Bioinspired Hydrogenase Models: The Mixed-Valence Triiron Complex \([\text{Fe}_{3}(\text{CO})_{7}(\mu-\text{edt})_{2}]\) and Phosphine Derivatives \([\text{Fe}_{3}(\text{CO})_{7-x}(\text{PPh}_{3})_{x}(\mu-\text{edt})_{2}]\) (\(x = 1, 2\)) and \([\text{Fe}_{3}(\text{CO})_{5}(\kappa^{2}-\text{diphosphine})(\mu-\text{edt})_{2}]\) as Proton Reduction Catalysts

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**ABSTRACT:** The mixed-valence triiron complexes \([\text{Fe}_{3}(\text{CO})_{7-x}(\text{PPh}_{3})_{x}(\mu-\text{edt})_{2}]\) (\(x = 0\sim2\); edt = SCH₂CH₂S) and \([\text{Fe}_{3}(\text{CO})_{5}(\kappa^{2}-\text{diphosphine})(\mu-\text{edt})_{2}]\) (diphosphine = dpv, dppe, dpb, dpn) have been prepared and structurally characterized. All adopt an anti arrangement of the dithiolate bridges, and PPh₃ substitution occurs at the apical positions of the outer iron atoms, while the diphosphine complexes exist only in the dibasal form in both the solid state and solution. The carbonyl on the central iron atom is semibridging, and this leads to a rotated structure between the bridged diiron center. IR studies reveal that all complexes are inert to protonation by HBF₄·Et₂O, but addition of acid to the pentacarbonyl complexes results in one-electron oxidation to yield the moderately stable cations \([\text{Fe}_{3}(\text{CO})_{5}(\text{PPh}_{3})_{2}(\mu-\text{edt})_{2}]^{+}\) and \([\text{Fe}_{3}(\text{CO})_{5}(\kappa^{2}-\text{diphosphine})(\mu-\text{edt})_{2}]^{+}\), species which also result upon oxidation by \([\text{Cp}_2\text{Fe}]^{2+}\). The electrochemistry of the formally Fe(I)–Fe(II)–Fe(I) complexes has been investigated. Each undergoes a quasi-reversible oxidation, the potential of which is sensitive to phosphine substitution, generally occurring between 0.15 and 0.50 V, although \([\text{Fe}_{3}(\text{CO})_{5}(\text{PPh}_{3})_{2}(\mu-\text{edt})_{2}]^{+}\) is oxidized at −0.05 V. Reduction of all complexes is irreversible and is again sensitive to phosphine substitution, varying between −1.47 V for \([\text{Fe}_{3}(\text{CO})_{5}(\mu-\text{edt})_{2}]^{+}\) and around −1.7 V for phosphine-substituted complexes. In their one-electron-reduced states, all complexes are catalysts for the reduction of protons to hydrogen, the catalytic overpotential being increased upon successive phosphine substitution. In comparison to the diiron complex \([\text{Fe}_{2}(\text{CO})_{6}(\mu-\text{edt})_{2}]^{+}\), \([\text{Fe}_{3}(\text{CO})_{5}(\mu-\text{edt})_{2}]^{+}\) catalyzes proton reduction at 0.36 V less negative potentials. Electronic structure calculations have been carried out in order to fully elucidate the nature of the oxidation and reduction processes. In all complexes, the HOMO comprises an iron–iron bonding orbital localized between the two iron atoms not ligated by the semibridging carbonyl, while the LUMO is highly delocalized in nature and is antibonding between both pairs of iron atoms but also contains an antibonding dithiolate interaction.

**INTRODUCTION**

Over the past decade there has been intense interest in the chemistry of dithiolate-bridged diiron complexes,¹−₅ since they closely resemble the two-iron unit of the H-cluster active site of iron-only hydrogenases.⁶−⁸ As a result of these studies important advances have been made in our understanding of how this enzyme site functions,⁹−₁₂ however, many challenges remain. Most notably, while it is relatively easy to prepare complexes which bear a close structural resemblance to the H-cluster site, the preparation of good functional models has not yet been achieved. Thus, while virtually all diiron(I) dithiolate-bridged complexes are able to act as catalysts for the reduction of protons to hydrogen under reducing conditions, they are generally characterized by high overpotentials and poor turnover numbers and frequencies.

In 2005, Pickett and co-workers reported the serendipitous isolation of the tetrairon cluster \([\text{Fe}_{4}(\text{CO})_{8}(\mu_{1}-\text{SCH}_{2})_{3}\text{CMe}_{2}]^{+}\) (A) formed upon reaction of Bosnich’s thiol with \([\text{Fe}_{6}(\text{CO})_{12}]^{+}\).¹³ This is a rare example of a linear 66-electron cluster being characterized by three metal–metal bonds¹⁴−¹⁹ and is formally a mixed-valence complex comprised

**Received:** July 15, 2013  
**Published:** March 5, 2014
of a chain of Fe(1)−Fe(II)−Fe(II)−Fe(1) centers. Importantly with respect to functional modeling of the hydrogenase active site, while the one-electron-reduction product $A^-$ was shown to be only a moderate catalyst for proton reduction, addition of a second electron resulted in formation of $A^2^-$, which was shown to be an excellent electrocatalyst, dihydrogen elimination being at least 500 times greater than that found in related [Fe$_2$(CO)$_6$(μ-dithiolate)] complexes. Later detailed electrochemical and DFT studies shed some light onto the high activity of $A^2^-$. Thus, it is proposed that upon addition of two electrons the central iron−iron bond of $A$ is cleaved, which in turn leads to rotation of the iron tricarbonyl groups and formation of bridging carbonyls and vacant coordination sites, the latter being able to bind protons efficiently and thus leading to high electrocatalytic ability (Scheme 1).

