ORGANOMETALLICS

Redox Chemistry of Noninnocent Quinones Annulated to 2Fe2S Cores

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Supporting Information

ABSTRACT: Noninnocent ligands that are electronically coupled to active catalytic sites can influence the redox behavior of the catalysts. A series of $(\mu$ -dithiolato)Fe₂(CO)₆ complexes, in which the sulfur atoms of the μ -dithiolato ligand are bridged by 5-substituted (Me, OMe, Cl, *t*-Bu)-1,4-benzoquinones, 1,4-naphthoquinone, or 1,4-anthraquinone, have been synthesized and characterized. In addition, the bisphosphine complex derived from the 1,4-naphthoquinone-bridged complex has also been prepared and characterized. Cyclic voltammetry of these complexes shows two reversible



one-electron reductions at potentials 0.2 to 0.5 V less negative than their corresponding parent quinones. In the presence of acetic acid two-electron reductions of the complexes result in conversion of the quinones to hydroquinone moieties. EPR spectroscopic and computational studies of the one-electron-reduced complexes show electron delocalization from the semiquinones to the 2Fe2S moieties, thereby revealing the "noninnocent" behavior of these ligands with these catalysts.

INTRODUCTION

The splitting of water consists of two half-reactions: oxidation to form molecular oxygen and the reduction of protons to molecular hydrogen. One broad class of catalysts for the latter half-reaction is inspired by the active sites of [FeFe]-hydrogenases,¹⁻³ which are extremely efficient enzymes for reversible reduction of protons to hydrogen with exceptionally high turnover rates at very modest overpotential.^{4,5} The common feature of this class of catalysts is a butterfly 2Fe2S core as depicted schematically in Chart 1. In addition to the





advantage of earth-abundant elements iron and sulfur comprising the core, a wide range of ligands can be bound to the iron centers and a variety of functional moieties can be attached to the sulfur atoms to tune the reduction potentials, facilitate geometry reorganizations, shuttle protons, accelerate electron transfer, and electronically couple ligands to the 2Fe2S core. According to a recent search of the CSD^{6,7} more than 600 catalysts of this class have been synthesized and characterized, and all catalyze the reduction of protons to hydrogen under appropriate conditions.⁸ In most cases, H₂ production occurs at potentials substantially more negative than the thermodynamic potential.^{9,10}

For example, we have studied H₂ production using benzene and hydroquinone moieties annulated to 2Fe2S cores.^{11–13} These complexes are excellent catalysts for H₂ production from weak acids. The mechanism for catalysis is shown in Scheme 1. Notably it features protonation most favored at iron after 2e⁻ reduction to generate a μ -bridged hydride. A further 1e⁻ reduction is needed to render the complex sufficiently hydridic to react with acetic acid. Because of this extra 1e⁻ reduction, these catalysts suffer from a > 0.5 V overpotential.

The H-cluster of [FeFe]-hydrogenase features a 4Fe4S cluster, which is part of the redox chain connecting the active site to the surface of the enzyme, and addition of an electron to a model of the H-cluster shows that the electron is delocalized over the entire H-cluster.^{14,15} Consequently, a number of examples have been reported in the literature^{16–18} in which an easily reduced moiety is incorporated into active site mimics. If the easily reduced moiety is electronically coupled with the 2Fe2S catalytic site,¹⁹ and protonation occurs at the 2Fe2S

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Scheme 1. Mechanism of Electrocatalytic Production of Hydrogen from a Weak Acid by Hydroquinone Complexes^{*a*}



^{*a*}Potentials are for the molecule with R = OMe.





core, a complex with the desired activity might be obtained. We now report active site mimics **2–4** (Chart 2) in which readily reducible quinone moieties are electronically coupled to the 2Fe2S core in an effort to design active H₂ catalysts with low overpotential. Such complexes appear promising considering electronic couplings with metals have been reported for related ligands: 1,2-dithiolenes,^{20–28} 1,2-benzenedithiolates,^{29,30} 1,2benzoquinone (catecholates),^{31–33} and 1,2-dithiolatonaphthoquinone.³⁴ Furthermore **2a** was reported before³⁵ and is more easily reduced than the corresponding benzene or hydroquinone complexes.^{13,35}

