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Preparation and Protonation of $\text{Fe}_2(\text{pdt})(\text{CNR})_6$, Electron-Rich Analogues of $\text{Fe}_2(\text{pdt})(\text{CO})_6$

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Abstract

The complexes $\text{Fe}_2(\text{pdt})(\text{CNR})_6$ ($\text{pdt}^{2-} = \text{CH}_2(\text{CH}_2\text{S}^-)_2$) were prepared by thermal substitution of the hexacarbonyl complex with the isocyanides RNC for $\text{R} = \text{C}_6\text{H}_4\text{-4-OMe}$ (**1**), $\text{C}_6\text{H}_4\text{-4-Cl}$ (**2**), Me (**3**). These complexes represent electron-rich analogues of the parent $\text{Fe}_2(\text{pdt})(\text{CO})_6$. Unlike most substituted derivatives of $\text{Fe}_2(\text{pdt})(\text{CO})_6$, these isocyanide complexes are sterically unencumbered and have the same idealized symmetry as the parent hexacarbonyl derivatives. Like the hexacarbonyls, the stereodynamics of **1–3** involve both turnstile rotation of the $\text{Fe}(\text{CNR})_3$ as well as the inversion of the chair conformation of the pdt ligand. Structural studies indicate that the basal isocyanide has nonlinear CNC bonds and short Fe–C distances, indicating that they engage

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Notes

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Supporting Information

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Additional experimental details and coordinates for DFT optimized structures for **3** and $[\mathbf{3H}]^+$; DFT-calculated barriers for protonation of **3** (PDF)

Crystallographic details (CIF)

in stronger Fe–C π -backbonding than the apical ligands. Cyclic voltammetry reveals that these new complexes are far more reducing than the hexacarbonyls, although the redox behavior is complex. Estimated reduction potentials are $E_{1/2} \approx -0.6$ ($[2]^{+/0}$), -0.7 ($[1]^{+/0}$), and -1.25 ($[3]^{+/0}$). According to DFT calculations, the rotated isomer of **3** is only 2.2 kcal/mol higher in energy than the crystallographically observed unrotated structure. The effects of rotated versus unrotated structure and of solvent coordination (THF, MeCN) on redox potentials were assessed computationally. These factors shift the redox couple by as much as 0.25 V, usually less. Compounds **1** and **2** protonate with strong acids to give the expected μ -hydrides $[H1]^+$ and $[H2]^+$. In contrast, **3** protonates with $[HNEt_3]BAr^F_4$ ($pK_a^{MeCN} = 18.7$) to give the aminocarbyne $[Fe_2(pdt)(CNMe)_5(\mu-CN(H)Me)]^+$ ($[3H]^+$). According to NMR measurements and DFT calculations, this species adopts an unsymmetrical, rotated structure. DFT calculations further indicate that the previously described carbyne complex $[Fe_2(SMe)_2(CO)_3(PMe_3)_2(CCF_3)]^+$ also adopts a rotated structure with a bridging carbyne ligand. Complex $[3H]^+$ reversibly adds MeNC to give $[Fe_2(pdt)(CNR)_6(\mu-CN(H)Me)]^+$ ($[3H(CNMe)]^+$). Near room temperature, $[3H]^+$ isomerizes to the hydride $[(\mu-H)Fe_2(pdt)(CNMe)_6]^+$ ($[H3]^+$) via a first-order pathway.

Graphical Abstract

INTRODUCTION

Over the preceding several years, compounds of the type $Fe_2(SR)_2(CO)_{6-x}L_x$ have been examined in considerable detail.^{1,2} In contrast to the parent hexacarbonyls, the substituted derivatives are susceptible to oxidation and protonation,^{3,4} two reaction modes characteristic of the hydrogenases.⁵ Indeed, the work is mainly motivated by interest in the chemistry of the $[FeFe]$ -hydrogenases, which feature a $Fe_2(SR)_2(CO)_3(CN)_2(R,SFe)$ active site. Synthetic analogues of this site most often include disubstituted species, e.g., $Fe_2(SR)_2(CO)_4L_2$, but tri- and tetrasubstituted derivatives have also been prepared.¹ The tetrasubstituted species are often subject to significant steric congestion as is evident in the unusual acid–base properties of $Fe_2(pdt)(CO)_2(dppv)_2$ and $Fe_2(pdt)(CO)_2(PMe_3)_4$ ($pdt^{2-} = CH_2(CH_2S^-)_2$, $dppv = cis-C_2H_2(PPh_2)_2$, Figure 1).^{6,7} In other work, bulky dithiolates have been shown to stabilize unusual, but biomimetic coordination geometry at one of the Fe centers.⁸ These precedents point to the desirability of examining electron-rich analogues of $Fe_2(SR)_2(CO)_6$, but without the steric constraints imposed by phosphines and other bulky ligands.

In this project, we sought replicas of $\text{Fe}_2(\text{pdt})(\text{CO})_6$ where the symmetry and noncongestion of the parent hexacarbonyl derivatives are preserved, but the basicity and redox properties are modified. A hypothetical electron-rich, nonbulky target is the acetonitrile complex $\text{Fe}_2(\text{pdt})(\text{NCMe})_6$. Such a species is unlikely to be isolable since even $\text{Fe}_2(\text{pdt})(\text{CO})_5(\text{NCMe})$ is very labile.⁹ One might also envision $[\text{Fe}_2(\text{pdt})(\text{CN})_6]^{6-}$ since polyanionic cyanometallates are known, e.g., $[\text{Ni}(\text{CN})_4]^{4-}$ and $\{[(\text{NC})_5\text{Co}]_2\text{C}_2(\text{CO}_2\text{Me})_2\}^{6-}$.¹⁰ Approaches to $[\text{Fe}_2(\text{pdt})(\text{CN})_6]^{6-}$ would necessarily need to be indirect since $[\text{Fe}_2(\text{pdt})(\text{CN})_2(\text{CO})_4]^{2-}$ is unreactive toward cyanide, although the diferrous polycyanides may be more realistic targets.¹¹ For generating a hexasubstituted diiron dithiolate, isocyanides represent a compromise between cyanide and nitriles,¹² while also featuring a modest steric profile virtually isosteric with CO in the vicinity of the metal center. It is known that four CO ligands in $\text{Fe}_2(\text{pdt})(\text{CO})_6$ can be replaced by isocyanide ligands.^{13–16} Several poly(isocyanide) analogues of metal carbonyl complexes are known. These species include analogues of mono- and dimetallic carbonyls. A few clusters are also known, e.g., $\text{Ni}_4(\text{CNBu-}t)_7$ and $\text{Pt}_7(\text{CNBu-}t)_{12}$.¹⁷ Studies on homoleptic and polyisocyanide complexes remain an active area,¹⁸ but the theme has not been applied to hydrogenase models.

RESULTS AND DISCUSSION

$\text{Fe}_2(\text{pdt})(\text{CNAr})_6$

At room temperature, mixing solid $\text{Fe}_2(\text{pdt})(\text{CO})_6$ and a slight excess of $\text{MeOC}_6\text{H}_4\text{NC}$ (AnNC) results in a vigorous reaction, evidenced by gas evolution and the formation of a deep red oil. According to its ^1H NMR spectrum, the crude product consisted mainly of a 1:1 mixture of $\text{Fe}_2(\text{pdt})(\text{CNAn})_6$ (**1**) and $\text{Fe}_2(\text{pdt})(\text{CO})_2(\text{CNAn})_4$. When heated in refluxing toluene, a 1:6 mixture of $\text{Fe}_2(\text{pdt})(\text{CO})_6$ and AnNC gave **1** quantitatively (eq 1).

