Electronic Supplementary Material (ESI) for Dalton Transactions.

Mononuclear Iron Carbonyl Complex [Fe(μ-bdt)$(CO)_2(PTA)_2$] with bulky phosphine ligand: A model for the [FeFe] hydrogenase enzyme active site with an inverted redox potential

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Supporting Information

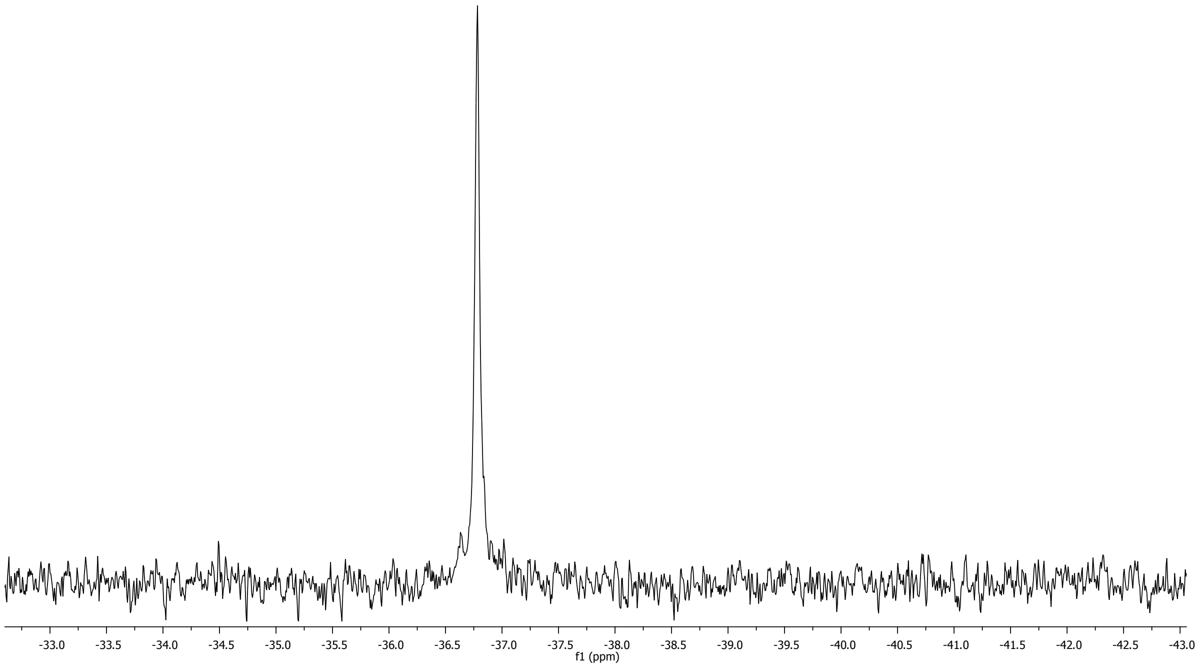

Figure S1. ^{31}P NMR of Complex **1** in $CDCl_3$.