RESULTS AND DISCUSSION

Synthesis and Structure. A synthesis of the dithiobenzoquinone metal complex **2a** has been reported previously.³⁵ In this previous synthesis, shown schematically in Scheme 2 as method A for a general quinone, the photocycloaddition of the quinone to the disulfide complex $S_2Fe_2(CO)_6$ (**5**) yields the corresponding hydroquinone complex of type 7. Oxidation of the hydroquinone complex 7 with 2,3-dichloro-5,6-dicyano-1,4benzoquinone, DDQ, provided the benzoquinone complex **2a**. We have since reported¹³ an alternative synthesis of hydroquinones of type 7, shown as method B in Scheme 2. In method B the quinone is reacted with the dithiol complex (HS)₂Fe₂(CO)₆ (**6**) catalyzed by piperidine to yield the hydroquinone complex 7. Oxidation of these hydroquinones Scheme 2. Methods A and B for Preparation of the Quinone Metal Complexes in this Study



Table 1. DDQ Oxidation of Hydroquinone 2Fe2S Complexes to the Corresponding Quinone Metal Complexes 2b-e and 3a as Shown in Scheme 2

reaction time (min)	isolated yield (%)
90	81
90	95
60	77
60	90
120	83
	reaction time (min) 90 90 60 60 120

with DDQ provided the corresponding quinones 2b-e and 3a in 77–90% isolated yields (Table 1).

Naphthoquinone adduct **3a** proved especially stable, easily obtainable, and easy to work with, so subsequent reactions are reported for this complex. Quinone metal complex **3a** could be reduced back to the hydroquinone adduct with sodium cyanoborohydride in 86% yield, but due to its facile air oxidation, pure samples of the hydroquinone were difficult to prepare.

Treatment of naphthoquinone adduct 3a with excess Ph_3P and Me_3NO , similar to the previous studies of benzoquinone complexes,³⁵ afforded the corresponding bis-phosphine 3b in 19% isolated yield. An ORTEP drawing of the molecular structure of 3b is shown in Figure 1. An interesting feature of the structure of 3b is that the quinone moiety is face-to-face with a phenyl ring from each of the triphenylphosphine ligands with 3.5884(10) Å separating the centroid of each ring plane.

Anthraquinone **q4** did not afford the corresponding hydroquinone metal complex, but instead yielded the anthraquinone metal complex **4** directly in 57% pure isolated yield.

Electrochemistry. Figure 2 shows the voltammograms of the quinone-containing catalysts **2b**, **3a**, and **4** along with the voltammograms of the corresponding free quinones **q2b**, **q3**, and **q4** (Chart 3). In metal complexes with redox-active ligands in which the electronic interaction between the metal and the ligands is weak, initial reduction can occur either at the metal or at the ligand depending on the inherent reduction potentials of the separated sites^{36,37} and giving rise to redox behavior



Figure 1. Structure of **3b** with displacement ellipsoids at the 50% probability level. The structure has 2-fold rotational symmetry; the numbered half of the molecule indicates the asymmetric unit.



Figure 2. Voltammograms of ca. 0.5 mM quinone metal complexes 2b, 3a, and 4 as well as the corresponding organic quinones: q2b, q3, and q4. The currents have been divided by the concentrations of the compounds to normalize for slight variations in concentration. Dichloromethane with 0.10 M n-Bu₄NPF₆, glassy carbon working electrode, 0.10 V/s.



analogous to the separated species. The extent that the voltammograms differ from those of the separated species

reflects the electronic interaction between the component parts. Ligands that alter the redox chemistry of metal complexes are said to behave "noninnocently" and can have important consequences for the chemistry of such systems.^{20,31,38}