These results prompted us to consider other mixed-valence iron thiolate clusters as potential electrocatalysts for proton reduction. In an early paper on the synthesis of diiron dithiolate complexes, Huttner and co-workers reported that while reaction of HS(CH$_2$)$_n$SH ($n$ = 2, 3) with [Fe$_3$(CO)$_{12}$] afforded predominantly the diiron complexes [Fe$_2$(CO)$_6$(μ-S-(CH$_2$)$_n$S)], in both cases smaller amounts of the trinuclear materials [Fe$_3$(CO)$_6$(μ-S(CH$_2$)$_n$S)$_2$] could also be isolated. No later reports detail these mixed-valence complexes, and consequently we were drawn to investigate them as possible electrocatalysts for proton reduction. Herein we describe our studies in this area which have focused on the ethanedithiolate (edt) complex [Fe$_3$(CO)$_7$(μ-edt)$_2$] (1), some aspects of which have previously been communicated.

## RESULTS AND DISCUSSION

### Synthesis [Fe$_3$(CO)$_7$(μ-edt)$_2$] (1)

Huttner and coworkers initially reported the preparation of [Fe$_3$(CO)$_7$(μ-edt)$_2$] (1) in <1% yield from a 1:1 reaction between 1,2-ethanethiol and [Fe$_3$(CO)$_{12}$] in toluene at 70 °C, raising the yield to 5% upon doubling the amount of 1,2-ethanethiol. We were not able to reproduce this latter yield following Huttner’s method, our best yield being less than 2%. In an attempt to prepare 1 in larger amounts, we reacted 2 equiv of Collman’s reagent, Na$_2$[Fe(CO)$_4$], with 1,2-ethanethiol at room temperature in thf over 24 h. This resulted in isolation of 1 after chromatographic workup as a red solid in 5% yield, the major product (27%) being [Fe$_2$(CO)$_6$(μ-edt)] (Scheme 2). While it is not clear to us why this method gives better results, it has been repeated many times and is fully reproducible. Characterization data are in accord with those reported earlier. In the $^1$H NMR spectrum, four broad high-field resonances were assigned to the methylene protons of the edt bridges. The 13C NMR spectrum has not previously been reported. Singlets at 37.7 and 36.2 ppm are assigned to the edt bridges, while the low-field region consists of five singlets in a 1:2:1:1:2 ratio. That at 221.5 ppm is assigned to the carbonyl bound to the central iron atom, while the other resonances are attributed to apical (intensity 1) and basal (intensity 2) carbonyls bound to the other iron atoms. These observations show that the solid-state structure (see below) is maintained in solution. The IR spectrum shows a series of strong absorptions between 2073 and 1975 cm$^{-1}$ together with a weak absorption at 1904 cm$^{-1}$, which we attribute to the carbonyl on the central iron atom. This latter assignment was subsequently corroborated by DFT calculations (see later), which revealed a semibridging ν(CO) band at 1899 cm$^{-1}$ in excellent agreement with the experimental data.

### Reactivity of [Fe$_3$(CO)$_7$(μ-edt)$_2$] (1) toward PPh$_3$

Phosphine substitution has been extensively utilized in work on diiron hydrogenase biomimetics, primarily in order to increase the electron density on the metal center and thus facilitate proton binding. Heating a benzene solution of 1 and PPh$_3$ resulted in the slow consumption of starting materials with concomitant formation of four new products identified as follow.
after chromatographic separation. Two of these were the desired substituted triiron complexes \([\text{Fe}_3(\text{CO})_6(\text{PPh}_3)_{\delta}(\mu-\text{edt})_2]\) (2) (23%) and \([\text{Fe}_3(\text{CO})_6(\text{PPh}_3)_{\delta}(\mu-\text{edt})_2]\) (3) (12%) (Scheme 3). Yields of both were dependent upon the reaction time, and it was clear that they were formed sequentially. Two further products were also isolated, binuclear \([\text{Fe}_2(\text{CO})_3(\text{PPh}_3)_{\delta}(\mu-\text{edt})_2]\) (22%) \(38\) and \(\text{Ph}_2\text{P}=\text{S} (30\%)). Competition between carbonyl substitution and iron–iron bond scission is a recurring feature of reactions in 1 and \([\text{Fe}_3(\text{CO})_6(\mu-\text{pdt})_2]\) with mono- and bidentate phosphines. \(39\)

Characterization of the desired triiron complexes was relatively straightforward. In the IR spectrum of 2 the low-energy carbonyl absorption now appears at 1882 cm\(^{-1}\), while in 3 it is seen at 1869 cm\(^{-1}\). The energies of these semibridging \(\nu(\text{CO})\) bands compare well with the DFT computed values of 1886 and 1873 cm\(^{-1}\). The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of 2 shows two singlets at 65.0 and 52.7 ppm in an approximate 3:1 ratio, which we attribute to the coexistence of isomers. This is seen at 52.7 ppm in an approximate 3:1 ratio, which we attribute to the coexistence of isomers. This is supported by the \(^1\text{H}\) NMR spectrum, in which a doubling of the expected peaks is seen. The major isomer shows four clear methylene resonances between \(\delta 2.5\) and 1.0, each appearing as a pseudodoublet \((J = ca. 7–8 \text{ Hz})\) consistent with monosubstitution. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of 3 consists of three singlets at 63.8, 61.5, and 53.1 ppm in an approximate 2.5:3:1 ratio, which we attribute to two isomers; the resonance at 61.5 ppm is attributed to overlapping singlets. The existence of only two isomers is easily surmised from the \(^1\text{H}\) NMR spectrum, which shows two pairs of methylene resonances in an approximate 2.5:1 ratio.

