it is commercially available in isotopically labeled forms. Once isolated, $\text{K}_2[\mathbf{1}]$ undergoes anion exchange to afford the corresponding Et_4N^+ and PPN^+ salts. In contrast to the use of Et_4NCN , substitution using KCN proceeds via the readily isolated intermediate $\text{K}[\text{Fe}_2(\text{xdt})(\text{CO})_5(\text{CN})]$.

The coordination of the boranes to $[\mathbf{1}]^{2-}$ and $[\mathbf{3}]^{2-}$ suppresses reactions at the Fe-CN sites, which complicated previous studies on the protonation and redox of these very appealing

models. Capping the Fe–CN sites with boranes allowed for straightforward protonation of $[1(\text{BAR}_3)_2]^{2-}$ to give the μ -hydrido derivatives $[\text{H1}(\text{BAR}_3)_2]^-$. Unlike $[\text{H1}]^-$, $[\text{H1}(\text{BAR}_3)_2]^-$ was readily isolated and handled. In solution, $[\text{H1}(\text{BAR}_3)_2]^-$ exists as a mixture of isomers, the distribution of which is similar for $[(\mu\text{-H})\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{CN}^t\text{Bu})_2]^+$.³²

Dihydrogen bonds between a metal hydrides and a protic group is a key interaction in the evolution and oxidation of hydrogen by H_2 ases. “Hydridic hydrides” are expected to form dihydrogen bonds with acids.³⁶ Indeed, crystallographic study of the $[\text{FeFe}]\text{-H}_2$ ase model $[\text{HFe}_2(\text{Hadt})(\text{CO})_2(\text{dppv})_2]^{2+}$, which contains both an N-protonated adt and terminal iron hydride, reveals a short $\text{NH}\cdots\text{HFe}$ distance of 1.8 Å ($\text{dppv} = \text{cis-C}_2\text{H}_2(\text{PPh}_2)_2$).¹² Similarly, NMR measurements indicate intermolecular dihydrogen bonding between $[(\text{CO})\text{-(CNBAR}^{\text{F}}_3)_2\text{Fe(H)(pdt)Ni(dppe)}]^-$ and Me_3NH^+ .²³ In contrast, we show in this work that the bridging hydride in $[\text{FeFe}]\text{-H}_2$ ase models do not engage in intramolecular hydrogen bonding.³⁷ Underscoring the nonhydridic nature of $\text{Fe}^{\text{II}}(\mu\text{-H})\text{Fe}^{\text{II}}$ species, we observed no interaction between $[\text{H1}(\text{BAR}_3)_2]^-$ and Me_3NH^+ , despite an electrostatic driving force.

The strengths of the hydrogen bonds from the protein to the two CN^- cofactors differ, as reflected by the distances between hydrogen-bonded heteroatoms. The $\text{Fe}^{\text{distal}}\text{-CN}\cdots\text{N}$ (lysine ϵ -ammonium) distance is 2.74 Å, whereas the $\text{Fe}^{\text{proximal}}\text{-CN}\cdots\text{O}$ (serine hydroxyl) distance is 2.92 Å.¹³ To simulate the disparate nature of these two hydrogen-bonding interactions, attempts were made to bind 1 equiv of a Lewis acid to $[1]^{2-}$. The reaction of 1 equiv of BAR^{F}_3 and $\text{BAR}^{\text{F}*}_3$ with $(\text{Et}_4\text{N})_2[1]$ gave intractable products. The targeted asymmetrically protected dicyanide complex was obtained by combining the bulky borane $\text{BAR}^{\text{F}*}_3$ and $\text{K}_2[1]$. We propose that this adduct is stabilized by binding of K^+ to the uncapped FeCN center. This interaction is consistent with the solvent dependence of the IR spectra of $\text{K}_2[1(\text{BAR}^{\text{F}*}_3)]$ and $\text{K}_2[1(\text{BAR}^{\text{F}*}_3)_2]$. In CH_2Cl_2 solutions, $\text{BAR}^{\text{F}*}_3$ coordinates strongly to Fe-CN , whereas in MeCN solutions K^+ appears to compete with $\text{BAR}^{\text{F}*}_3$ for coordination to Fe-CN . The IR spectrum of $(\text{Et}_4\text{N})_2[1(\text{BAR}^{\text{F}*}_3)_2]$ was found not to vary with solvent.