The voltammograms of the free quinones and the quinonecontaining metal complexes each show two reversible oneelectron processes with similar separations between the peaks. For the free quinones the first peak is reduction of the neutral quinone to the anion-radical semiquinone, and the second peak corresponds to reduction to the dianion. Similarly, the peaks of the quinone-containing metal complexes are assigned to reduction predominantly of the quinone moiety in the complex to the anion radical and dianion. The primary electrochemical effect of appending the quinone to the metal complex is a substantial positive shift of the potentials in the metal complexes, +0.402-0.468 V for E°_1 and +0.223-0.416 V for E°_2 (results summarized in Table 2). Thus the S₂Fe₂(CO)₆

Table 2. Standard Potentials of Quinone Metal Complexesin Comparison to the Corresponding Quinones

molecule	E°_{1}/V	E_{2}°/V	$\Delta E^{\circ}{}_{1}{}^{b}$ /V	$\Delta E^{\circ}{}_{2}{}^{b}/V$
q2b ^a	-1.028	-1.457		
$2b^a$	-0.626	-1.234	-0.402	-0.223
$q2c^{c}$	-1.041	-1.587		
$2c^{c}$	-0.552	-1.202	-0.489	-0.385
q2d ^c	-1.083	-1.640		
$2d^{c}$	-0.661	-1.315	-0.422	-0.325
$q2e^{c}$	-0.794	-1.469		
$2e^{c}$	-0.424	-1.240	-0.370	-0.224
$q3^a$	-1.174	-1.675		
3a ^a	-0.718	-1.293	-0.456	-0.382
$3b^c$	-1.082	-1.714	-0.092	0.039
$q4^a$	-1.207	-1.667		
4 ^{<i>a</i>}	-0.739	-1.251	-0.468	-0.416

^{*a*}Determined by simulations of cyclic voltammograms obtained in 0.10 M n-Bu₄NPF₆/CH₂Cl₂ with a 0.3 cm diameter glassy carbon working electrode. Potentials referred to the Fc⁺/Fc potential also determined in dichloromethane. The quinone-containing metal complexes were not stable in acetonitrile. Diffusion coefficients used in simulations are not reported, as there was uncertainty in the concentrations due to evaporation of solvent. ^{*b*}Potential of quinone minus potential of quinone metal complex. ^{*c*}Determined by averaging the potential of maximum current for the anodic and cathodic peaks.

portion acts as a very strong electron-withdrawing substituent on the quinone. This substituent effect indicates that the $S_2Fe_2(CO)_6$ "group" is roughly equivalent to three chlorine atoms, as judged by the observation that the potential for oneelectron reduction in acetonitrile of trichloro-1,4-benzoquinone is 0.43 V less negative than that of 1,4-benzoquinone itself.³⁹

The dianions produced by electrochemical reduction of **2b**, **3a**, and **4** render reduction localized primarily on the $S_2Fe_2(CO)_6$ portion of the molecule more difficult. For example, the overall two-electron reduction¹² potential for the benzenedithiolato complex **8** (Chart 4) is -1.47 V vs Fc⁺/ Fc (Fc = ferrocene) in dichloromethane (DCM), but as Figure 2 shows, further reduction of the quinonedithiolato metal complexes $2b^{2-}$, $3a^{2-}$, and 4^{2-} is not observed in the potential range of these scans to around -2 V.

Thus the quinone-containing complexes are easily reduced, even more so than the free quinones, with E°_{1} values falling in the range -0.424 to -0.739 V vs Fc⁺/Fc. The reduced complexes potentially could catalyze the reduction of protons

Chart 4. (μ -Benzenedithiolato)Fe₂(CO)₆



to form hydrogen through a series of electron transfers and protonations (perhaps coupled) at iron. However, we find that protonation of the reduced complexes is favored at the quinone moiety, probably at the stage of the anion radical depending on the strength of the acid. To illustrate this, Figure 3 shows