Compound **1** is soluble in aromatic solvents, giving deep red solutions that are moderately air-sensitive. Its IR spectrum features ν_{CN} bands ranging from 2113 to 1943, versus 2128 cm^{-1} for free MeNC (Figure 2). The ^1H NMR spectrum displays two peaks with 1:2 ratio for pdt, and a singlet for OMe, suggesting that both the turnstile rotation of FeL_3 subunit and the pdt flipping are fast on the NMR time scale, similar to the behavior of $\text{Fe}_2(\text{pdt})(\text{CO})_6$ and most of its derivatives.¹⁹ From 4-chlorophenylisocyanide ($^{\text{Cl}}\text{ArNC}$), the complex $\text{Fe}_2(\text{pdt})(\text{CNC}_6\text{H}_4\text{Cl})_6$ (**2**) was prepared. The chlorophenyl derivative crystallized more readily than the anisyl derivative **1**.

$\text{Fe}_2(\text{pdt})(\text{CNMe})_6$

Substitution of $\text{Fe}_2(\text{pdt})(\text{CO})_6$ with MeNC proceeded more slowly than with aryl isocyanides. The di- and tetrasubstituted derivatives had previously been obtained under mild conditions,^{13,20} but complete substitution of the CO ligands required refluxing toluene over the course of 3 days. The product, $\text{Fe}_2(\text{pdt})(\text{CNMe})_6$ (**3**), was isolated as a deep red

solid that is very sensitive to air. In its FT-IR spectrum, broad ν_{CN} bands are observed over the range 2150–1900 cm^{-1} , both as toluene and CH_2Cl_2 solutions (Figure 2, see Supporting Information). At room temperature, **3** degrades in CH_2Cl_2 solutions; for this reason experiments using this solvent were conducted at low temperatures where the compound is stable. Relative to ν_{CN} of 2165 cm^{-1} for MeNC,^{21,22} the low energies of these CN bands reflect the electron-rich character of the $[\text{Fe}(\text{I})]_2$ center.

In contrast to the phosphine-substituted derivatives $\text{Fe}_2(\text{pdt})(\text{CO})_{6-x}(\text{PR}_3)_x$, **3** spontaneously undergoes substitution with minimal thermal activation. Upon stirring in solution under 1 atm of CO, **3** carbonylates within minutes at room temperature to give a mixture of $\text{Fe}_2(\text{pdt})(\text{CO})_2(\text{CNMe})_4$ and $\text{Fe}_2(\text{pdt})(\text{CO})_3(\text{CNMe})_3$.²⁰

NMR Studies

The ^1H NMR shifts for the methylene groups, especially the SCH_2 signals, correlate qualitatively with the donor properties of the coligands on the Fe_2 center (Figure 3): for $\text{Fe}_2(\text{pdt})\text{L}_6$, $\delta(\text{SCH}_2) = 2.16$ ($\text{L} = \text{CO}$), 2.08 ($\text{L} = \text{AnNC}$), 2.11 ($\text{L} = ^{\text{Cl}}\text{ArNC}$), and 1.71 ($\text{L} = \text{MeNC}$).

The dynamic behavior of **1** was examined by variable temperature NMR measurements. The onset of decoalescence commences below 0 °C. At ≈ -90 °C, the doublets in the phenyl region have split into a 1H:1H (overlapping) 4H:1H:1H (overlapping) and 4H doublets. This pattern is at least consistent with slow turnstile rotation and slowed pdt flipping. These two processes are probably coupled such that turnstile rotation occurs upon flipping of the pdt backbone.

The dynamic behavior of **3** was also examined by variable temperature NMR measurements. At -85 °C, the $\text{Fe}-\text{CNCH}_3$ resonance splits into three signals with an intensity ratio of 1:3:2. The multiplicity probably results from the overlap of two peaks, since the expected signal ratio is 1:1:2:2. The ^{13}C NMR spectrum, which shows two singlets for CNMe (δ 182, $\text{Fe}-\text{CNMe}$; δ 30, $\text{Fe}-\text{CNMe}$) at ambient temperature, splits at -85 °C into two peaks with a 2:4 ratio. In the region assigned to the methylene groups in pdt^{2-} , four signals are observed in the ratio 1:2:1:2. These results are consistent with both fast turnstile rotation of the $\text{Fe}(\text{CNMe})_3$ subunits, as observed in the carbonyls, and rapid folding of the pdt^{2-} ligand.^{19,23} The effect of MeCN on the DNMR properties of **3** were examined for two reasons: (i) the MeNC ligands are labile in **3** (e.g., they are readily displaced by CO), and (ii) MeCN subtly but noticeably affects the cyclic voltammetry of **3**. The DNMR properties of a $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$ solution of **3** are similar to those recorded in CD_2Cl_2 alone. No signals were observed for free MeNC at low temperatures.

Crystallographic Studies

Recrystallization of **3** from benzene solution afforded X-ray quality crystals of $\text{Fe}_2(\text{pdt})(\text{CNMe})_6 \cdot 1.3(\text{C}_6\text{H}_6)$ (Figure 4). The $\text{Fe}(1)-\text{Fe}(2)$ distance of 2.540 Å is similar to $\text{Fe}-\text{Fe}$ distances in other $\text{Fe}_2(\text{pdt})(\text{CO})_{6-x}\text{L}_x$ species.²⁴ The structure of **2** was also confirmed by X-ray crystallography (Figure 5). The molecule has a crystallographically imposed plane of symmetry bisecting the two Fe centers and relating sulfur atoms and pairs of basal MeNC

ligands. As shown in Table 1, the Fe–C bond lengths correlate with the expected trends in π -backbonding by these ligands. Both the Fe–S and Fe–Fe bond lengths in $\text{Fe}_2(\text{pdt})(\text{CNMe})_6$ are slightly longer than those in $\text{Fe}_2(\text{pdt})(\text{CNC}_6\text{H}_4\text{Cl})_6$ and $\text{Fe}_2(\text{pdt})(\text{CO})_6$, consistent with the electron-donating ability of the MeNC ligands. One pair of S–Fe–C_{apical} angles is slightly greater (105°) than the other (101°).

In **2**, the $\text{CNC}_6\text{H}_4\text{Cl}$ ligands in the basal positions exhibit ring–ring distances of 3.55–3.65 Å, suggesting π – π interaction between the aromatic rings. A similar effect had been observed in $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{CNC}_6\text{H}_4\text{-4-I})_2$.¹⁵ Indicative of the stabilizing influence of this π -stacking, this $(\text{CNC}_6\text{H}_4\text{I})_2$ species adopts an unusual cis-dibasal structure. In contrast, the isocyanide ligands are nonadjacent in $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{CNBu-}i)_2$, occupying the apical sites¹⁴ as is typical for $\text{Fe}_2(\text{pdt})(\text{CO})_4\text{L}_2$ derivatives.

The nonlinearity of the CNC cores of isocyanide ligands qualitatively indicates their participation in π -backbonding.²⁵ In both **1** and **3**, the CNC angles for the apical isocyanide ligands deviate only a few degrees from linearity. More pronounced distortions are observed for the basal ligands. In **3**, the two basal isocyanide ligands most distant from the unique CH_2 of pdt^{2-} are markedly bent, with C–N–C(Me) angles of 166°. This finding provides structural evidence that the electronic desymmetrization imposed by the pdt^{2-} ligand biases the electron density of the two Fe centers. Complexes with strongly bent RNC ligands generally exhibit ν_{CN} bands near 1900 cm^{-1} as seen for the lowest energy $\nu_{\text{C}\equiv\text{N}}$ band for **3**.²¹ The bending of the basal RNC ligands is consistent with the shortened Fe–C_{basal} distances, a difference that is more pronounced in these (RNC)₆ complexes than the parent hexacarbonyl compounds. These points are discussed further in the DFT section below.