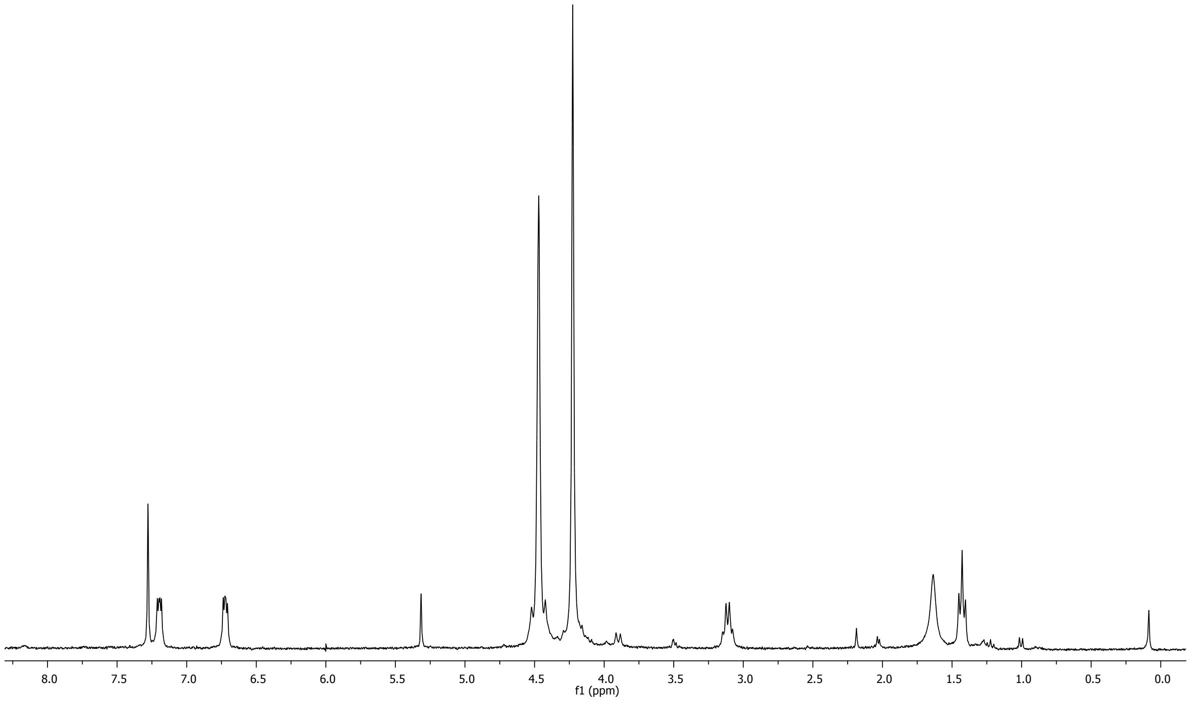

Figure S2. ^{1}H NMR of Complex **1** in $CDCl_3$.

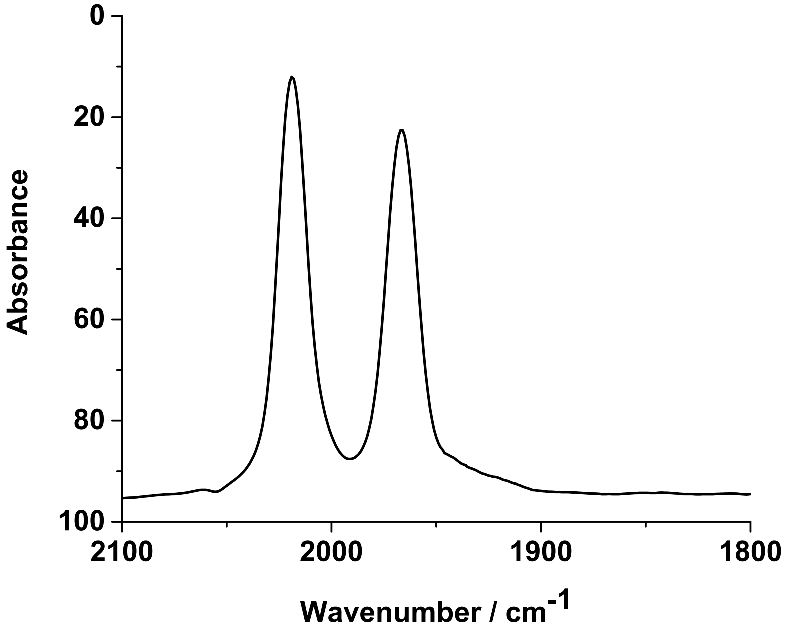

Figure S3. FTIR spectrum for complex **1** in dichloromethane.

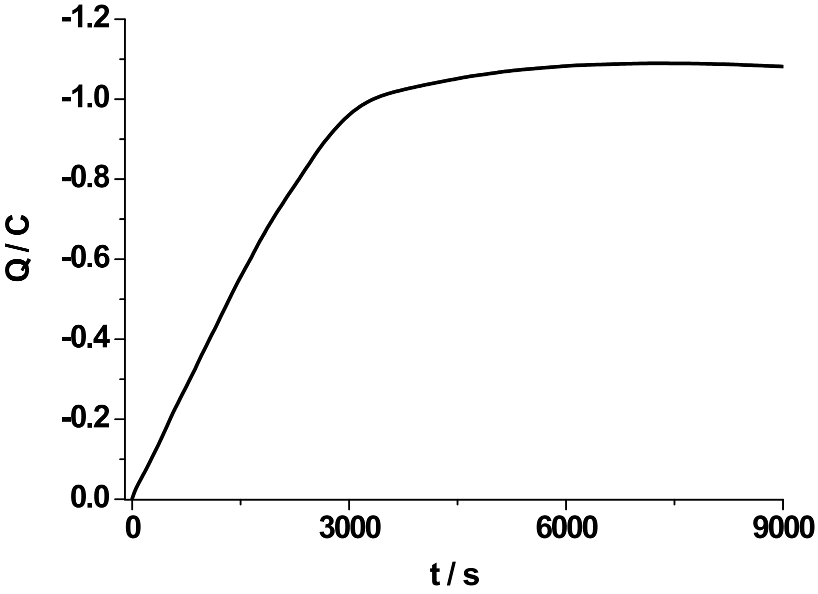

Figure S4. Controlled potential coulometry for complex **1** (0.47 mM) at -2.05 V in CH_3CN.