Figure 3. Voltammograms of 0.48 mM 3a with additions of 0, 1, and 5 mM acetic acid. Mercury-film working electrode. Other conditions are as in Figure 2

voltammograms of 0.49 mM 3a obtained with 0, 1, and 5 mM of added acetic acid ($pK_a = 22.4$ in acetonitrile).⁴⁰ With no acid, the voltammogram is the same as seen in Figure 2. Addition of 1 mM acid causes a small increase in the first reduction peak, and the second reduction peak is replaced by a much larger quasireversible reduction peak near -1.5 V. Scheme 3 illustrates an explanation for the increases in reduction current with the addition of acid. First, the addition of 1 mM acid is stoichiometrically sufficient to convert the quinone-ligand to its hydroquinone form, as shown in Scheme 3. Second, from our previous studies¹³ of the reduction of the related hydroquinone complexes, it is known that the hydroquinone complexes undergo a quasireversible two-electron reduction near -1.5 V. The reduction near -1.5 V in Figure 3 then includes the oneelectron reduction of the semiquinone complex and the twoelectron reduction of the hydroquinone complex. In the presence of 5 mM acid, the first reduction peak is still larger, as determined by the protonation equilibrium, the next reduction corresponding to the hydroquinone becomes higher and sharper, and a new peak appears near -1.9 V. This new catalytic peak corresponds to the reduction of acetic acid to dihydrogen and acetate as catalyzed by the in situ generated hydroquinone-containing complex, as previously reported.¹³ The catalytic peak is not present until the ratio of acetic acid

Scheme 3. Proposed Reduction Processes of the Methoxybenzoquinone Metal Complex 2b in the Presence of Acetic Acid^a



^aThe hydroquinone complex at bottom right undergoes reversible two-electron reduction at -1.315 V and catalyzes the reduction of protons from acetic acid to hydrogen at around -2 V, as shown in Scheme 1.¹³

concentration to that of the complex exceeds 2, for it is only then that there is excess acetic acid in the diffusion-kinetic layer. For ratios less than or equal to 2, the acetic acid is consumed to form the hydroquinone.⁴¹

When a stronger acid was used (benzoic acid; $pK_a = 20.4$), the same effects as those in Figure 3 were seen. Conversely, higher concentrations of the weaker acid (2-bromophenol; pK_a = 23.9) were required to see reduction to the hydroguinone. Quinone-containing catalysts 2b and 4 behaved in an analogous way when studied with acetic acid.

The reduction of the quinone moiety rather than H₂ production as pointed out above shows that protonation at oxygen of the reduced species occurs rather than at the 2Fe2S moiety. This could be due to the lack of electronic communication between moieties in the reduced species as reported before for a bma (bma = 2,3-bis(diphenylphosphino)maleic anhydride) complexed through a bridging apical S to a 2Fe2S moiety.^{18,42} To determine whether there is electronic communication between reduced semiquinone and 2Fe2S moieties, electron paramagnetic resonance (EPR) spectroscopic and computational studies of these species were undertaken.

EPR of the One-Electron-Reduced Complexes. The cyclic voltammograms indicate that the first two reductions of the quinone metal complexes are predominantly quinone in character, although shifted substantially less negative from the reduction potentials of the uncomplexed quinones. To probe the delocalization of charge and spin density to the 2Fe2S core in the reduced complexes, EPR spectroscopic experiments were performed on the electrochemically produced anion-radicals from 2b,c,d,e and 3a,3b (Figure 4) and compared with the spectra obtained from the parent organic semiquinones of q2b,c,d,e and q3 (the EPR spectra obtained for the organic semiquinone anion-radicals agree well with those reported in the literature).⁴³ The g_{av} values and hyperfine splitting constants were obtained for both the organic semiquinones



Figure 4. EPR Spectra for the semiquinone obtained on electrochemical reduction of 2b, 2c, 2d, 2e, 3a, and 3b.