Redox Reactions

The redox properties of the hexa-(isocyanide) and hexacarbonyl compounds are very different. One clear indication is that the hexacarbonyls are unaffected by Fc^+ , whereas treatment of **2** with Fc^+ results in immediate reaction. When conducted in the presence of CNAr^{Cl} , this reaction afforded $[\text{Fe}_2(\text{pdt})(\text{CNAr}^{\text{Cl}})_7](\text{BF}_4)_2$ in high yield. The dication in this dark green salt appears to be analogous to the known $[\text{Fe}_2(\text{pdt})(\text{CNMe})_7]^{2+}$.¹³

Cyclic voltammetry (CV) studies reveal that oxidations of **1** and **2** are complex, apparently the result of ligand dissociation. Efforts focused on the chlorophenyl derivative **2**, which is assumed to be similar to **1**. To minimize the possibility of solvent and anion coordination, measurements were conducted on THF solutions using $\text{NBu}_4[\text{BAR}^{\text{F}}_4]$ electrolyte ($\text{Ar}^{\text{F}} = \text{C}_6\text{H}_3\text{-3,5-(CF}_3)_2$).²⁷

In the CV for **2**, Faradaic current commences at about –0.58 V, and at least two further anodic processes are observed, at –0.45 and –0.29 V (Figure 6). In the reducing direction, prominent features are observed at –0.71 and –1.13 V. The complexity of this CV persists over multiple scans. We conclude that the oxidation of **2** generates at least two electroactive species, perhaps via coordination of solvent and disproportionation. The CV simplifies upon addition of excess CNAr^{Cl} such that a quasireversible couple appears at –0.67 V ($i_{\text{pc}}/i_{\text{pa}} = 0.5$), but the irreversible event near –1.1 V is retained. The partially reversible couple at –0.67 V is assigned to $[\mathbf{2}]^{+/0}$. The irreversible process at ~ -1.2 V is assigned to reduction of

$[\text{Fe}_2(\text{pdt})(\text{CNAr}^{\text{Cl}})_7]^{2+}$. The CV of a saturated solution ($<10^{-3}$ M) of $[\text{Fe}_2(\text{pdt})(\text{CNAr}^{\text{Cl}})_7](\text{BF}_4)_2$ (which is poorly soluble in THF), exhibits a reversible couple at -1.25 V (Supporting Information). Addition of greater amounts of CNAr^{Cl} did not affect the relative currents of the two reduction waves.

The CV for **3** was simpler than that observed for **2**. An ostensible reversible couple is observed near -1.2 V (Figure 7). Smaller processes are detectable at -1.0 and -1.8 V indicative of secondary reactions, which are of unknown origin. At slow scan rates (12.5 mV/s), the dominant feature at -1.2 V resolves into two overlapping processes, with $E_{1/2} = -1.2$ and -1.3 V. The two redox couples are tentatively assigned as $[\mathbf{3}]^{+/0}$ for the rotated and unrotated isomers of **3** (see next section). DFT calculations (see below) predict that these couples for these isomers differ by 0.15 V in THF solution. Upon addition of excess MeCN to this THF solution, only one event is observed at -1.31 V. The effect of solvent coordination (THF, MeCN) was examined computationally for all possible isomers; the redox potentials shifted as much as 0.29 V for THF (cathodically), but only by 0.06 V for MeCN.

DFT Characterization of $[\text{Fe}_2(\text{pdt})(\text{CNMe})_6]^z$ ($z = 0, 1+$)

The structure of **3** and its derivatives were examined using the DFT/B-P86/TZVP/COSMO computational setup. All other computational data presented in this work were obtained by the same protocol (see Experimental Section). As a starting point, the structure and HOMO of **3** were examined. A striking aspect of **3** is its close structural similarity to $\text{Fe}_2(\text{pdt})(\text{CO})_6$,²⁸ despite their differing chemical properties. The interatomic distances are very similar (Table 1). The fractional electronic occupations per single atom, including the 2-electron Fe–Fe bonding HOMO are also similar (Figure 8). The NBO analysis revealed π -back-donation from Fe to CNMe, as is also indicated both by short Fe–C distances and the nonlinearity of the MeN–C angles. Both features are reproduced computationally: the Fe–C(basal)_{avg} distances are about 0.02 Å shorter than C(apical)_{avg} (Table 1). The strong π -interaction is enhanced by the electron-releasing character of the Me substituents.

The IR spectrum of **3** was also computed at the BP86/TZVP level. The frequency range associated with the ν_{CN} normal modes was computed to be 1983 – 2117 cm^{-1} , which is reasonably consistent with the observed spectrum (Figure 9). The atomic partial charges are qualitatively compatible with the reducing power and basicity for **3** as indicated by the greater electron density residing on the ligands.

Using DFT, we investigated the possibility that the rotated isomer of **3** exists in significant equilibrium concentrations at room temperature. The energy of the rotated isomer is elevated by only 2.2 kcal/mol, suggesting that it is indeed reasonable that the rotated isomer is populated or at least forms readily. Furthermore, rotated-**3** would be particularly susceptible to fast electron-transfer since it is preorganized in the geometry expected for $[\mathbf{3}]^+$. In the optimized structure for rotated-**3**, the C–N–Me angles reveal that the distorted Fe center is the stronger π -donor, with the average C–N–C(Me) angle of 141.8° (Figure 10). The NBO charges on Fe unrotated-**3** are both -0.342 , whereas for the rotated form, the values are -0.405 and -0.307 (rotated Fe center).

Computations confirm that $[3]^+$ contains a bridging isocyanide ligand $[\text{Fe}_2(\text{pdt})(\text{CNMe})_5(\mu\text{-CNMe})]^+$. This structure is a typical “rotated” mixed-valence Fe(II)Fe(I) species, often referred to as “ H_{ox} -models”.^{29,30} The DFT-calculated structures highlight the greater bending of the C–N–Me ligands in rotated- 3^0 vs rotated- 3^+ (Figure 10). The Fe– $\mu\text{-C}(\text{NMe})$ distances differ by 0.4 Å, vs ~1 Å difference was observed for Fe– $\mu\text{-C}(\text{O})$ bonds in the H_{ox} models of the type $[\text{Fe}_2(\text{pdt})(\mu\text{-CO})\text{L}_5]^+$.²⁹ In the enzyme from *D. desulfuricans*, the Fe– $\mu\text{-C}$ distances differ by 0.7 Å.³¹

Relative energies were calculated for the couples $[\text{rotated-}3]^+ / [\text{unrotated-}3]^0$ and $[\text{rotated-}3]^+ / [\text{rotated-}3]^0$ (Scheme 1). These calculations suggest that the rotated- 3 would be a more potent reducing agent than the parent by 0.15 V. Since the CV studies raised the possibility of coordination by solvent (THF, MeCN), the energies for the couple $[\text{Fe}_2(\text{pdt})(\mu\text{-CNMe})-(\text{CNMe})_4(\text{solvent})]^+ / \text{Fe}_2(\text{pdt})(\text{CNMe})_5(\text{solvent})$ were thus calculated. These results are summarized in eq 2 (see Supporting Information for data on individual isomers).