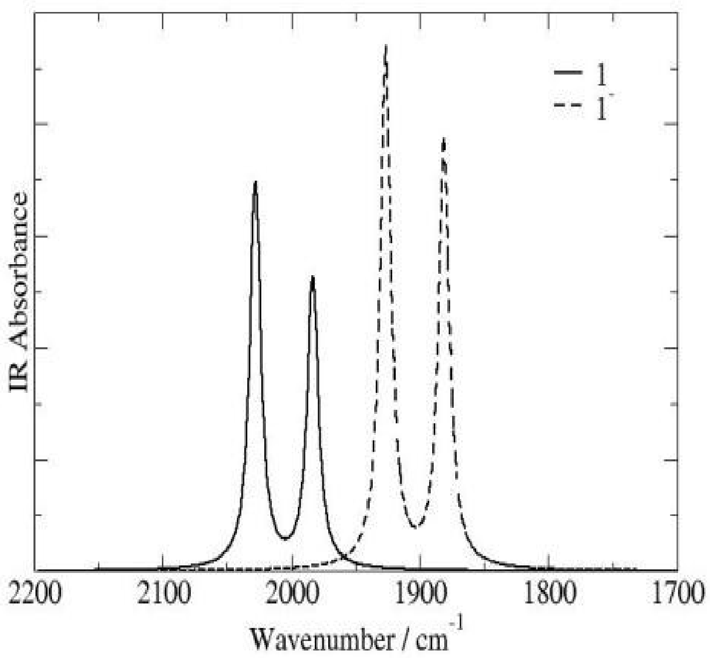

Figure S5. Calculated FTIR spectra of complex **1** (Fe(II)) and 1^{-} (Fe(I)).

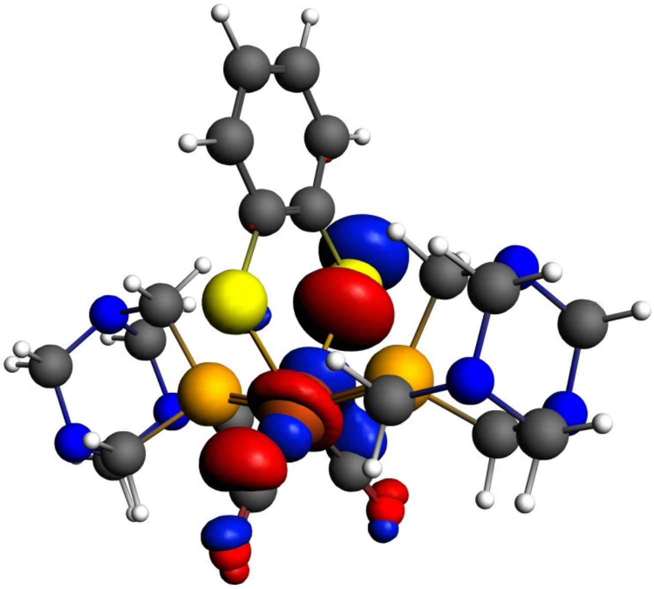

Figure S6. Orbital isocontour plot at 0.05 e$^-$/Å^3 of the HOMO of complex **1$^-$**.

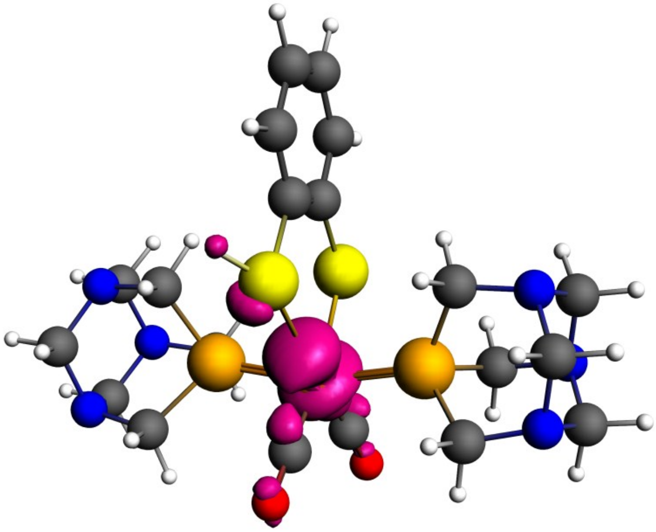

Figure S7. Isocontour plot at 0.005 e$^-$/Å^3 of the unpaired spin density of complex **1SH**.

Table S1. Crystallographic parameters and refinement details for complex **1**.