Reactivity of \([\text{Fe}_3(\text{CO})_6(\mu-\text{edt})_2]\) (1) toward Diphosphines. Addition of diphosphines to the diiron center of hydrogenase biomimetics has been extensively studied and leads to an increase in electron density at the center, thus promoting protonation, but also binding of the diphosphines in a chelating manner affords steric and electronic differentiation of the two iron atoms. \(31\)–\(37\) Heating 1 in benzene with a range of diphosphines led to the isolation after chromatography of two product types, namely the desired triiron complexes \([\text{Fe}_3(\text{CO})_6(\kappa^2\text{-diphosphine})(\mu-\text{edt})_2]\) (4–7) (Scheme 4) to-

\[
\begin{align*}
\text{Ph}_2\text{P}X\text{P}\text{P}X\text{P} &\quad \Delta \quad \text{C}_6\text{H}_6 \\
\text{Fe}_3(\text{CO})_6(\kappa^2\text{-diphosphine})(\mu-\text{edt})_2 &\quad \text{Scheme 4}
\end{align*}
\]

gather with the diiron species \([\text{Fe}_2(\text{CO})_3(\kappa^2\text{-diphosphine})(\mu-\text{edt})_2]\) \((\text{diphosphine} = \text{dppv, dppe, dpbb})\). \(35,39\) The latter result is more easily prepared upon addition of the same diphosphines to \([\text{Fe}_3(\text{CO})_6(\mu-\text{edt})_2]\) and will be reported more fully elsewhere. \(39\)

The triiron complexes 4–7 were isolated in moderate yields (20–40%) as air-stable red crystalline solids. They are readily characterized by their IR spectra, which show three absorption bands: a sharp and strong absorption at ca. 2025 cm\(^{-1}\), a broad strong absorption at ca. 1950 cm\(^{-1}\), and a weak absorption at ca. 1830 cm\(^{-1}\). The last band shows that the semibridging carbonyl is still present. The \(^1\text{H}\) NMR spectra are generally uninformative but are consistent with the proposed formulation. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra are more useful; in all cases, these consist only of a sharp singlet at room temperature, showing the existence of a single isomer. For example, the spectrum of \([\text{Fe}_3(\text{CO})_6(\kappa^2\text{-PPh}_{11}\text{CCHPPh}_{11})(\mu-\text{edt})_2]\) (4) consists only of a singlet at 81.6 ppm and cooling to \(-60^\circ\text{C}\) in \(\text{CD}_2\text{Cl}_2\) results in no significant broadening. Thus, we conclude that coordination of the diphosphine occurs exclusively in the basal positions of one of the outer iron atoms, a supposition that is supported both by crystallography and by DFT calculations (vide infra).

While this work was in progress, Schollhammer and co-workers reported the preparation of a diphosphine complex, \([\text{Fe}_3(\text{CO})_6(\kappa^2\text{-diphosphine})(\mu-pdt)]\) \((\text{diphosphine} = 1,3,5,7\text{-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane})\), related to 4–8 as a low-yield product from the reaction of \([\text{Fe}_3(\text{CO})_6(\mu-\text{pdt})]\) with the diphosphine in refluxing toluene. \(40\) In light of the work described here, it seems probable that this results from the reaction of small amounts of \([\text{Fe}_3(\text{CO})_6(\mu-\text{pdt})]\) in the diiron starting material.

Structural Studies. Crystallographic studies were carried out on 1–4, the results of which are summarized in Figure 1 and Table 1. Data for 3 are relatively poor but nevertheless show clearly the sites of phosphine substitution and thus are included here. The diphosphine complex 4 contains a crystallographic plane of symmetry that includes the three iron atoms and the semibridging carbonyl.

All clusters contain an approximately linear triiron core \([\text{Fe}(1)\cdots\text{Fe}(2)\cdots\text{Fe}(3)\text{ }151.50(6)\cdots154.77(3)^\circ]\) and an anti arrangement of dithiolate ligands. Iron–iron bond distances of 2.5385(8)–2.5842(4) Å compare well with the Fe(1)–Fe(II) bond length of 2.543(5) Å found in \([\text{Fe}_4(\text{CO})_6(\mu-3\text{-SCH}_2\text{C}(\text{CH}_3)\text{Me})_2]\) \(13\) but are shorter than the Fe(II)–Fe(II) contact of 2.651(9) Å in the same molecule. In 2 and 3 phosphine substitution occurs at the apical site(s) of the external Fe(1) centers lying approximately \(trans\) to the metal–metal bond (Fe–Fe–P 150.27(9)–154.11(8)°). In contrast, the diphosphine in 4 occupies basal sites at the iron center that is bound to the semibridging carbonyl and subtends a bite angle of 86.71(4)°. A feature of all complexes is the bending of the carbonyl bound to the Fe(II) center (Fe(2)–C–O 160.4(3)–168.2(8)°) (see below), while the Fe(2)–C bond distances of 1.75(1)–1.774(4) Å are somewhat shorter than those for the carbonyls bound to the Fe(1) centers, with the exception of the unique carbonyl at the Fe(3)(diphosphine) center in 4 (Fe(1)–C–C 1.754(5) Å). Again a similar but less pronounced effect is seen in \([\text{Fe}_3(\text{CO})_6(\mu-3\text{-SCH}_2\text{C}(\text{CH}_3)\text{Me})_2]\), where the Fe(2)–C bond length is 1.771(3) Å. \(13\)

The structure of 1 is very similar to that of anti-[Ru(III)(CO)\(6\)(\mu-\text{edt})_2] reported by Adams and Yamamoto. \(41\) Importantly, the bond angle at the central metal site of 151.52(3)° is virtually identical with those in 1–4, while the central carbonyl is also bent (Ru(2)–C–O 166.4(8)°). This has been attributed to a semibridging interaction with a second ruthenium atom (Ru(1)–C 2.713(9) Å). Similar interactions are seen in 1–3, with Fe(1)–C(4), Fe(1)–C(3), and Fe(3)–C(3) bond lengths of 2.576(4), 2.61(1), and 2.57(1) Å, respectively. In 4 this interaction is even shorter (Fe(1)–C(2) 2.433(4) Å), suggesting that the increase in electron density at the iron(I) center upon phosphine addition enhances the semibridging interaction. Formation of a semibridging carbonyl is believed to be a key feature of proton reduction by hydrogenase enzymes, \(1\)–\(5\) and a number of biomimetic Fe(I)–Fe(II) complexes contain this feature. \(42\)–\(45\)
Acid Addition and Chemical Oxidation. A key step in the electrocatalytic conversion of protons to hydrogen at the active center is the coordination of the proton(s). The hexacarbonyl complexes \([\text{Fe}_2(\text{CO})_6(\mu\text{-dithiolate})]\) are protonated only when especially strong acids are used, and thus phosphine substitution is typically employed in order to increase the proton-binding properties of binuclear models. Before embarking on electrocatalytic studies, we therefore decided to investigate the reactions of 1–4 with acids.