Protonation of $\text{Fe}_2(\text{pdt})(\text{CNR})_6$

The arylisocyanide complexes **1** and **2** are protonated with the strong acid $[\text{H}(\text{OEt})_2\text{BAr}^{\text{F}}_4]$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$). These reactions produce the hydrides $[(\mu\text{-H})\text{Fe}_2(\text{pdt})(\text{CNAr})_6]^+$, indicated by ^1H NMR signals near $\delta -15$. The spectra also show separate signals for two types of ArNC groups in a 2:1 ratio. These data indicate that $[(\mu\text{-H})\text{Fe}_2(\text{pdt})(\text{CNAr})_6]^+$ adopts a rigid biotetrahedral structure typical of many related μ -hydride complexes.⁴

Protonation of **3** proceeded cleanly with 1 equiv of $[\text{HNEt}_3]\text{BAr}^{\text{F}}_4$, a weak acid ($\text{p}K_{\text{a}}^{\text{MeCN}} = 19$),³² which is unreactive toward **1** and **2**. When conducted at -78°C in CD_2Cl_2 solution, protonation of **3** produced an air-sensitive blue species, labeled $[3\text{H}]^+$. The ^1H NMR spectrum of this intermediate is complex but can be fully assigned (Figure 11). A doublet and quartet appear, respectively, at $\delta 3.34$ and $\delta 8.33$, with integrated intensity 3:1 and an apparent $J_{\text{HH}} = 4.8$ Hz. Comparable NMR shifts and couplings are observed for the aminocarbene $[\text{Cp}_2\text{Co}_2(\mu\text{-PMe}_2)_2(\mu\text{-CNMe}(\text{H}))]^+$.³³ The low-field portion of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displays a signal at $\delta 340$ as well as resonances at $\delta 166$, $\delta 165$, and $\delta 164$. The ^{13}C NMR signal at $\delta 340$ is also consistent with a bridging aminocarbene ligand,^{34,35} indicating that protonation occurs at the MeNC ligand. The unmodified MeNC ligands in $[3\text{H}]^+$ exhibit ^1H NMR resonances in the ratio 1:2:2. These data are consistent with the formulation $[\text{Fe}_2(\text{pdt})(\text{CNMe})_5\{\mu\text{-CN}(\text{H})\text{-Me}\}]^+$, which adopts a rotated structure (Scheme 2). Unlike the situation for **3**, turnstile rotation of the $\text{Fe}(\text{CNMe})_3$ subunit in $[3\text{H}]^+$ is inhibited even at 25°C , as seen in oxidized species of the general formula $\text{Fe}_2(\text{pdt})\text{L}_5(\mu\text{-CO})]^{2+}$.^{14,36} The data also rule out degenerate exchange between the Fe centers (eq 3). N-protonation selectively produces only one of the two orientational isomers (N–H pointing toward $\text{Fe}(\text{CNMe})_3$ or $\text{Fe}(\text{CNMe})_2$ subunits).

(3)

Upon warming its solutions to near room temperature, $[3H]^+$ isomerizes to the hydride $[(\mu-H)Fe_2(pdt)(CNMe)_6]^+$ ($[H3]^+$). The structure of this species is indicated by its 1H NMR spectrum, showing two peaks with a 1:2 ratio for $FeCNMe$ and a hydride signal at $\delta -17.2$, as expected.¹⁴ The NMR data indicate that $[H1]^+$, $[H2]^+$, and $[H3]^+$ are structurally similar.

Isomerization of $[Fe_2(pdt)(CNMe)_5(\mu-CNMe(H))]^+$ to $[(\mu-H)Fe_2(pdt)(CNMe)_6]^+$

1H NMR measurements at room temperature show that $[3H]^+$ converts mainly (~80%) to $[H3]^+$ as well as to another species (~20%). The new minor species displays a doublet at δ 3.75 ($J_{HH} = 4.8$ Hz) and four singlets (δ 3.46, 3.42, 3.31, 3.30) with a ratio of 1:1:2:2, along with a broadened downfield NH peak at δ 10.1. These data indicate that the two iron centers are inequivalent, the complex is C_s -symmetric, and the apical/basal $CNMe$ exchange is slow. These results are consistent with the assigned structure of a bioctahedral μ -aminocarbyne $[Fe_2(pdt)(CNMe)_6\{\mu-CN(H)-Me\}]^+$ ($[3H(CNMe)]^+$), an adduct of $[3H]^+$. Rotational barriers are also high for related μ -aminocarbyne complexes.^{35,37} The ready formation of $[3H(CNMe)]^+$ indicates the lability of **3** and is relevant to the complexities observed electrochemically.

The kinetics for the conversion of $[3H]^+$ to $[H3]^+$ were examined by monitoring the rate of the disappearance of $[3H]^+$ by 1H NMR spectroscopy. Over the course of hours, $[3H]^+$ disappeared concomitant with the growth of the hydride $[H3]^+$. Throughout the conversion, the concentration of $[3H(CNMe)]^+$ remained low and fairly constant. The isomerization to the hydride follows first-order behavior with a rate constant $k_1 = 1.93(2) \times 10^{-4} s^{-1}$ (Figure 12). After the CD_2Cl_2 solution stood at room temperature for 24 h, $[H3]^+$ was the exclusive product, indicating that even $[3H(CNMe)]^+$ converts to the hydride under these conditions.

The adduct $[3H(CNMe)]^+$ was generated by the addition of 20 equiv of $MeNC$ to $[3H]^+$ (CD_2Cl_2 , $-78^\circ C$) followed by warming the sample to $25^\circ C$. The reaction is fairly clean, with >85% NMR yield at $25^\circ C$. Under these conditions $[3H(CNMe)]^+$ is stable for hours, showing that the hydride $[H3]^+$ forms from the unsaturated aminocarbyne $[3H]^+$, not from $[3H(CNMe)]^+$. In comparison to $[3H]^+$, the $CN(H)Me$ signal at δ 10.07 is shifted downfield by ca. 2 ppm in $[3H(CNMe)]^+$.

DFT Studies on the Protonation of $Fe_2(pdt)(CNMe)_6$

According to the calculations, N-protonation of **3** by HOTf would have a very low barrier, as is typical for protonation of amines and imines³⁸ (Supporting Information). In contrast, protonation at Fe or at the Fe–Fe bond would be expected to proceed via a significant barrier

due to higher reorganizational energies involved.³⁸ The following barriers were calculated for protonation at Fe: apical (12.7 kcal/mol), basal position (11.5 kcal/mol), and Fe–Fe bond (7.8 kcal/mol) (Supporting Information). A higher barrier of ca. 14 kcal/mol is also indicated for C-protonation of an apical isocyanide. The thermodynamic stabilities of the protonated derivatives of **3** were investigated by DFT (Scheme 3). The overall picture is consistent with the experimental observation that the kinetic product of protonation is the aminocarbyne $[3H]^+$, not the thermodynamic product $[H3]^+$. Two scenarios can be envisioned for the conversion of **3** into aminocarbyne $[3H]^+$. N-protonation of a basal (bent) MeNC ligand in **3** would produce a basal aminocarbyne, poised to migrate to the bridging site. The related migration of basal ligand to the bridging site has been found to be facile.³⁹ Alternatively, N-protonation could occur directly at the μ -CNMe ligand in the rotated isomer of **3**. Both processes give the same result. The protonation *trans*-[Mo(CNMe)₂(dppe)₂] proceeds analogously to **3**. The kinetic product is the aminocarbyne [Mo(CNMe)-(CN(H)Me)(dppe)₂]⁺, which subsequently rearranges to the hydride [HMo(CNMe)₂(dppe)₂]⁺.^{40,41}

With a focus on the aminocarbyne $[3H]^+$, the two rotamers (with respect to the MeNH center) are nearly equal in energy at 8.6 and 9.4 kcal/mol. The two Fe–C distances differ by 0.2 Å, with the shorter bond being to the rotated Fe center. In the optimized structure, two basal CNMe ligands are slightly distorted, perhaps indicating steric repulsions with the N(H)Me group. The basal CNMe ligands at the other Fe are normal (Figure 12).