In terms of ligand properties, how does $\text{CNBAR}^{\text{F}}_3^-$ compare with related ligands? The answer depends on the method of measurement. Using the criterion of ν_{CO} , CNBAR_3^- is less basic than PMe_3 .³¹ Similar ranking is indicated when comparing the $\text{pK}_a^{\text{MeCN}}$ of the corresponding hydrido complexes.³⁸ On the other hand, in terms of redox properties, the $[\text{H1}(\text{BAR}_3)_2]^{2-/1-}$ couple (ca. -1.7 V vs $\text{Fc}^{0/+}$) is far more cathodic than the couple $[\text{HFe}_2(\text{pdt})(\text{CO})_4(\text{PMe}_3)_2]^{+/0}$ (-1.39 V).³⁹

Now that adt^{2-} has been established as the dithiolate cofactor, the question remains: what steps are required to convert $[\text{Fe}_2(\text{adt})(\text{CO})_4(\text{CN})_2]^{2-}$ and $[(\mu\text{-H})\text{Fe}_2(\text{adt})(\text{CO})_4(\text{CN})_2]^-$ into functioning catalysts? Previously the barrier to this activation was the interfering reactivity of the cyanide ligands, which are both bases and potentially bridging ligands. This distracting behavior has been addressed with the introduction of the borane protecting groups, yet the diferrous hydride remains bridging. One obvious gap is the absence of the 4Fe-4S cluster–ligand on the proximal Fe center. Beyond that omission, the rotated structure may require a more protein-like environment, especially a hydrogen-bonding interaction directed at a basal cyanide on the distal Fe.^{3,4}

Experimental Section

Materials and Methods

Standard Schlenk or glovebox techniques were used. Solvents used for syntheses were high-performance liquid chromatography grade, further purified by using an alumina filtration system (Glass Contour Co., Irvine, CA), and were deoxygenated prior to use. NMR solvents were purchased from Cambridge Isotope Laboratories, dried with CaH_2 , and stored under nitrogen over activated molecular sieves. The preparations of $(\text{Et}_4\text{N})_2[\mathbf{1}]$ and $(\text{Et}_4\text{N})_2[\mathbf{3}]$ are described elsewhere.^{24,42} BAr^{F}_3 was purchased from Boulder Scientific and twice sublimed under vacuum at 90 °C prior to use. BPh_3 was prepared by pyrolysis of $\text{HNMe}_3\text{BPh}_4$.⁴³ The preparations of $\text{BAr}^{\text{F}*}_3$ and BAr^{F}_3 have been reported. IR spectra were recorded using a PerkinElmer Spectrum 100 FT-IR instrument using a CaF_2 solution cell. These data are reported in cm^{-1} . Elemental analyses were conducted at the University of Illinois Microanalysis Laboratory. Cyclic voltammetry was performed under nitrogen at room temperature using a CHI 630D potentiostat with glassy carbon working electrode, Pt wire counter electrode, pseudoreference electrode Ag wire, and with ferrocene as an internal standard. NMR spectra were recorded on a Varian Mercury 500 MHz spectrometer, and the ^1H NMR chemical shifts were referenced to the residual protons of deuterated solvents. ^{11}B (recorded on a Varian 400 MHz instrument) and ^{19}F NMR spectra were referenced to external standards of $\text{BF}_3\cdot\text{Et}_2\text{O}$ and 1% CFCl_3 in CDCl_3 , respectively.

$\text{K}_2[\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{CN})_2]$, $\text{K}_2[\mathbf{1}]$ —A Schlenk flask was charged with $\text{Fe}_2(\text{pdt})(\text{CO})_6$ (1.0 g, 2.6 mmol), KCN (0.51 g, 7.8 mmol), and MeCN (100 mL). The mixture was heated at reflux for 28 h, with monitoring by IR spectroscopy. The mixture was filtered through Celite, and the filtrate was evaporated under vacuum. The resulting solid was washed with Et_2O (50 mL) and hexanes (50 mL) and then dried under vacuum. Yield: 0.91 g (76%). Anal. Calcd for $\text{C}_9\text{H}_6\text{Fe}_2\text{K}_2\text{N}_2\text{O}_4\text{S}_2\cdot 0.33\text{CH}_3\text{CN}$ (found): C, 24.49 (24.35); H, 1.49 (1.64); N, 6.81 (6.88). IR (MeCN): 2077, 1967, 1928, 1890.