In no case did we find any evidence for the formation of a protonated species. Addition of a slight excess of HBF\(_4\)·Et\(_2\)O to a dichloromethane solutions of 1 resulted in no discernible change, while dark red 2 resulted in a slow lightening of the solution with concomitant growth of some new IR bands; however, this species showed limited stability and decomposed slowly. Addition of HBF\(_4\)·Et\(_2\)O to 3 in air resulted in a rapid lightening of the solution and the appearance of new IR bands at 2042 vs, 2021 m, and 1988 m cm\(^{-1}\). Attempts to observe this compound by NMR spectroscopy were unsuccessful, and the excessively broadened spectrum was attributed to the generation of a paramagnetic species. Thus, we considered that the “protonation” product of 3 was rather an oxidation product.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1–4

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product. This was confirmed upon addition of 1 equiv of \([\text{Cp}_2\text{Fe}]\left[\text{PF}_6\right]\) to a dichloromethane solution of 3, which resulted in the generation of \([\text{Fe}_3(\text{CO})_7(\mu-\text{PhPh}_2)(\mu-\text{edt})_2]\left[\text{PF}_6\right] \ (3^{+} \left[\text{PF}_6\right])\), having an IR spectrum identical to that generated upon HBF\(_4\) addition. The lack of a semibridging carbonyl band shows that some structural rearrangement has occurred upon oxidation. Unfortunately, we have not been able to obtain 3\(^+\) in a pure state. Addition of HBF\(_4\)-Et\(_2\)O to 4 followed a similar course: an immediate lightening of the dark red solution with concomitant formation of a new species characterized by IR bands at 2071 vs, 2015 s, 1984 m, 1954 m, and 1908 w cm\(^{-1}\) with limited stability. As was the case for 3, addition of \([\text{Cp}_2\text{Fe}]\left[\text{PF}_6\right]\) led to the generation of an indistinguishable IR spectrum and for 5 and 6 similar changes were noted upon addition of HBF\(_4\)-Et\(_2\)O.

Electronic Structure Calculations. In order to better understand the nature of the mixed valency and also in an attempt to interpret the electrochemical studies (see below), we have carried out a series of density functional calculations on 1–4. For all four compounds the optimized structure was that seen crystallographically, suggesting that for 2–4 the observed phosphine substitution position(s) was the thermodynamic isomer. For related dinuclear complexes containing chelating diphenyls both apical–basal and dibasal isomers coexist in solution,\(^{31-37}\) the relative energies being on the order of 0.5–1.5 kcal mol\(^{-1}\). Using DFT we have calculated the energy difference between the observed dibasal form of 4 and its basal–apical isomer, the difference of 5.7 kcal mol\(^{-1}\) in favor of the dibasal isomer equating to \(K_{eq} = 5.6 \times 10^{-5}\), in accord with our observation of a single isomer.

Phosphine substitution appears to have little impact on the nature of both the HOMO and LUMO (see the Supporting Information for full details), and thus only those for 1 are shown (Figure 2). The HOMO (Figure 2a) is best described as an iron–iron bonding orbital that is localized on the pair of iron atoms not ligated by the semibridging carbonyl ligand, although there is a small antibonding component across the second iron–iron bond. This suggests that partial depopulation of this orbital (oxidation) should lead to an elongation of one of the metal–metal bonds and result in a significant loss of symmetry. In 2 and 4 the introduced phosphine ligand lies remote to the significant iron–iron bonding contribution in the HOMO, and hence one might expect that it plays little part in the nature of the oxidation process. In contrast to the HOMO, the LUMO (Figure 2b) is highly delocalized in nature. It is clearly antibonding about both iron–iron bonds and also displays an antibonding dithiolate interaction (in-phase lone pair) at the iron–iron vector ligated by the semibridging carbonyl. Consequently, a one-electron reduction might be expected to result in a slight elongation of both metal–metal bonds and perhaps also some elongation of some of the iron–sulfur bonds. It is noteworthy that the degree of the iron–sulfur antibonding interactions noted in the LUMOs of 2–4 is somewhat reduced in comparison to that in 1, suggesting that the potential for sulfur–iron bond rupture upon reduction of the substituted clusters is reduced. The HOMO–LUMO gap is sensitive to the degree of phosphine substitution, decreasing from 3.01 eV in 1 to 2.95 and 2.80 eV in 2 and 3, respectively, while the HOMO–LUMO gap in 4 of 3.28 eV is significantly larger.

Adams and Yamamoto have previously shown that \(\text{anti-}[\text{Ru}_n(\text{CO})_x(\mu-\text{edt})_2]\) formed upon addition of 1,2,5,6-tetra-thiaocyclooctane to \([\text{Ru}_3(\text{CO})_7(\mu-\text{edt})_2][\text{PF}_6]\) converts into the thermodynamically favored \(\text{syn}\) product upon heating (Scheme 5).

**Scheme 5**

These isomers are structurally quite different, the most notable changes upon isomerization being (i) a significant lengthening of the ruthenium–ruthenium bonds of ca. 0.16 Å, (ii) a far more acute Ru–Ru–Ru bond angle of 73.55(2)\(^\circ\), and (iii) loss of the semibridging carbonyl interaction, while in the \(\text{syn}\) isomer both binuclear subunits contain nonrotated RuL\(_3\) mieties. In \(\text{syn-}[\text{Ru}_n(\text{CO})_x(\mu-\text{edt})_2]\) the formally nonbonded Ru–Ru interaction is 3.4148(6) Å, which while being long could still be indicative of some direct interaction between these two atoms. DFT calculations (Figure 3) confirmed that for ruthenium the \(\text{syn}\) isomer lies 2.9 kcal mol\(^{-1}\) lower in enthalpy than the \(\text{anti}\) isomer. In contrast to the facile isomerization of \(\text{anti-}[\text{Ru}_n(\text{CO})_x(\mu-\text{edt})_2]\), heating a toluene solution of 1 resulted in no discernible change. A DFT calculation on the triiron system showed that the \(\text{syn}\) isomer is lower in enthalpy than the \(\text{anti}\) isomer, the difference of 1.1 kcal mol\(^{-1}\) being less than that found for the ruthenium complex. It is not clear why 1 does not undergo such an isomerization. It may be that the more radially contacted iron(I) centers cannot interact over the 3.53 Å computed for the internuclear Fe–Fe distance in the \(\text{syn}\) isomer, or it may simply be that the activation barrier is too high.