Other Diiron Carbyne Complexes

The cation $[Fe_2(SMe)_2(CO)_3(PMe_3)_2(CCF_3)]^+$ represented the first reported carbyne derivative of a diiron dithiolate. Isolated as its BF_4^- salt, this species arises via a multistep pathway from the tetrafluoroethylene complex $Fe_2(SMe)_2(CO)_4(PMe_3)_2(C_2F_4)$, culminating in fluoride abstraction with BF_3 .⁴² This cation was described as a terminal carbyne complex, but our DFT calculations suggest otherwise (Figure 13). Since crystallographic studies of the related $Fe_2(SMe)_2(CO)_6(\mu-\eta^1, \eta^1-C_2F_4)$ and $Fe_2(SMe)_2(CO)_6(\mu-C(F)CF_3)$ complexes⁴² show that the *SMe* groups adopt the *anti* disposition, this conformation was adopted in our calculations. There were 12 rotamers of $[Fe_2(SMe)_2(CO)_3(PMe_3)_2(CCF_3)]^+$ evaluated with attention to the orientation of the *SMe* groups (Supporting Information). The energies of these isomers fall into three ranges (see Supporting Information): (1) In the range 0–6.5 kcal/mol are 10 isomeric μ -carbyne complexes with no obvious steric interactions between the ligand substituents. (2) At 12.3 and 12.7 kcal/mol are two μ -carbyne complexes with mutually *cis* *PMe*₃ ligands, which sterically clash with an equatorial *SMe* group. (3) At 24.3 kcal/mol is the terminal carbyne complex originally proposed.⁴²

On the basis of these results, a revised ground state structure is assigned, featuring a bridging carbyne ligand and *cis*-basal *PMe*₃ groups (Figure 13).

CONCLUSIONS

Relative to $Fe_2(pdt)(CO)_6$, the complexes $Fe_2(pdt)(CNR)_6$ exhibit enhanced basicity, reducing power, and lability. These attributes are all desirable from the perspective of new reactivity. The electronic structure and stereodynamics are also instructive. The DNMR properties of **3** indicate both the flipping of the *pdt* and the turnstile rotating of the

Fe(CNMe)₃ sites occur in the same temperature regime. It is logical to suggest that these processes are coupled, such that the turnstile rotation is inhibited by the steric clash between the unique CH₂ of pdt with the apical ligand.

In terms of its reducing power, the highly negative [3]⁺⁰ couple is noteworthy. To provide context, the oxidation of Fe₂(pdt)(CO)₆ has only been achieved with [N(C₆H₃-2,4-Br)₃]SbCl₆⁴³ (*E* = 1.36 V⁴⁴), and even then the cation abstracts chloride from [SbCl₆]⁻, usually considered an inert anion. The [Fe₂(pdt)(CO)₅(CNMe)]⁺⁰ couple is observed at 0.57 V, a shift of nearly 200 mV versus the [Fe₂(pdt)(CO)₆]⁺⁰ couple (Table 2). Otherwise, the replacement of CO by MeNC shifts the redox potential by ca. 300 mV/substitution.⁴⁵ Similar trends in *E*_p are observed for the Cr(CNR)_{6-x}(CO)_x complexes.⁴⁶ As established in this work, the electrochemistry of Fe₂(pdt)-(CNR)₆ complexes is complex, probably resulting from the involvement of [Fe₂(pdt)(CNR)₇]²⁺ and {(pdt)[Fe-(CNR)₅]₂]²⁺ and related solvento species, some of which have been previously identified.¹³ These protonation studies also revealed the lability of the MeNC ligand.

In terms of its protonation, Fe₂(pdt)(CNMe)₆ behaves analogously to *trans*-Mo(CNR)(L)(Ph₂PCH₂CH₂PPh₂)₂ (L = CNR, N₂, CO).^{22,47} Both the Mo(0) and [Fe(I)]₂ species undergo kinetic protonation at RMC to give unstable aminocarbene species, which isomerize to a thermodynamic hydrido complex.^{40,48} The conversion of the aminocarbene [3H]⁺ to the hydride [H3]⁺ follows first-order kinetics and probably involves intramolecular rearrangement. DFT calculations provide insights into this pathway. Isomeric with [3H]⁺ is [*term*-HFe₂(pdt)(CNMe)₅(μ-CNMe)]⁺, which contains a basal terminal hydride, and is only 8 kcal/mol higher in energy. The rearrangement of terminal hydrides, especially basal terminal hydrides, to μ-hydrides is known to be facile in related systems.^{39,49} Overall, the combined experimental and computational results highlight the indirect path followed in the conversion of the diiron(I) complex to its diiron(II) μ-hydride derivative (Scheme 4). The following question arises: is such a pathway general? That is, do all diiron dithiolates protonate at ligands prior to formation of the μ-hydrides? Surely, the basicity of Fe–Fe bonds and steric distortions strongly influence the rate of μ-hydride formation.⁵⁰ In terms of the intimate details for protonation of Fe₂(pdt)(CO)₂(PMe₃)₄ at least, spectroscopic evidence indeed favors initial protonation at ligands prior to protonation at metal.⁷

In one of the more striking findings, this work provides some guidance for the synthesis of reduced diiron dithiolato complexes with a biomimetic structure. Recall that the active site adopts a rotated structure wherein the two Fe sites are differentiated, leaving one Fe center with an open apical coordination site, poised for interaction with substrates. In the prototypical Fe₂(pdt)(CO)₆ and its simple substituted derivatives, the rotated structure is destabilized by 9–12 kcal/mol above the unrotated structure.⁵² Early calculations suggested that electronic factors were modest, so most efforts to stabilize the rotated state have focused on steric effects.^{8,53} The rotated structure is only adopted in Fe(I)Fe(I) species with a combination of bulky dithiolates,^{8,50} which do not exist in nature, and unsymmetrical substitution. The present work suggests that the rotated structure is stabilized by a collection of strong donor ligands.

EXPERIMENTAL SECTION

All manipulations were performed under an inert atmosphere using standard Schlenk and then glovebox techniques, unless otherwise noted. Reagents were purchased from Sigma-Aldrich. $\text{Fe}_2(\text{pdt})(\text{CO})_6$, $^9\text{HNEt}_3[\text{BAr}^{\text{F}}_4]$, and $[\text{H}(\text{Et}_2\text{O})_2][\text{BAr}^{\text{F}}_4]^{54}$ were prepared by literature methods. Solvents were HPLC-grade and dried by filtration through activated alumina or distilled under nitrogen over an appropriate drying agent. Other commercial reagents were used as received without further purification. NMR spectra were acquired using Varian 500 and 600 MHz spectrometers. NMR signals are quoted using the δ scale and referenced to the residual solvent signal. FT-IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. Electrochemical data were collected using CH Instruments 600D potentiostats. Cyclic voltammetry was conducted under an inert atmosphere in the solvents and electrolytes indicated in the figure caption with *iR* compensation, a freshly polished glassy carbon electrode (diameter = 1 cm), a Ag wire quasireference electrode, and a Pt counter electrode. Redox couples are referenced versus internal $\text{Fc}^{+/0}$. All CVs were recorded starting from the highly negative potentials where the background Faradaic current was zero, except for $[\text{Fe}_2(\text{pdt})(\text{CNArCl})_7](\text{BF}_4)_2$, which was recorded starting from the positive potentials.