$\text{K}[\text{Fe}_2(\text{pdt})(\text{CO})_5(\text{CN})]$, $\text{K}[\mathbf{2}]$ —A two-necked Schlenk flask was charged with $\text{Fe}_2(\text{pdt})(\text{CO})_6$ (0.50 g, 1.30 mmol), 0.9 equiv of KCN (0.076 g, 1.17 mmol), and MeCN (50 mL). The mixture was heated at reflux for 6 h, with monitoring by IR spectroscopy. The mixture was filtered through Celite, and the filtrate was dried under vacuum. The resulting oil was extracted into Et_2O , and product was precipitated with pentane. The resulting solid was collected by filtration, washed with pentane (50 mL), and dried under vacuum. Yield: 0.42 g (85%). Anal. Calcd for $\text{C}_9\text{H}_6\text{Fe}_2\text{KNO}_5\text{S}_2$ (found): C, 25.55 (25.62); H, 1.43 (1.71); N, 3.31 (3.17). IR (MeCN): 2092, 2031, 1976, 1956, 1946, 1916.

$(\text{Et}_4\text{N})_2[\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{CNBAr}^{\text{F}}_3)_2]$, $(\text{Et}_4\text{N})_2[\mathbf{1}(\text{BAr}^{\text{F}}_3)_2]$ —A slurry of $(\text{Et}_4\text{N})_2[\mathbf{1}]$ (2.40 g, 3.74 mmol) in CH_2Cl_2 (50 mL) was treated with BAr_3 (3.88 g, 7.57 mmol) in CH_2Cl_2 (10 mL). After stirring the reaction solution for 30 min, the solvent was evaporated to yield a red oil, which a red powder upon standing under vacuum. The product was triturated with pentane (3×10 mL) and crystallized from CH_2Cl_2 (10 mL) layered with Et_2O (10 mL) and pentane (30 mL). Yield: 5.25 g (99%). Anal. Calcd for $\text{C}_{61}\text{B}_2\text{Fe}_2\text{S}_2\text{H}_{46}\text{O}_4\text{N}_4\text{F}_{30}$ (found): C, 43.97 (43.50); H, 2.78(3.07); N, 3.36 (3.60). IR (CH_2Cl_2): 2136, 1990, 1954, 1922. ^1H

NMR (CD₂Cl₂): δ 3.10 (16 H, m, (CH₃CH₂)₄N), 1.73 (4 H, t, SCH₂CH₂CH₂S), 1.48 (2 H, m, SCH₂CH₂CH₂), 1.23 (24 H, t, (CH₃CH₂)₄N). ¹¹B NMR (CD₂Cl₂): δ -14. ¹⁹F NMR (CD₂Cl₂): δ -134 (d, o-F), -162 (t, p-F), -167 (t, m-F). Crystals suitable for X-ray diffraction were obtained by the slow diffusion of pentane into a THF solution of (Et₄N)₂[I(BAr^F₃)₂] at -30 °C.

(Et₄N)₂[Fe₂(pdt)(CO)₄(CNBAr^F₃)₂], (Et₄N)₂[1(BAr^F₃)₂]—A solution of (Et₄N)₂[1] (0.16 g, 0.25 mmol) in CH₂Cl₂ (10 mL) was treated dropwise with a solution of BAr^F₃ (0.20 g, 0.50 mmol) in 10 mL of CH₂Cl₂. The solvent was evaporated to yield a red oil, which was extracted into CH₂Cl₂ (5 mL). The extract was layered with pentane (20 mL) and cooled at -30 °C for 2 d, producing a red oil. The filtrate was decanted off, and the oil was triturated with pentane (3 × 10 mL) to produce a red solid. Yield: 0.34 g (95%). Anal. Calcd for C₆₁H₅₈B₂F₁₈Fe₂N₄O₄S₂ (found): C, 50.51 (50.82); H, 4.03 (4.04); N, 3.86 (4.15). IR (CH₂Cl₂): 2147, 1986, 1947, 1915. ¹H NMR (CD₂Cl₂): δ 6.41 (12 H, t, *m*-ArH), 3.09 (16H, m, (CH₃CH₂)₄N), 1.70 (4 H, t, SCH₂CH₂CH₂S), 1.42 (2 H, m, SCH₂CH₂CH₂), 1.22 (24 H, t, (CH₃CH₂)₄N). ¹¹B NMR (CD₂Cl₂): δ -15. ¹⁹F NMR (CD₂Cl₂): δ -99.9 (s, o-F), -117.1 (s, p-F).