Table 3. EPR Spectroscopic Parameters of Metal Complex Radical Anions (Parameters for Uncomplexed Organic Semiquinones in Parentheses)

semiquinone complex	$g_{ m av}$	$a_{\rm H}^{\ a}$ (MHz)
2b•-	2.0177 (2.009)	-1.1 (-2.5)
2c•-	2.017 (2.008)	-2.80 (-5.32)
2d•-	2.017 (2.008)	-3.1 (-5.5)
2e ^{•-}	2.016 (2.008)	-4.4 (-6.9)
naphthosemiquinone complex	g_{av}	$a_{\rm P}~({\rm MHz})$
3a•-	2.017 (2.008)	
3b*-	2.017 (2.008)	-4.1

 a All $a_{\rm H}$ values reported are for proton connected to the C6 position of the quinone.

and semiquinone metal complexes under the same conditions $(a_{\rm H} \text{ values are known to change with solvent})^{43-45}$ and are reported in Table 3.

Comparison of the parent organic semiquinone g values with those of the corresponding semiquinone metal complexes shows an increase in g_{av} values for the complexed semiquinone from 2.008 to 2.016-2.017. This suggests greater spin-orbit coupling, attributable to delocalization of the unpaired electron from the semiquinone moiety to the 2Fe2S moiety. In addition, the $a_{\rm H}$ values for the uncomplexed organic semiquinones are reduced to approximately half their values in the corresponding 2Fe2S complexed species. This provides further evidence for delocalization of the unpaired electron from the quinone to the 2Fe2S moiety. Comparison of the EPR spectra of the semiquinone obtained from 3a with that from 3b, in which there are now phosphine ligands coordinated to the metals, shows a dramatic difference. The former shows a broad singlet, but the latter a distinct triplet. The additional hyperfine is due to splitting by the two equivalent ³¹P nuclei of the Ph₃P ligands, demonstrating spin density on the P₂Fe₂S₂ moiety. The observed phosphorus hyperfine is 4.1 MHz.

Density functional theory (DFT) computations of the structures and hyperfine constants compare favorably with the experimental values. As observed experimentally, the ¹H hyperfine constants of the complexes are calculated to fall to about half the values of the uncomplexed organic semiquinones. Since the hydrogen atoms are situated on the node of the SOMO (singly occupied molecular orbital), the hyperfine splitting is proportional to the spin density on the carbon atom, which is calculated to fall to about half the value of the uncomplexed organic semiquinone as the spin density is delocalized to the metals in the complexes.

The hyperfine constant due to the phosphorus atoms in $3b^{\bullet-}$ is low in comparison to most other hydrogenase active site mimics with bound phosphine ligands.^{46–48} These previous cases differ from the present case in that the previous EPR studies are performed on the radical *cations* of the complexes in two instances and for the radical anion *protonated* at the metal–metal bond in the third instance, and the SOMOs of these species are calculated to be primarily on the iron atoms. In the radical anion of the present case of $3b^{\bullet-}$ the SOMO is primarily on the semiquinone portion of the molecule and delocalized to the iron atoms, so there is a smaller percentage of metal character. Examination of the SOMO of $3b^{\bullet-}$, shown in Figure 5, identifies an additional reason for the modest hyperfine



Figure 5. Calculated SOMO of 3b^{•-}.

splitting by ³¹P. That is, just as the protons are situated on the node of the semiquinone π orbital, the phosphines are situated on the node of the SOMO at the metal d orbitals. Furthermore, the metal orbital portion of the SOMO has δ symmetry with respect to the Fe–P bond, so there is no π back-bonding from this orbital to the phosphines. Thus the phosphine splitting in the EPR is solely due to spin polarization on the iron atoms and not due to spin delocalization onto the phosphorus atoms.