Crystallographic data for $\text{Fe}_2(\text{pdt})(\text{CNC}_6\text{H}_4\text{Cl})_6$ were collected on a Bruker D8 Venture instrument equipped with a four-circle kappa diffractometer and Photon 100 detector, and crystallographic data for compound $\text{Fe}_2(\text{pdt})(\text{MeNC})_6$ were collected on a Bruker X8 Kappa four-circle diffractometer equipped with an APEX-II CCD detector.

Synthesis of $\text{Fe}_2(\text{pdt})(\text{CNC}_6\text{H}_4\text{OMe})_6$ (**1**)

A Schlenk flask fitted with a reflux condenser was charged with $\text{Fe}_2(\text{pdt})(\text{CO})_6$ (186 mg, 0.50 mmol) and 4-methoxyphenyl isocyanide (540 mg, 4.0 mmol). Toluene (5 mL) was added, resulting in a red solution, which was heated at reflux for 15 h at 120 °C (oil bath temperature). After being cooled to 25 °C, the dark brownish red mixture was evaporated under vacuum to yield a dark red residue. The residue was extracted into CH_2Cl_2 (10 mL), and this solution was filtered through a plug of Celite. The filtrate was evaporated under vacuum, and the resulting viscous oil residue was washed with pentane (15 mL). Yield: 0.41 g (0.40 mmol, 80%). ^1H NMR (500 MHz, CD_2Cl_2): 7.05 (d, $^3J_{\text{HH}} = 8.6$ Hz, 12H), 6.66 (d, $^3J_{\text{HH}} = 8.8$ Hz, 12H), 3.73 (s, 18H, OMe), 2.08 (br s, 4H, pdt), 1.85 (br s, 2H, pdt). FT-IR (CH_2Cl_2): $\nu_{\text{CN}} = 2107, 2064, 2012, 1935\text{ cm}^{-1}$.

$\text{Fe}_2(\text{pdt})(\text{CNC}_6\text{H}_4\text{Cl})_6$ (**2**)

Compound **2** was obtained analogously to **1**, except that the product crystallized readily. Yield: 0.35 g (0.34 mmol, 68%). Crystals suitable for X-ray analysis were obtained by diffusion of pentane into a CH_2Cl_2 solution of the product at $-30\text{ }^\circ\text{C}$. ^1H NMR (500 MHz, CD_2Cl_2): 7.15 (d, $^3J_{\text{HH}} = 8.7$ Hz, 12H), 7.01 (d, $^3J_{\text{HH}} = 8.6$ Hz, 12H), 2.11 (br s, 4H, pdt), 1.85 (br s, 2H, pdt). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CD_2Cl_2): 189.9 (CNAr), 131.6 (CNAr), 130.3 (CNAr), 129.6 (CNAr), 126.7 (CNAr), 31.5 ($-\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$), 24.7 ($\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$). FT-IR (CH_2Cl_2): $\nu_{\text{CN}} = 2107, 2062, 2042, 2001\text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{45}\text{H}_{30}\text{Cl}_6\text{Fe}_2\text{N}_6\text{S}_2$ (found): C, 51.81 (51.41); H, 2.9 (2.82); N, 8.06 (7.86).

Protonation of $\text{Fe}_2(\text{pdt})(\text{CNC}_6\text{H}_4\text{Cl})_6$

A J-Young tube was charged with **2** (10.4 mg, 10 μmol) and $[\text{H}(\text{OEt}_2)_2]\text{BAr}^{\text{F}}_4$ (10 mg, 10 μmol). CD_2Cl_2 (0.5 mL) was condensed onto the sample by vacuum transfer at -193°C . Upon warming to room temperature, the sample color changed from dark green to red. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.40 (d, $^3J_{\text{HH}} = 7.4$ Hz, 4H), 7.29 (d, $^3J_{\text{HH}} = 7.3$ Hz, 8H), 7.23 (d, $^3J_{\text{HH}} = 7.2$ Hz, 4H), 7.16 (d, $^3J_{\text{HH}} = 7.2$ Hz, 8H), 2.44 (br s, 4H, pdt), 2.15 (br s, 2H, pdt), -15.14 (s, $\mu\text{-H}$).

$\text{Fe}_2(\text{pdt})(\text{CNMe})_6$ (**3**)

A Schlenk flask fitted with a reflux condenser was charged with $\text{Fe}_2(\text{pdt})(\text{CO})_6$ (0.74 g, 2 mmol), toluene (20 mL), and MeNC (1.08 mL, 20 mmol). The deep red solution was heated at reflux under an argon atmosphere for 3 days. Additional MeNC (0.4 mL) was added to the reaction mixture once every 24 h to compensate for evaporative loss of MeNC. The progress of the reaction was monitored by ^1H NMR spectroscopy. Solvent was then removed under vacuum, and the red solid residue was mixed with C_6H_6 (60 mL), and heated to 80°C for ca. 20 min. After being cooled to ca. 40°C , the mixture was cannula-filtered, and the deep red filtrate was evaporated, yielding a dark red solid, which was washed with pentane (30 mL). Yield: 0.87 g (1.54 mmol, 77%). Crystals suitable for X-ray analysis were obtained by cooling a saturated benzene solution of the product. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.35 (s, 7.8H, benzene), 3.35 (s, 18H, CNMe), 1.71 (br s, 4H, pdt), 1.56 (br s, 2H, pdt). ^1H NMR (500 MHz, CD_2Cl_2 , -85°C): 3.53 (s, 3H, CNMe), 3.33 (s, 9H, CNMe), 3.21 (s, 6H, CNMe), 2.28 (s, 1H, pdt), 2.00 (s, 2H, pdt), 1.66 (s, 1H, pdt), 1.24 (s, 2H, pdt). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CD_2Cl_2): 182.6 (CNMe), 30.2 (CNMe, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$), 24.1 ($-\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}-$). FT-IR (CH_2Cl_2): ν_{CNMe} 2142, 2092, 2065, 1953 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{N}_6\text{Fe}_2\text{S}_2 \cdot 1.3(\text{C}_6\text{H}_6)$ (found): C, 48.4 (49.16); H, 5.67 (5.48); N, 14.85 (14.70).

$[\text{Fe}_2(\text{pdt})(\text{CNC}_6\text{H}_4\text{Cl})_7](\text{BF}_4)_2$ (**[2](BF₄)₂**)

A solution was prepared with **2** (209 mg, 200 μmol), 4-chlorophenyl isocyanide (41 mg, 300 μmol), and CH_2Cl_2 (5 mL). This solution was treated dropwise with a solution of FcBF_4 (120 mg, 440 μmol) in MeCN (10 mL) at room temperature. After stirring at room temperature for 1 h, the solvent was evaporated under vacuum, and the green residue was extracted into CH_2Cl_2 (10 mL). This extract was filtered through a Celite plug. The dark green filtrate was concentrated to ca. 2 mL and then diluted with pentane (10 mL). A dark green solid precipitate was collected and was stored under vacuum. Yield: 238 g (176 μmol , 88%). ^1H NMR (500 MHz, CD_2Cl_2): δ 7.65 (d, $^3J_{\text{HH}} = 8.3$ Hz, 4H), 7.54 (d, $^3J_{\text{HH}} = 8.7$ Hz, 4H), 7.50–7.40 (m, 20 H), 2.88 (t, $^3J_{\text{HH}} = 2.9$ Hz, 4H, pdt), 2.40 (m, 2H, pdt). FT-IR (CH_2Cl_2): ν_{CNAr} = 2170, 2154, 2060 cm^{-1} . ESI-MS: Calcd m/z = 588.4, found 588.6. Anal. Calcd for $\text{C}_{52}\text{H}_{34}\text{B}_2\text{Cl}_7\text{-F}_8\text{Fe}_2\text{N}_7\text{S}_2$ (found): C, 46.11 (45.74, 45.49); H, 2.53 (2.62, 2.69); N, 7.24 (6.94, 7.07).