K₂[Fe₂(pdt)(CO)₄(CN)(CNBAr^F₃)], K₂[1(BAr^F₃)₂]—A solution of K₂[1] (26 mg, 0.058 mmol) in MeCN (20 mL) was treated over the course of 2 h dropwise with a MeCN solution (10 mL) of BAr^F₃ (50 mg, 0.052 mmol). The solvent was then removed under vacuum and the residue was extracted into 5 mL of Et₂O. The extract was passed through Celite and then evaporated under vacuum to yield a tacky red solid, which was triturated with pentane (3 × 10 mL). Yield: 50 mg (68%). Anal. Calcd for C₄₅BFe₂S₂H₆O₄N₂F₂₇K₂·0.33CH₃CN·OEt₂ (found): C, 39.66 (40.03); H, 1.14 (0.88); N, 2.17 (2.03). IR (MeCN): 2096, 2081, 1990, 1978, 1942, 1931, 1913, 1888. IR (CH₂Cl₂): 2100, 1990, 1927.

K₂[Fe₂(pdt)(CO)₄(CNBAr^F₃)₂], K₂[1(BAr^F₃)₂]—A solution of K₂[1] (24 mg, 0.052 mmol) in MeCN (5 mL) was treated with a solution of BAr^F₃ (100 mg, 0.11 mmol) in MeCN (10 mL). The solvent was then removed under vacuum. The residue was extracted into 5 mL of Et₂O, and this extract was treated with 20 mL of pentane, precipitating a red oil that was triturated with pentane (3 × 10 mL) to yield a red solid. Yield: 84 mg (68%). IR (MeCN) 2098, 1991, 1959, 1947, 1932, 1909. IR (CH₂Cl₂): 2119, 1989, 1951, 1916.

Et₄N[(μ -H)Fe₂(pdt)(CO)₄(CNBAr^F₃)₂], Et₄N[H1(BAr^F₃)₂]—A solution of (Et₄N)₂[1(BAr^F₃)₂] (0.282 g, 0.169 mmol) in ether (50 mL) was treated with HCl in ether (0.093 mL, 2 M, 0.186 mmol). The reaction solution color became lighter, and a colorless precipitate formed. The reaction solution was stirred for 30 min and was filtered through a plug of Celite to remove Et₄NCl. The filtrate was collected, the solvent was evaporated to ca. 10 mL, and pentane (20 mL) was added. The resulting red solid was extracted into ether (10 mL), and this extract was layered with pentane (30 mL) to yield yellow microcrystals. Yield: 107 mg (44%). Anal. Calcd for C₅₃B₂Fe₂S₂H₂₇O₄N₃F₃₀ (found): C, 41.41 (41.29); H, 1.77 (1.75); N, 2.73 (2.66). IR (CH₂Cl₂): 2185, 2071, 2051, 2022. ¹H NMR (CD₂Cl₂): δ -13.7 (s, Fe-H), -16.4 (s, Fe-H), -19.0 (s, Fe-H). ¹⁹F NMR (CD₂Cl₂): δ -134.8 (dd, o-F),

–134.9 (m, *o*-F), –160.4 (t, *p*-F), –160.8 (t, *p*-F), –160.9 (t, *p*-F), –166.2 (m, *m*-F), –166.5 (td, m-F), –166.6 (td, m-F). ^{11}B NMR (CD_2Cl_2): δ –15.