Nevertheless, delocalization of the unpaired electron from the quinone to the 2Fe2S moiety is established. Agreement of the calculated $a_{\rm H}$ values shown in Table 4 with the experimental

Table 4. Calculated EPR Spectroscopic Hyperfine Splittings and Spin Densities (Uncomplexed Organic Semiquinones in Parentheses)

		spin density (%)	
semiquinone complex	$a_{\rm H}~({\rm MHz})$	Fe ^a	C^b
2b•-	2.4 (5.0)	18.32	1.4 (4.7)
2c•-	3.3 (6.0)	18.8	2.8 (6.2)
2d•-	3.3 (6.3)	18.7	3.0 (6.3)
2e•-	4.3 (7.2)	15.6	4.3 (8.9)
		spin density (%)	
naphthosemiquinone complex	$a_{\rm P}~({\rm MHz})$	Fe ^a	C^b
3a•-		22.7	0.8 (2.0)
3b•-	-7.3	17.4	1.3 (2.0)

^{*a*}The sum of both iron centers. ^{*b*}Mulliken spin density for the carbon atom in the C6 position of the parent quinone and the corresponding carbon in the naphthoquinone analogues.

values shown in Table 3 supports the calculation of the spin density distribution. As shown in Table 4, the calculated spin density on the carbon α to the remaining proton in **2b**,c,d,e shows reduction of spin density in the metal-complexed semiquinones as compared to the uncomplexed organic semiquinones. This Fe spin density can be varied based on the functionalization of the quinone moiety, as shown in Table 4.

CONCLUSIONS

Oxidation of hydroquinones annulated to 2Fe2S moieties provided the corresponding quinone complexes in good yield. Communication between the quinone and 2Fe2S moieties was shown by the considerable positive shift in the reduction potentials. The quinones were demonstrated to electronically communicate with the 2Fe2S moieties through cyclic voltammetry, EPR spectroscopy, and DFT computations. This interaction in the semiquinones could be tuned by changing functionalization of the quinone moiety. Thus the spin density on the metal centers changes from 16% to 23% by changing from chloroquinone to naphthoquinone, with intermediate values for methyl, methoxy, and tert-butyl-1,4benzoquinone. Despite this electronic communication, initial 2e⁻ reduction in the presence of acid gave the corresponding hydroquinone product, and further reduction was required for the production of molecular hydrogen.¹³ These systems demonstrate that quinone π -systems linked in this way with the sulfur atoms of the 2Fe2S core behave noninnocently in their electronic interactions, reduce the reduction potentials of the complexes, but protonate on oxygen rather than at the 2Fe2S, resulting in initial ligand not proton reduction.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an atmosphere of prepurified nitrogen by using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (THF) and hexane were purified by distillation under nitrogen from sodium/benzophenone ketyl. Dichloromethane was distilled from calcium hydride under nitrogen. Acetonitrile was distilled once from P_2O_5 and then freshly distilled from CaH₂ under N₂ before use. Ethanol was distilled from magnesium under nitrogen. LiBEt₃H (1 M in THF), trifluoroacetic acid, 1,4-anthraquinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, sodium cyanoborohydride, Me₃NO·2H₂O, PPh₃, and PMe₃ (1.0 M in THF) were purchased from Aldrich Chemical Co. and used as received. Hydroquinones of type 7 were synthesized as previously reported.¹³

¹H and ¹³C NMR spectra were obtained with a Bruker DRX-500 spectrometer (chemical shifts refer to TMS). IR spectra were obtained on a Nicolet Impact 410 spectrometer. UV–vis data were collected on an Agilent 8453. All photochemical reactions were carried out utilizing a Rayonet Srinivasan-Griffith apparatus.

Single-crystal X-ray intensity data for **3b** were obtained using an Agilent Technologies XCalibur diffractometer using graphite-monochromated Mo K α radiation and a crystal temperature of 150 K. The structure of **3b** was solved by direct methods with SIR-2004 and refined by full-matrix least-squares on F^2 using SHELXTL.^{49–51}