**Electrochemical Studies.** Cyclic voltammetry (CV) of 1–6 in dichloromethane under an argon atmosphere was carried out, important features being summarized in Table 2. CVs for 1–3 are shown in Figure 4. On scanning first to positive potentials, oxidation takes place at \(E_{1/2} = 0.50\) V for 1, \(E_{1/2} = 0.15\) V for 2, and \(E_{1/2} = -0.05\) V for 3. The peak current for oxidation of 3 is significantly smaller than for 1 and 2, suggesting that fewer electrons are transferred for this complex. Normalizing peak current by dividing by the square root of the scan rate reveals that twice as many electrons are transferred at low in comparison to high scan rates (Supporting Information); thus, we suggest a one-electron transfer at fast scan rates, tending to two electrons as the electrochemical time scale is increased. The limited stability of the oxidation product does not allow the number of electrons transferred to be determined using chronocoulometry experiments.

Of more importance in the context of proton reduction catalysis is the reduction behavior of the complexes. As expected, reduction potentials for 1–3 shift to more negative values with increased phosphine substitution (Figure 4). A
The reduction behavior of the complexes in the presence of protons was investigated in the presence of the strong acid HBF₄. For 1–3 in dichloromethane the principal catalytic response is observed at approximately the potential of the first reduction, at −1.5 V for 1, −1.8 V for 2, and −1.95 V for 3 (with 10 equiv of acid). The CVs of 2 with sequential addition of molar acid equivalents are presented in Figure 5, along with a plot of limiting catalytic current vs acid concentration for 1 and 2. Although the catalytic activity of 2 takes place at more negative potentials as a consequence of its reduction potential, the catalytic peak currents obtained are higher than for unsubstituted 1. Simulations reveal this is a consequence of the higher basicity of 2 and hence its more rapid protonation (Supporting Information). In excess acid some reduction currents are noted at potentials less negative than for the primary catalytic process, starting at −1.1 V. This suggests that the electron that is removed is not lost in the substituted iron center, an observation in accord with the electronic structure calculations, which show the HOMO is delocalized over all three iron atoms. Complexes 4–6 show an irreversible reduction between −1.68 and −1.88 V, a potential range comparable with that of 2 and 3, and the reduction is irreversible at all scan rates.

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We attribute this peak to a decomposition product (P3) of 2− (or 22−), resulting from scission of an Fe−S bond (vide supra). Hence, the catalytic response at the same potential is likely due to proton reduction associated with P. A suggested catalytic scheme is presented in Figure 5c. The peak at −2.3 V may be attributed to further reduction products, but direct reduction of the acid at the electrode also occurs in this potential region, making interpretation difficult.

We find catalytic currents for 2 are marginally higher than for 3, indicating that further PPh3 substitution does not result in faster proton reduction catalysis. This may be a result of slower protonation for 3− than for 2−, but if so this must be due to steric rather than electronic effects. The bulky PPh3 group may prevent ready access for the proton to the Fe−Fe bond, or steric interactions between the edt bridge and the PPh3 may prevent elongation of the Fe−Fe bond to accommodate a bridging hydride. Alternatively, this may be a consequence of the stability inferred on the 3H catalytic intermediate species by the bulky phosphine ligands. For example, the species [(μ-H)Fe2(pdt)(CO)2(dppv)] has sufficient stability to be isolated, due to the basicity and steric bulk of phosphines. Both computational and experimental studies suggest that this bridging hydride is a spectator, rather than an intermediate, in hydrogen evolution catalysis, although the exact mechanisms are unclear. It may be that a similar mechanism takes place for 2 and the rate-limiting step is not initial protonation of 3− but subsequent steps involving the 3H intermediate. For 2 we observe that the limiting current maintains a linear relationship with acid addition up to 10 equiv (Figure 5b), suggesting that under these conditions the rate-limiting step is acid dependent.

Figure 5. (a) CV of 0.5 mM 2 in 0.1 M TBAPF6 in dichloromethane under Ar at a scan rate of 0.1 V s−1. The black trace indicates the neutral complex only, and then HBF4 is added in 0.5 mM increments. (b) Plot of experimental limiting catalytic current against molar equivalents of HBF4 added for 1 (black triangles) and 2 (black circles) and simulated limiting catalytic currents for 1 (open triangles) and 2 (open circles) from DigiSim (see the Supporting Information). (c) Suggested ECEC mechanism of H+ reduction with 2 and catalytic process at −2.0 V attributed to the decomposition product P. Parameters are described further in the Supporting Information. Values in red denote parameters that differ between 1 and 2.
Thus, in this regime it appears that one of the protonation steps, rather than \( \text{H}_2 \) elimination, is rate limiting. Further studies, including determination of scan rate dependence and the use of acids of different \( pK_a \) values would be required to further understand this mechanism and the difference in behavior of 2 and 3.

In dichloromethane, sequential addition of HBF\(_4\) to \( 4-6 \) results in irreproducible CVs, suggesting that the complexes are unstable under these conditions; thus, we are unable to provide a direct comparison of the influence of asymmetric substitution on the protonation or catalytic behavior of these complexes.