$\text{Et}_4\text{N}[\text{i-H}]\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{CNBAR}^{\text{F}\#}_3)_2$, $\text{Et}_4\text{N}[\text{H1}(\text{BAR}^{\text{F}\#}_3)_2]$ —A solution of $(\text{Et}_4\text{N})_2[\text{1}(\text{BAR}^{\text{F}\#}_3)_2]$ (100 mg, 0.069 mmol) in THF (1 mL) was treated with a solution of HCl in ether (0.1 mL, 2M, 0.2 mmol), resulting in the color of the solution lightening and the appearance of some solid precipitate. The reaction solution was cooled to $-30\text{ }^\circ\text{C}$ to precipitate Et_4NCl and was then filtered through a plug of Celite. The solution was evaporated under vacuum, and the resulting oil was triturated with pentane ($3 \times 10\text{ mL}$) and left to dry under vacuum overnight, yielding a red solid. Yield: 91 mg (99%). Anal. Calcd for $\text{C}_{53}\text{H}_{39}\text{B}_2\text{F}_{18}\text{Fe}_2\text{N}_3\text{O}_4\text{S}_2$ (found): C, 48.18 (48.51); H, 2.97 (3.17); N, 3.18 (3.16). IR (CH_2Cl_2): 2194, 2066, 2046, 2012. ^1H NMR (CD_2Cl_2): δ –16.41 (s, Fe-*H*), –19.16 (s, Fe-*H*). ^{19}F NMR (CD_2Cl_2): δ –100.6 (s, *o*-F), –100.8 (s, *o*-F), –116.1 (s, *p*-F), –116.3 (s, *p*-F).

$\text{p}K_{\text{a}}$ Determinations

Solutions of $(\text{Et}_4\text{N})_2[\text{1}(\text{BAR}^{\text{F}\#}_3)_2]$ and $\text{Ph}_3\text{NHBAR}^{\text{F}\#}_3 \cdot 2\text{Et}_2\text{O}$ or $(\text{Et}_4\text{N})_2[\text{1}(\text{BAR}^{\text{F}\#}_3)_2]$ and $\text{PyHBAR}^{\text{F}\#}_3$ were prepared in MeCN with approximate $[\text{1}(\text{BAR}_3)_2]^{2-}/\text{acid}$ ratios of 1:2, 1:1, and 2:1 and examined by ^{19}F NMR spectroscopy. Solutions reached equilibrium at room temperature over 24 h. The $\text{p}K_{\text{a}}$ was then determined using the Henderson–Hasselbach equation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Active site of [FeFe] H₂ase (PDB 3C8Y) depicting hydrogen bonding environment to the cyanide ligands.

Figure 2. Thermal ellipsoid plot of [1(BArF₃)₂]²⁻ at 50% probability and with H atoms omitted for clarity. Pentafluorophenyl groups are deemphasized for clarity.

Figure 3.

IR spectra of $K_2[1]$ in MeCN (top), $K_2[1(\text{BAr}^{\text{F}*}_3)]$ in CH_2Cl_2 (middle), and $K_2[1(\text{BAr}^{\text{F}*}_3)_2]$ in CH_2Cl_2 (bottom).

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Figure 5. Cyclic voltammograms of (Et₄N)₂[1] and (Et₄N)₂[1(BAr^F₃)₂] (1 mM solutions in CH₂Cl₂) with 100 mM Bu₄NPF₆ as electrolyte recorded at 0.1 V/s.

Scheme 1.

Table 1
IR Bands in the ν_{CN} and ν_{CO} Regions for Et_4N^+ and K^+ Salts of $[\mathbf{1}]^{2-}$, $[\mathbf{2}]^-$, and $[\mathbf{3}]^{2-}$

compound	ν_{CN} (cm^{-1})	ν_{CO} (cm^{-1})
$(\text{Et}_4\text{N})_2[\mathbf{1}]^a$	2075	1964, 1924, 1885
$\text{K}_2[\mathbf{1}]^a$	2077	1967, 1928, 1890
$\text{Et}_4\text{N}[\mathbf{2}]^b$	2094	2029, 1974, 1955, 1941, 1917
$\text{K}[\mathbf{2}]^a$	2092	2031, 1976, 1956, 1946, 1916
$(\text{Et}_4\text{N})_2[\mathbf{3}]^a$	2075	1969, 1925, 1892
$\text{K}_2[\mathbf{3}]^a$	2078	1969, 1929, 1893

^a MeCN solution.

^b THF solution, ref 10.