Oxidation of 12 to $Fe_2(CO)_6(\mu-S_2C_{10}H_4O_2)$, **3a**. To a solution of 12 (100 mg, 0.20 mmol) in CH₂Cl₂ (40 mL) was added 2,3-dichloro-5,6dicyano-1,4-benzoquinone (55 mg, 0.22 mmol). The solution was then stirred at room temperature for 2 h. The solvent was removed under vacuum, and the residue was separated by flash silica gel column chromatography by using a hexanes/CH₂Cl₂ (2:1, v/v) solvent mixture as eluant to give **3a** (83 mg, 83%): dark crystals, which were recrystallized from dichloromethane and hexane; ¹H NMR (CDCl₃, 23 °C, 500 MHz) δ 8.00 (s, 1H), 7.72 (s, 1H); ¹³C NMR (CDCl₃, 23 °C, 125 MHz) δ 206.2 (s, Cq, Fe(CO)₃), 177.6 (C=O), 167.1 (s, Cq, C–SFe), 134.3 and 127.1 (s, CH), 131.5 (s, Cq); IR (KBr) cm⁻¹ 2086 (100), 2039 (100), 2023 (100), 1980 (100) [ν (C \equiv O)], 1663 (90) [ν (C \equiv O)]; MS (EI) m/z (relative intensity) 500 (M⁺, 1), 472 (M⁺ – CO, 14), 444 (M⁺ – 2 CO, 20), 416 (M⁺ – 3 CO, 2), 388 (M⁺ – 4 CO, 12), 360 (M⁺ – 5 CO, 22), 332 (M⁺ – 6 CO, 36), 288 (3), 276 (18), 244 (5), 232 (7), 176 (Fe₂S₂⁺, 24), 166 (7), 56 (Fe⁺, 1). Anal. Calcd for C₁₆H₄Fe₂O₈S₂: C, 38.43; H, 0.81. Found: C, 38.37; H, 0.99.

Syntheses of 2b-e follow an analogous method to that for 3a, and experimental details can be found in the Supporting Information.

Reduction of **3a** to the Corresponding Hydroquinone. To a solution of **3a** (100 mg, 0.20 mmol) in EtOH (40 mL) was added sodium cyanoborohydride (14 mg 0.22 mmol). The solution was then stirred at room temperature for 6 h. The solvent was removed under vacuum, and the residue was separated by flash silica gel column chromatography by using CH_2Cl_2 as eluent to give the corresponding hydroquinone (83 mg, 83% yield): dark crystals, which were recrystallized from dichloromethane and hexane.

Synthesis of $Fe_2(CO)_4(PPh_3)_2(\mu-S_2C_{10}H_4O_2)$, **3b**. Me₃NO·2H₂O (133 mg, 1.20 mmol) was added to a solution of **3a** (100 mg, 0.20 mmol) and PPh₃ (315 mg, 1.20 mmol) in CH₃CN solvent (40 mL). The solution was stirred at room temperature for 12 h. The solvent was then removed under vacuum, and the residue was separated by flash silica gel column chromatography (hexanes/CH₂Cl₂, v/v = 2:3) to afford complex **3b** as dark red crystals (37 mg, 19%), which were recrystallized dichloromethane and hexane: ¹H NMR (CDCl₃, 23 °C, 500 MHz) δ 7.49 and 7.18 (s each, 1:1 H); ¹³C NMR (CDCl₃, 23 °C, 125 MHz) δ 214.7 (t, Cq, Fe(CO)₂), 177.0 (C=O), 165.4 (s, Cq, C-SFe), 135.6 and 135.3 (d, CP of PPh₃), 133.3 and 128.5 (t each, CH of PPh₃), 132.5 and 125.6 (s, CH), 131.8 (s, Cq), 129.7 (s, CH of PPh₃); IR (KBr) cm⁻¹ 2004 (100), 1960 (80), 1940 (90) [ν (C=O)], 1662 (10) [ν (C=O)]. Anal. Calcd for C₅₀H₃₄Fe₂O₆P₂S₂: C, 62.00; H, 3.54. Found: C, 61.65; H, 3.76.