**CONCLUDING REMARKS**

Since it has been suggested that a rotated structure encompassing a semibridging carbonyl is essential for effective catalytic activity in hydrogenase biomimetic molecules, various synthetic routes have been explored to produce such a structure. Here we report the electrochemical and electrocatalytic activity of triiron complexes with this structural feature in their neutral form. In comparison to their diiron analogues the complexes are catalytic at decreased overpotential; for example, electrocatalytic proton reduction by \([\text{Fe}_3(\text{CO})_9]^{2-}\) (1) takes place at 0.36 V less negative potentials than that when \([\text{Fe}_2(\text{CO})_9]^{2-}\) is the catalyst. Substitution with PPh\(_3\) or diphosphines does not increase the basicity of the complexes sufficiently to allow significant protonation of the neutral molecule in dichloromethane. The first step in the catalytic cycle is therefore reduction of the complex in an EC-initiated mechanism. Phosphines push the catalytic response to more negative potentials; however, the payoff is that higher catalytic currents can be achieved, as the rate-limiting step is protonation of the anion.

Recently a number of other groups have utilized triiron clusters as proton reduction catalysts,\(^{52-55}\) most notably the bicapped 50-electron cluster \([\text{Fe}_5(\mu_3-S)_2(\text{CO})_9]^{5-}\).\(^{52,53,55}\) Linear triiron complexes 1–6 are considerably less stable to one-electron reduction than \([\text{Fe}_3(\mu_3-S)_2(\text{CO})_9]^{-}\), which undergoes a reversible one-electron reduction on the voltammetric time scale, and the monooanionic product has been detected spectroscopically,\(^{55}\) although it is not stable enough to isolate with bulk electrolysis due to CO ligand loss.\(^{52}\) On addition of a second electron at more negative potential \([\text{Fe}_3(\mu_3-S)_2(\text{CO})_9]^{2-}\) undergoes a rapid structural rearrangement with proposed Fe–S bond scission and formation of a bridging carbonyl across one iron–iron bond.\(^{53}\) \([\text{Fe}_3(\mu_3-S)_2(\text{CO})_9]^{2-}\) undergoes proton reduction catalysis via an EEC mechanism at the potential of the first reduction, in a mechanism similar to that proposed for 2. Catalytic processes at more negative potentials were attributed to the carbonyl-loss decomposition product of the monoanion and further reduction and protonation of the \([\text{H}_2\text{Fe}_3(\mu_3-S)_2(\text{CO})_9]^{-}\) intermediate from the primary catalytic cycle. The linear complexes described herein have reduction behavior very different from that of \([\text{Fe}_3(\mu_3-S)_2(\text{CO})_9]^{-}\), exhibiting irreversible reduction even at fast voltammetric scan rates. Reversibility is not improved in CO-saturated solutions, indicating that ligand loss is not a primary decomposition pathway. Electron uptake for 1–6 appears to be a two-electron process in the absence of acid, and as for \([\text{Fe}_3(\mu_3-S)_2(\text{CO})_9]^{-}\), we suggest that iron–sulfur bond rupture takes place. The linear complexes do not have the stability conferred by the cyclic structure; therefore, fragmentation into diiron and monooiron is a likely result.

Although they are not structural models for the hydrogenase enzyme active site, the triiron complexes described here have several features which make them potential functional models. The enzyme operates via the Fe\(^{2+}\)Fe oxidation states, as do the triiron complexes, while in contrast, most hydrogenase mimics operate via the FeFe\(^{2+}\) oxidation states. Further, the presence of the third iron center results in a HOMO—LUMO gap smaller than that for analogous diiron species. The difference in potential between the first oxidation and first reduction of neutral 1 is 1.97 V, in contrast to 2.70 V for \([\text{Fe}_3(\text{CO})_9]^{2-}\).\(^{23}\) Similarly, the values are 1.87 V for 2, in comparison to 2.60 V for \([\text{Fe}_3(\text{CO})_9(\text{PPh}_3)]^{2-}\), and 1.77 V for 3, in comparison to 2.45 V for \([\text{Fe}_3(\text{CO})_9(\text{PPh}_3)]^{2-}\) (for experiments carried out under the same conditions).\(^{23}\) In the enzyme the catalysis of proton reduction and hydrogen oxidation takes place reversibly and is close to the thermodynamic potential; thus, the difference in energy between the HOMO and LUMO must be very small. By designing biomimetics with a smaller HOMO—LUMO gap, we can hope to come closer to the catalytic performance of the enzyme. Unfortunately, the instability of the reduced forms of the complexes described here negates their use as viable proton reduction catalysts. Nevertheless, this work points toward the potential of small low-valent molecular clusters, especially those with mixed-valence states, to act as proton reduction catalysts.

**EXPERIMENTAL SECTION**

General Procedures and Starting Materials. Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Reagent-grade solvents were dried using appropriate drying agents and distilled prior to use by standard methods. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on a Bruker DPX 400 instrument. Mass spectra were recorded on a Varian Mat 312 mass spectrometer. Elemental analyses were performed by Microanalytical Laboratories, University College London. Collman’s reagent and phosphines were purchased from Strem Chemical Inc. and used without further purification.

Preparation of \([\text{Fe}_3(\text{CO})_9(\mu_3-S)]^{2-}\) (1). To a suspension of \(\text{Na}_4[\text{Fe}_3(\text{CO})_9]^{2-}\) (ca. 2.183 g, 10.20 mmol) in thf (30 mL) was added dropwise a solution of 1,2-ethanedithiol (0.479 g, 5.10 mmol) in thf (30 mL). After the mixture was stirred for 24 h at room temperature, the solvent was removed in vacuo and the residue extracted with hexane and filtered on Kieselguhr. The filtrate was concentrated under reduced pressure and the residue extracted with hexane and filtered on Kieselguhr. The filtrate was concentrated under reduced pressure to give an orange gum, which was chromatographed by TLC on silica gel. Elution with hexane developed two bands. The faster-moving orange band gave \([\text{Fe}_3(\text{CO})_9(\mu_3-S)]^{2-}\) (512 mg, 27%) as red crystals, while the slower-moving band afforded \([\text{Fe}_3(\text{CO})_9(\mu_3-S)]^{2-}\) (1; 90 mg, 5%) as deep red crystals after recrystallization from hexane/CH\(_2\)Cl\(_2\) at 4 °C. IR (CH\(_2\)Cl\(_2\)); 2703 s, 2040 vs, 1974 s, 1904 w cm\(^{-1}\); \(^1H\) NMR (CD\(_2\)Cl\(_2\)); 2.59 (br, 2H), 2.34 (br, 2H); 1.30 (br, 2H); 0.88 (br, 2H). \(^{31}\)C (\(^1\)H) NMR (CD\(_2\)Cl\(_2\)); 221.5 (1,ICO), 211.6 (2,ICO), 207.3 (3,ICO), 206.7 (4,ICO), 206.0 (5,ICO). 37.8 (6,CH\(_3\)), 36.2 (6,CH\(_3\)).