$[(\mu\text{-H})\text{Fe}_2(\text{pdt})(\text{CNMe})_6]\text{BAr}^{\text{F}}_4$ (**[H3]BAr^F₄**)

A Schlenk flask was charged with $\text{Fe}_2(\text{pdt})(\text{CNMe})_6 \cdot 1.3(\text{C}_6\text{H}_6)$ (56 mg, 100 μmol), $[\text{HNEt}_3]\text{BAr}^{\text{F}}_4$ (100 mg, 100 μmol), and CH_2Cl_2 (10 mL). The solution was stirred at room temperature for 24 h and filtered, and the deep red filtrate was evaporated under vacuum.

The residue was extracted into CH_2Cl_2 (2 mL), and the resulting red solution was diluted with pentane (5 mL) to precipitate an oil, which solidified upon removal of traces of solvent under vacuum. ^1H NMR (500 MHz, CD_2Cl_2): δ 3.58 (s, 6H, apical-CNMe), 3.33 (s, 12H, basal-CNMe), 2.03 (t, $^3J_{\text{HH}} = 5.9$ Hz, 4H, pdt), 1.84 (m, 2H, pdt), -17.21 (s, $\mu\text{-H}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2): 164.6 (apical-CNMe), 163.3 (basal-CNMe), 30.9 (apical-CNMe), 30.4 (basal-CNMe), 29.4 (pdt), 21.6 (pdt). FT-IR (CH_2Cl_2): ν_{CNAr} 2200, 2180, 2151 cm^{-1} . Anal. Calcd for $\text{C}_{47}\text{H}_{37}\text{BF}_{24}\text{Fe}_2\text{N}_6\text{S}_2$ (found): C, 42.49 (42.08); H, 2.81 (2.86); N, 6.33 (6.80).

Protonation of $\text{Fe}_2(\text{pdt})(\text{CNMe})_6$ with $\text{HNEt}_3[\text{BARF}_4]$

A J-Young tube was charged with $\text{Fe}_2(\text{pdt})(\text{CNMe})_6 \cdot 1.3(\text{C}_6\text{H}_6)$ (5.6 mg, $10\text{ }\mu\text{mol}$) and $[\text{HNEt}_3]\text{BARF}_4$ (10 mg, $10\text{ }\mu\text{mol}$). CD_2Cl_2 (0.5 mL) was vacuum transferred onto these solids at $-193\text{ }^\circ\text{C}$. After warming to $-78\text{ }^\circ\text{C}$, the sample converted to a deep blue solution. ^1H NMR (600 MHz, CD_2Cl_2 , $-40\text{ }^\circ\text{C}$): δ 8.32 (m, 1H, CN(*H*)Me), 3.70 (s, 3H, apical-CNMe), 3.51 (s, 6H, basal-CNMe), 3.31 (3H, 6H, 6H, CNMe), 3.34 (d, $^3J_{\text{HH}} = 4.8$ Hz, 3H, CN(*H*)Me), 3.28 (s, 6H, basal-CNMe), 2.26 (m, 1H, pdt), 2.14 (m, 4H, pdt), 1.72 (m, 1H, pdt); signals at δ 7.70, 7.53 and 2.55, 0.99 were assigned to BARF_4 and NEt_3 . $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CD_2Cl_2 , $-20\text{ }^\circ\text{C}$): 340.2 (CN(*H*)Me), 165.9 (basal-CNMe), 165.2 (apical-CNMe), 164.9 (basal-CNMe), 42.4 (CN(*H*) Me), 30.9 (CNMe), 30.7 (CNMe), 30.4 (CNMe), 30.3 (pdt), 21.9 (pdt). This compound isomerizes to the μ -hydride $[\text{Fe}_2(\text{CNMe})_6(\mu\text{-H})]^+$ over the course of 24 h. This isomerization process was monitored by ^1H NMR spectroscopy at $25\text{ }^\circ\text{C}$. After protonation of **3** at $-78\text{ }^\circ\text{C}$ in CD_2Cl_2 solution with 1 equiv of $\text{HNEt}_3[\text{BARF}_4]$, the sample was thermally equilibrated at $25\text{ }^\circ\text{C}$, and the product distribution was then monitored by ^1H NMR spectroscopy.

In-Situ Generation of $[\text{Fe}_2(\text{pdt})(\text{CNMe})_6\{\mu\text{-CN}(\text{H})\text{Me}\}]\text{BARF}_4$ ($[\text{3H}(\text{CNMe})]\text{BARF}_4$)

A J-Young tube was charged with $\text{Fe}_2(\text{pdt})(\text{CNMe})_6 \cdot 1.3(\text{C}_6\text{H}_6)$ (5.6 mg, $10\text{ }\mu\text{mol}$) and $[\text{HNEt}_3]\text{BARF}_4$ (10 mg, $10\text{ }\mu\text{mol}$) in the glovebox. CD_2Cl_2 (0.5 mL) was vacuum transferred at $-193\text{ }^\circ\text{C}$. The sample was initially warmed to $-78\text{ }^\circ\text{C}$ to form $[\text{3H}]^+$ and refrozen at $-193\text{ }^\circ\text{C}$. Excess MeNC (40 equiv) was vacuum transferred onto the cold mixture. The sample mixture, which turned from a blue solution to a brown solution instantly upon warming to room temperature, was characterized by ^1H NMR spectroscopy. ^1H NMR (500 MHz, CD_2Cl_2): 10.1 (br s, 1H, CN(*H*)Me), 3.74 (d, $^3J_{\text{HH}} = 4.8$ Hz, 3H, CN(*H*)Me), 3.46 (s, 3H, apical-CNMe), 3.42 (s, 3H, apical-CNMe), 3.31 (s, 6H, basal-CNMe), 3.30 (s, 6H, basal-CNMe), 2.31 (br m, 6H, pdt). In the presence of excess MeNC, $[\text{3H}(\text{CNMe})]^+$ is stable at room temperature for hours. After removal of excess MeNC under vacuum and addition of fresh CD_2Cl_2 , it converted to $[\text{H3}]\text{BARF}_4$ after standing at $25\text{ }^\circ\text{C}$ overnight.

DFT Methods

Calculations were carried out with the TURBOMOLE suite of programs.⁵⁵ The pure functional BP86 was used,⁵⁶ in conjunction with a valence triple- ζ basis set with polarization on all atoms (TZVP),⁵⁷ a level of theory that has proven to be suitable to reliably investigate hydrogenase models.⁵⁸ The resolution-of-the-identity technique has been adopted to speed up computations, since expensive four-center integrals (describing the

classical electron–electron repulsive contribution to the total energy) are approximated through a combination of two three-center integrals.⁵⁹

Each stationary point was characterized by means of full vibrational analysis. IR simulations were performed with the same full-electron TZVP basis set that was employed to investigate energies and structures of structures of interest, without need of using scaling factors (usually necessary for functionals other than BP86, to correct the harmonic potential shape). Transition-state search was carried out according to a pseudo-Newton–Raphson procedure, starting from the optimization of a guessed transition-state structure, in which the degrees of freedom associated with the reaction coordinate (RC) are originally frozen. After performing the vibrational analysis of the constrained structures, the negative eigenmode associated with the RC is followed, in order to locate the first-order saddle point corresponding to genuine transition-state structure. In the case under investigation, the adoption of $E_{\text{solv}}(\text{SCF})$ values afforded the closest match of theory with experimental oxidation potentials. In particular,

$E_{\text{solv}}(\text{SCF})$ is referred to the energy difference between the gas-phase optimized reduced and the oxidized structures, including an implicit solvent model. Absolute oxidation potentials were obtained using the Nernst equation and have been referred to the Fc^+/Fc couple at -5.09 V (CH_2Cl_2), -5.20 V (THF), and -4.92 V (MeCN). The COSMO approach was used to treat implicitly the presence of three different solvents (CH_2Cl_2 , THF, MeCN), by considering a polarizable continuum medium characterized by their respective dielectric constants, $\epsilon = 8.93$, 7.58 , and 37.5 .⁶⁰

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Structure of the active site of the [FeFe]-hydrogenase, the dicyanide precursor to that active site, and a pdt-based model complex with four phosphine ligands.