*Fe*₂(*CO*)₆(μ -S₂C₁₄*H*₆O₂), **4**. Dark crystals. Single crystals were obtained by recrystallization from dichloromethane and hexane: ¹H NMR (CDCl₃, 23 °C, 500 MHz) δ 8.50, 8.02, and 7.70 (s each, 1:1:1 H); ¹³C NMR (CDCl₃, 23 °C, 125 MHz) δ 206.3 (s Cq, Fe(CO)3, 177.3 (C=O), 168.6 (s, Cq, C–SFe), 134.7 and 127.8 (s, Cq), 130.3, 130.2, and 130.0 (s each, CH); IR (KBr) cm⁻¹ 2085 (100), 2044 (100), 2015 (100), 2002 (100), 1990 (100) [ν (C=O)], 1664 (70) [ν (C=O)]. Anal. Calcd for C₂₀H₆Fe₂O₈S₂: C, 43.67; H, 1.10. Found: C, 43.52; H, 1.35.

Electrochemistry. For electrochemical experiments, the source and treatment of the solvent and supporting electrolyte have been described earlier.⁵² Experiments were conducted in acetonitrile or dichloromethane with 0.10 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as supporting electrolyte. Electrodes, cells, instrumentation, and electrochemical procedures have been described.⁵² In the present study the potentiostat was an EG&G PAR model 2273. The working electrode was a glassy carbon electrode (0.071 cm^2) or a mercury-film on a gold-disk electrode (0.080 cm^2) prepared as described earlier).¹⁰ Its area was ascertained by studies of the oxidation of ferrocene, whose diffusion coefficient is known. Evaluation of solution resistance was carried out as described earlier,⁵² and the resistance was partially compensated by electronic resistance compensation with the remainder of the resistance applied when simulating the data. The laboratory reference electrode was a silver wire in contact with 0.010 M AgNO₃, 0.10 M NBu₄PF₆, and acetonitrile (AgRE). Its potential was frequently determined with respect to the reversible ferrocenium/ferrocene couple, in dichloromethane, and all potentials are referred to ferrocene. Voltammetric experiments were carried out at room temperature except for those in dichloromethane with added acid, for which the temperature was 298 K.

Digital simulations were conducted with DigiElch, version 3.0, a software package for the digital simulation of common electrochemical experiments (http://www.digielch.de).⁵³ The fitting routine in that program was used to establish the final best-fit parameter values for many of the variables.

EPR Spectroscopy. All EPR spectra were collected on species that were generated electrochemically *in situ* via bulk electrolysis in DCM with 0.5 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. The spectroelectrochemical cell was made of quartz with a platinum counter and working electrode and a Ag/AgNO₃ reference electrode. An X-band Bruker Elexsys E500 spectrometer was used for all spectra. Spectra were modeled with EasySpin software to extract hyperfine constants and g values.⁵⁴

COMPUTATIONAL METHODS

All computations were performed with ADF2009.01.55,56 Geometry optimizations and frequency calculations were carried out using the VWN functional with the Stoll correction implemented.57 All hyperfines reported were calculated using the OPBE density functional.⁵⁸ Recent comparisons of OPBE to other common functionals found it to be preferred for the prediction of nuclear magnetic constants⁵⁹ and the only functional to correctly predict the spin states of seven different iron complexes.⁵⁸ Our comparisons with other common functionals in the ADF package have also shown it to be among the best at predicting the oxidation and reduction potentials of several iron complexes and the pK_a values of the acids. A triple- ζ STO basis set with one polarization function (TZP), available in the ADF package, was used in all calculations. Relativistic effects were taken into account by using the scalar ZORA formalism for geometry optimizations and spin populations and the spin-orbit ZORÁ formalism for all hyperfine values,⁶⁰ implemented as part of the ADF2009.01 program. All electronic structures with unpaired spin were calculated using an unrestricted framework. Only low-spin complexes have been analyzed. Figure 5 was created with the program Visual Molecular Dynamics 1.9.61

ASSOCIATED CONTENT

Supporting Information

Characterization details of 2b-e, cyclic voltammograms of 2c,d,e and 3b, simulations of EPR spectra of metal-quinone anions, plot of catalytic current vs [HA] for 3a, tables of crystallographic information for 3b, optimized geometries of radical anions in a separate text file, instructions for viewing geometries, and example ADF input file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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