Preparation of \([\text{Fe}_3(\text{CO})_9(\text{PPh}_3)]^{2-}\) (2) and \([\text{Fe}_3(\text{CO})_9(\text{PPh}_3)(\mu_3-S)]^{2-}\) (3). A benzene solution (20 mL) of 1 (75 mg, 0.137 mmol) and PPh\(_3\) (36 mg, 0.137 mmol) was heated to 197 °C for 15 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH\(_2\)Cl\(_2\) (v/v 9/1) developed six bands. The first band was unreacted 1 (trace). The second to fifth bands afforded the following compounds in order of elution: \([\text{Fe}_3(\text{CO})_9(\text{PPh}_3)]^{2-}\) (18 mg, 22%) as red crystals, \([\text{Fe}_3(\text{CO})_9(\text{PPh}_3)(\mu_3-S)]^{2-}\) (2; 25 mg, 23%) as orange crystals, \([\text{Fe}_3(\text{CO})_9(\text{PPh}_3)(\mu_3-S)]^{2-}\) (3; 16 mg, 12%) as red crystals, and PPh\(_3\) (15 mg, 30%) as white crystals after recrystallization from hexane/CH\(_2\)Cl\(_2\) at ~20 °C. Spectral data for 2 are as follows. Anal. Calcd for \(\text{C}_{1385}\text{H}_{1238}\text{Fe}_{198}\text{O}_{226}\text{S}_{16}\): C, 42.99; H, 2.96.
Organometallics

Table 3. Crystallographic Data and Structure Refinement Details for 1–4

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<td>0.1027</td>
<td>0.0396</td>
</tr>
<tr>
<td></td>
<td>r2 0.1248</td>
<td>0.2600</td>
<td>0.2069</td>
<td>0.0854</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 0.0480</td>
<td>0.1181</td>
<td>0.2394</td>
<td>0.0661</td>
</tr>
<tr>
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<td>r2 0.1411</td>
<td>0.2787</td>
<td>0.2551</td>
<td>0.0903</td>
</tr>
<tr>
<td>largest peak, hole (e Å⁻³)</td>
<td>1.362, −0.649</td>
<td>1.045, −1.726</td>
<td>1.051, −0.631</td>
<td>1.430, −0.608</td>
</tr>
</tbody>
</table>

Found: C, 43.44; H, 3.07; IR (ν(CO), CH₂Cl₂): 2035 s, 2014, 33, 1356 C. 307 s, 2012 vs, 1963 vs, 1882 w cm⁻¹. ¹H NMR (CDCl₃): both isomers, δ 7.65 (m, 4H), 7.58 (m, 2H), 7.44 (m, 9H), 2.49 (m, 2H), 2.18 (m, 2H), 1.81 (m, 2H), 1.04 (m, 2H). ³¹P(¹H) NMR (CDCl₃): major isomer, δ 65.0 (s); minor isomer, δ 52.7 (s). Spectral data for 3 are as follows. Anal. Calc. for C₃₅H₃₀Fe₃O₅P₂S₄: C, 47.19; H, 3.77. Found: C, 53.69; H, 3.91. IR (ν(CO), CH₂Cl₂): 2008 s, 1965 vs, 1953 sh, 1912 m, 1869 w cm⁻¹. ¹H NMR (CDCl₃): δ 7.66 (m, 10H), 7.39 (m, 2H), 1.98 (m, 4H), 1.01 (m, 2H), 0.77 (m, 2H). ³¹P(¹H) NMR (CDCl₃): δ 63.8 (s), 61.5 (s).

Preparation of [Fe₃(CO)₅(μ₃-dppe)(μ- edt)] (4). A benzene solution (20 mL) of 1 (40 mg, 0.072 mmol) and cis-PCH₂CH₂PPH₂ (ddpb; 29 mg, 0.072 mmol) was heated to reflux for 4 h. The solvent was removed under reduced pressure, and the residue chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (v/v 4/1) gave three bands. The first band was unreacted 1 (3 mg; trace). The second band afforded [Fe₃(CO)₅(μ₃-dppe)(μ- edt)] [5 mg, 33%] as red crystals, after recrystallization from hexane/CH₂Cl₂ at −20 °C. Spectral data for 4 are as follows. Anal. Calc. for C₃₅H₃₀Fe₃O₅P₂S₄: C, 47.19; H, 3.62; Found: C, 47.37; H, 3.69. IR (ν(CO), CH₂Cl₂): 2024 vs, 1850 w cm⁻¹. ¹H NMR (CDCl₃): δ 7.44–7.33 (m, 20H, Ph), 2.36–2.35 (m, 4H, CH₄), 2.29–2.27 (m, 4H, CH₂), 1.81–1.79 (m, 4H, CH₂). ³¹P(¹H) NMR (CDCl₃): δ 71.0. ES-MS: m/z 913 [M⁺ + Na] (calc 913), 885 [M⁺ + Na + CO] (calc 885).

Preparation of [Fe₃(CO)₅(μ₃-dppb)(μ- edt)] (6). A benzene solution (20 mL) of 1 (40 mg, 0.072 mmol) and 1,2-PCH₂PPH₂PPh₂ (ddpb; 33 mg, 0.073 mmol) was heated to reflux for 3 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (v/v 4/1) gave three bands. The first band was unreacted 1 (2 mg; trace). The second band gave a trace amount of [Fe₃(CO)₅(μ- edt)] [μ- edt] (23 mg, 37%) as red crystals, after recrystallization from hexane/CH₂Cl₂ at −20 °C. Spectral data for 6 are as follows. Anal. Calc. for C₃₅H₃₀Fe₃O₅P₂S₄: C, 49.89; H, 3.43. Found: C, 49.95; H, 3.50. IR (ν(CO), CH₂Cl₂): 2024

dx.doi.org/10.1021/om000691q | Organometallics 2014, 33, 1356–1366
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SMART software. Data reduction was accomplished with SAINT collection, indexing, and initial cell re-regeneration with SHELXTL, V6.12. All non-hydrogen atoms were re-refined as isotropic.