Table 2
IR Bands for (Et₄N)₂[1(BAr₃)₂] and Related Complexes in CH₂Cl₂ Solution

compound	ν_{CN} (cm ⁻¹)	ν_{CO} (cm ⁻¹)
(Et ₄ N) ₂ [1]	2075	1964, 1924, 1885
(Et ₄ N) ₂ [1(BPh ₃) ₂]	2137	1984, 1946, 1911
(Et ₄ N) ₂ [3(BPh ₃) ₂]	2136	1986, 1949, 1914
(Et ₄ N) ₂ [1(BAr ^{F#} ₃) ₂]	2147	1986, 1947, 1915
(Et ₄ N) ₂ [1(BAr ^F ₃) ₂]	2136	1990, 1954, 1922
Fe ₂ (pdt)(CO) ₄ (PMe ₃) ₂ ³¹		1979, 1942, 1889
Fe ₂ (pdt)(CO) ₄ (CN ^t Bu) ₂ ³²	2145	1997, 1972, 1933

Table 3
IR Bands for $K_2[1]$ and $(Et_4N)_2[1]$ and Their BAr^{F*}_3 Adducts

compound	solvent	ν_{CN} (cm^{-1})	ν_{CO} (cm^{-1})
$(Et_4N)_2[1]$	MeCN	2075	1964, 1924, 1885
$K_2[1]$	MeCN	2077	1967, 1928, 1890
$K_2[1(BAr^{F*}_3)]$	MeCN	2096, 2081	1990, 1978, 1942, 1931, 1913, 1888
$K_2[1(BAr^{F*}_3)]$	CH_2Cl_2	2126, 2058	1985, 1950, 1905
$K_2[1(BAr^{F*}_3)_2]$	MeCN	2098	1991, 1959, 1947, 1932, 1910
$K_2[1(BAr^{F*}_3)_2]$	CH_2Cl_2	2119	1989, 1951, 1916
$(Et_4N)_2[1(BAr^{F*}_3)_2]$	MeCN	2098	1991, 1932
$(Et_4N)_2[1(BAr^{F*}_3)_2]$	CH_2Cl_2	2100	1990, 1928

Table 4
IR Bands in ν_{CN} and ν_{CO} Regions for $\text{Et}_4\text{N}[\text{H1}(\text{BAr}_3)_2]$ and Related Complexes

compound	solvent	ν_{CN} (cm^{-1})	ν_{CO} (cm^{-1})
$\text{Et}_4\text{N}[\text{H1}]$	MeCN	2118, 2112	2045, 2024, 1985
$\text{Et}_4\text{N}[\text{H1}(\text{BPh}_3)_2]$	CH_2Cl_2	2180	2064, 2043, 2009
$\text{Et}_4\text{N}[\text{H1}(\text{BAr}^{\text{F}\#}_3)_2]$	CH_2Cl_2	2194	2066, 2046, 2012
$\text{Et}_4\text{N}[\text{H1}(\text{BAr}^{\text{F}}_3)_2]$	CH_2Cl_2	2185	2071, 2051, 2022
$[(\mu\text{-H})\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{PMe}_3)_2]\text{BF}_4$ ³¹	CH_2Cl_2		2029, 1989
$[(\mu\text{-H})\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{CN}'\text{Bu})_2]\text{BF}_4$ ³²	CH_2Cl_2	2187	2076, 2060, 2028

Table 5
Redox Potentials (V) and Current Ratios of Adducts of $[1(\text{BAr}_3)_2]^{2-}$ and $[\text{HI}(\text{BAr}_3)_2]^-$ in CH_2Cl_2 vs $\text{Fc}^{0/+}$ (Scan Rate $\nu = 0.1 \text{ V/s}$)

BAr_3	$E_{1/2}$	$[1(\text{BAr}_3)_2]^{2-/-}$	$i_{\text{pa}}/i_{\text{pc}}$	$E_{1/2}$	$[\text{HI}(\text{BAr}_3)_2]^{-/2-}$	$i_{\text{pc}}/i_{\text{pa}}$	$E_{1/2}$	$[\text{HI}(\text{BAr}_3)_2]$	$i_{\text{pa}}/i_{\text{pc}}$
none	-0.79		irrev.						
BPh_3	-0.36		0.16	-1.72		irrev. (0.20) ^a			
BAr^{F}_3	-0.34		0.69	-1.76		0.21 (0.44) ^a	1.11		0.76
BAr^{F}_3	-0.23		0.82	-1.65		0.28 (0.51) ^a	1.24		0.57

^a $\nu = 1.0 \text{ V/s}$.