Figure 2. FT-IR spectra (CH₂Cl₂ solutions, note that the isocyanide complexes are insoluble in alkanes) in ν_{NC} region for **1** (green), **2** (black), **3** (red), and Fe₂(pdt)(CO)₆ (blue).

Figure 3. ¹H NMR signals for ptd²⁻ ligand in **1** (green), **2** (black), **3** (red), and Fe₂(ptd)(CO)₆ (blue, top).

Figure 4. Structure of $\text{Fe}_2(\text{pdt})(\text{CNMe})_6$ (**3**), with thermal ellipsoids drawn at 35%. Hydrogen atoms and cocrystallized benzene are omitted for clarity.

Figure 5. Structure of $\text{Fe}_2(\text{pdt})(\text{CNC}_6\text{H}_4\text{Cl})_6$ (2), with thermal ellipsoids drawn at 35%; hydrogen atoms and cocrystallized benzene are omitted for clarity.

Figure 6.

Cyclic voltammogram of **2** in THF (top, black). Cyclic voltammogram of **2** in THF and ≈ 200 equiv of CNAr^{Cl} (bottom, red). Conditions: 1 mM Fe₂(pdt)(CNAr^{Cl})₆, 40 mM Bu₄N[BAr^F₄], 100 mV s⁻¹ scan rate. Ferrocene is used as an internal standard. Annotations (V vs Fc^{0/+}): (black) A_a = -0.29, A_c = -0.37, B_a = -0.45, C_a = -0.58, D_c = -0.71, E_c = -1.13; (red) A_a = -0.37, B_a = -0.65, B_c = -0.71, C_c = -1.07 V.

Figure 7.
Cyclic voltammogram of $\text{Fe}_2(\text{pdt})(\text{CNMe})_6$ in THF solution. Conditions: 1 mM $\text{Fe}_2(\text{pdt})(\text{MeNC})_6$, 40 mM $\text{Bu}_4\text{N}[\text{BAr}^{\text{F}}_4]$, 12.5 mV s^{-1} scan rate.

Figure 8.
Top: HOMO (cutoff value: 0.035). Bottom: NBO partial charges (bold, next to atoms) and fractional atomic contributions to the HOMO (parentheses) of $\text{Fe}_2(\text{pdt})(\text{CNMe})_6$ and $\text{Fe}_2(\text{pdt})(\text{CO})_6$.

Figure 9.
DFT-computed (black) and experimental (red) IR spectra of **3** in the ν_{CN} region.

Figure 10. DFT-calculated structures of $[\text{Fe}_2(\text{pdt})(\text{CNMe})_5(\mu\text{-CNMe})]^z$ for $z = 0$ (left) and $1+$ (right, distances in Å). Hydrogen atoms were omitted for clarity.

Figure 11. 600 MHz ${}^1\text{H}$ NMR spectrum (CD_2Cl_2 , -40°C) of $[\mathbf{3H}]^+$ generated in situ from **3** and $[\text{HNEt}_3]\text{BAr}^{\text{F}}_4$.

Figure 12.

Top: Conversion of aminocarbyne $[3H]^+$ to the hydride $[H3]^+$. Bottom: Time course for isomerization of $[3H]^+$ to $[H3]^+$. $A_0 = [3H]^+$ at $t = 0$ s. $B_0 = [H3]^+$ at $t = 0$ s. $B = [H3]^+$ at time t .

Figure 13.

Left: originally proposed (top) and revised (bottom) structures of $[\text{Fe}_2(\text{SMe})_2(\text{CO})_3(\text{PMe}_3)_2(\text{CCF}_3)]^+$. DFT-calculated structure for minimized structure (distances in Å). Hydrogen atoms were omitted for clarity.

Scheme 1.

DFT-Calculated Redox Couples for the Rotated and Unrotated Isomers of 3

Scheme 2.

Reactions of **3** (Rotamers of $\mu\text{-CNMe}(\text{H})$ and $\mu\text{-CNMe}$ Substituents Are Nearly Equal in Energy)

Scheme 3. Structures (Relative Energy in kcal/mol) for Selected Lower-Energy Isomers Resulting from Protonation of **3^a**

^aThe two lowest energy isomers were observed spectroscopically.

Scheme 4.

DFT-Calculated Pathway for Conversion of $\text{Fe}_2(\text{pdt})(\text{CNMe})_6$ to $[\text{HFe}_2(\text{pdt})(\text{CNMe})_6]^+$

Table 1Selected Distances (Å) and Angles (deg) in Fe₂(pdt)(CO)₆,²⁶ 2, and 3 (DFT-Calculated Values in Brackets)

	Fe ₂ (pdt)(CO) ₆	Fe ₂ (pdt)(CNC ₆ H ₄ Cl) ₆ (2)	Fe ₂ (pdt)(CNMe) ₆ (3)
Fe–C(apical) _{avg}	1.802(1) [1.800]	1.812(12)	1.847(12) [1.808]
Fe–C(basal) _{avg}	1.799(2) [1.787]	1.807(5)	1.823(7) [1.790]
Fe–S _{avg}	2.252(3) [2.279]	2.261(2)	2.273(2) [2.292]
Fe–Fe	2.5103(11) [2.551]	2.530(2)	2.540(1) [2.562]
C–N–C _{apical}		165 (distal) ^a	177 (distal) ^a [165.1]
C–N–C _{basal}		172 (proximal)	173 (proximal)
		164, 175 (distal) ^a	176, 176 (distal) ^a
		166, 175 (proximal)	166, 166 (proximal) [150.3]

^aDistal Fe is nearest to the C–CH₂–C center. Proximal is the other Fe. These definitions conform to the labeling of Fe^d and Fe^p in the [FeFe]-hydrogenases.

Table 2

Reduction Potentials (V vs Fc⁺/Fc) for [Fe₂(pdt)(CO)_{6-n}(CNMe)_n]^{+/0} and Related Compounds in MeCN Solution^{45,51}

redox couple	<i>E</i> _{1/2} (V)
[Fe ₂ (pdt)(CO) ₆] ^{+/0}	0.76 (0.65 ⁵⁰)
[Fe ₂ (pdt)(CO) ₅ (CNMe)] ^{+/0}	0.57
[Fe ₂ (pdt)(CO) ₅ (PMe ₃)] ^{+/0}	0.23 (0.1 ⁵⁰)
[Fe ₂ (pdt)(CO) ₄ (CNMe) ₂] ^{+/0}	0.21
[Fe ₂ (pdt)(CO) ₄ (PMe ₃) ₂] ^{+/0}	−0.20 (−0.24 ⁵⁰)
[Fe ₂ (pdt)(CNMe) ₆] ^{+/0} ([3] ^{+/0})	−1.2 to −1.3