Preparation of [Fe(CO)₅(dppn)(μ-edt)] (7). A benzene solution (20 mL) of 1 (50 mg, 0.091 mmol) and bis(diphenylphosphino)arylene-dppn (dppn; 40.09 mg, 0.091 mmol) was heated to reflux for 12 h. The solvent was removed under reduced pressure and the residue chromatographed on silica gel. Elution with hexane/Cl₂CH₂ (v/v 4/1) gave three bands. The first band was unreacted dppn (trace). The second and third bands gave respectively [Fe(CO)₅(μ-edt)(dppn)] (25 mg, 33%) and [Fe(CO)₅(μ-edt)(dppn)] (7; 22 mg, 24%) as deep red crystals, after recrystallization from hexane/Cl₂CH₂ at −20 °C. Spectral data for 7 are as follows. Anal. Calc. for C₄₅H₃₀Fe₂O₅P₂S₂: C, 52.72; H, 3.57. IR (KBr, CH₂Cl₂): 2024 vs, 1951 vs, 1815 w cm⁻¹. For the dark red solution lightened immediately upon addition of acid and new IR bands at 2071 vs, 2015 s, 1978 m cm⁻¹, the product were unsuccessful. For this time there was also substantial decomposition. For the partial loss of one or both of these solvents during the experiment.

IR Studies of Addition of HBF₄⁻ to [Fe₂(CO)₉(edt)] and [CP₃FePF₆] to 1–6. All reactions were carried out in a similar manner and monitored by IR spectroscopy.

Protonation. A CH₂Cl₂ solution (ca. 1 mL) of 1–6 was made by dissolving 2.5 × 10⁻³ mmol of the complex under study, and 2 molar equiv of HBF₄·Et₂O (0.680 µL) was added to this solution in the presence of air. The resultant acid-containing solution was immediately transferred to an IR cell and monitored over time. For 4 no discernible change in the IR spectrum was noted. For 2 a slow (ca. 1 h) lightening of the solution lead to the generation of new IR bands at 2103 m, 2062 sh, 2039 vs, 2001 s, and 1955 w cm⁻¹, but over this time there was also substantial decomposition. For 3 a rapid (ca. 1 min) lightening of the solution occurred and new IR bands were observed at 2042 vs, 2021 m, and 1988 w cm⁻¹. This species also decomposed slowly, and all attempts to further characterize the product were unsuccessful. For 4 the dark red solution lightened immediately upon addition of acid and new IR bands at 2071 vs, 2015 s, 1984 m, 1954 m, and 1908 w cm⁻¹ were observed. These slowly decayed with concomitant decomposition of the product over approximately 3 h. Similar behavior was noted for 5 and 6, the products being characterized by IR bands at 2100 vs, 2048 s, 1972 m, and 1885 w cm⁻¹ and at 2099 vs, 2047 s, 1978 m, and 1880 w cm⁻¹, respectively.

Oxidation. [CP₃Fe][PF₆] (0.828 mg, 2.5 × 10⁻³ mmol) was dissolved in a minimum amount of CH₂Cl₂ and this solution was then added to the presence of air to a CH₂Cl₂ solution containing 2.5 × 10⁻³ mmol of 1–6 prepared as above. The mixture was immediately transferred to an IR cell and monitored over time. For 1 and 2 no significant changes were noted, while for 3–6 IR changes very similar to those noted above resulted, suggesting that the two reactions were generating the same products.

Electrochemistry. Electrochemistry was carried out in deoxygenated dichloromethane or acetonitrile with 0.1 M TBAPF₆ as reference electrode was a silver wire. All CVs were referenced to the analytical Hessian. The computed harmonic frequencies for the carbonyl stretching bands have been scaled using Radom’s scaling factor of 0.964.60 The charges associated with the non-hydrogen atoms in compounds 1–4 were determined by natural population analyses (NPA) at the B3LYP level of theory.64 The geometry-optimized structures have been drawn with the JIMP2 molecular visualization and manipulation program.65

ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving details of the X-ray crystallographic structure determinations of 1–4, HOMO and LUMO contour plots of the geometry-optimized structures of clusters 1–4 and the geometry-optimized structures of the isomeric clusters [Ru₃(CO)₉(μ-edt)]₃ the complete ref 60, atomic coordinates of all optimized stationary points, and additional electrochemical information and experiments (Figures S1–S5). This material is available free of charge via the Internet at http://pubs.acs.org. Crystal data for 1–4 are also available from http://www.ccdc.cam.ac.uk/conts/retrieving.html as supplementary publications CCDC 827724–827726 (mail, 12 Union Road, Cambridge CB2 1FZ, U.K.; fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research has been partially sponsored by the Ministry of Science and Information & Communication Technology, Government of the People’s Republic of Bangladesh. We thank University College London for the provision of a studentship (D.U.), the EPSRC for an Advanced Fellowship (K.B.H., Grant No EP/D070538/1), the Commonwealth Scholarship Commission (S.G.) and the European Commission for Erasmus Mundus doctoral (A.R.) and post-doctoral (S.B.M.) fellowships. G.H. thanks The Royal Society of Chemistry for an International Authors Grant, which allowed
this manuscript to be completed during his visit to the University of North Texas. M.G.R. acknowledges support from the Robert A. Welch Foundation (Grant B-1093-MGR) and NSF (CHE-0741936). We also thank Prof. Michael B. Hall (TAMU) for providing us a copy of his JIMP2 program, which was used to prepare the geometry-optimized structures reported here. M.G.R. also thanks Dr. David A. Hrovat (Center for Advanced Scientific Computing and Modeling, UNR) for helpful computational discussions.

REFERENCES