	1
Formula	$C_{20}H_{28}FeN_6O_2P_2S_2$
M_r	566.39
crystal system	Monoclinic
space group	$P\ 2_1/c$
a (Å)	6.7520(2)
b (Å)	20.5370(5)
c (Å)	17.4119(5)
α (deg)	90.00
β (deg)	100.934(2)
γ (deg)	90.00
V (Å^3)	2370.60(11)
Z	4
T (K)	150(2)
λ (Å)	0.71073
D_{calc} (g cm^{-3})	1.587
μ (mm^{-1})	0.979
F(000)	1176
goodness-of-fit	1.036
R1^a/wR2^b [$I > 2\sigma(I)$]	0.0603/0.1500
R1^a/wR2^b (all data)	0.0812/0.1628

Table S2. Proton affinities of complex **1** in kcal/mol.

PA of **1**/protonation site	**1SH**$^+$	**1NH1**$^+$	**1NH2**$^+$
BP86-D3/TZP	-73.7	-62.7	-63.8
BP86-D3, COSMO/TZP	-21.59	-6.4	-6.3

Calculation of redox potentials

The calculation of redox potentials in aqueous and organic solvents has recently gained attention. The use of an aqueous value of the standard hydrogen electrode (SHE) as a reference electrode for the redox potential of the Fc/Fc$^+$ couple in an non-aqueous solution is problematic. The absolute potential for the Fc/Fc$^+$ couple in most non-aqueous solvents is not easily available.

The structures of Fc and Fc$^+$ were optimized at the BP86-D3/def2-TZVP and B3LYP-D3/def2-TZVP levels, respectively. Solvation energies of the couple were studied using a COSMO solvation model for acetonitrile.

The reduction of the ferricenium radical cation by one electron converts it into the reduced, neutral form, ferrocene.

$$\mathrm{Fe(C_2H_5)_2^+(acetonitrile) + e^- \ (gas)} \longrightarrow \mathrm{Fe(C_2H_5)_2(acetonitrile)} \qquad \textbf{(1)}$$

$$\begin{tikzcd}
\mathrm{Fc^+(gas) + e^-(gas)} \arrow[r, "\Delta G(\mathrm{gas})"] \arrow[d, "\Delta G(\mathrm{solv.,\ Fc^+})"'] & \mathrm{Fc(gas)} \arrow[d, "\Delta G(\mathrm{solv.,\ Fc})"] \\
\mathrm{Fc^+(acn) + e^-(gas)} \arrow[r, "\Delta G(\mathrm{soln})"] & \mathrm{Fc(acn)}
\end{tikzcd}$$

The standard potential is related to the Gibbs free energy of reaction (1) in solution

$$E^0 = -\Delta G^0\,(soln)/nF$$

Where n is the number of electrons transferred (n = 1 in this case) and F is the Faraday constant (23.061 kcal mol^{-1} V^{-1}).

To calculate ΔG^0(soln), we use the thermodynamic cycle above which then gives

$$\Delta G^0(soln) = \Delta G^0\,(gas) + \Delta G^0\,(solv., Fc) - \Delta G^0(solv., Fc^+)$$

Table S3. Calculated absolute redox potential of the Fc^+/Fc reference electrode in acetonitrile.

Energies in kcal/mol	ΔG^0(gas)	ΔG^0(solv, Fc)	ΔG^0(solv, Fc^+)	ΔG^0(soln.)
BP86-D3/TZP	-158.43	-2.41	-8.06	-152.78
B3LYP-D3/TZP	-145.32	-2.58	-48.85	-99.05
Fc^+/Fc E^0 in V				
BP86-D3/TZP				-6.62
B3LYP-D3/TZP				-4.30

The IUPAC Commission on Electrochemistry has proposed that the ferricenium/ferrocene (Fc+/Fc) couple is to be used an internal reference for reporting electrode potentials in nonaqueous solutions.

The absolute redox potential of the Fc^+/Fc reference electrode in acetonitrile was calculated using B3LYP-D3. The use of the B3LYP functional with an implicit solvation model was shown to afford relative redox potentials with accuracy to those from cyclic voltammetry.[1]

The relative redox potentials of all catalyst complexes such as **1/1**$^-$ and **1/1**$^{2-}$ can thus be calculated in a similar way using the thermodynamic cycle above.

1. S. J. Konezny, M. D. Doherty, O. R. Luca, R. H. Crabtree, G. L. Soloveichik and V. S. Batista, *J. Phys. Chem*. C, 2012, **116**, 6349-6356.

Table S4. Calculated absolute and relative redox potentials of **1** / **1**$^{-}$.

Energies in kcal/mol	ΔG^0(gas)	ΔG^0(solv, **1**$^{-}$)	ΔG^0(solv, **1**)	ΔG^0(soln.)
BP86-D3/TZP	-33.05	-30.70	-15.51	-48.24
B3LYP-D3/TZP	-30.59	-35.01	-16.9	-51.70
Redox potential **1/1**$^{-}$ in V				
Absolute				
BP86-D3/TZP				-2.09
B3LYP-D3/TZP				-2.24
Relative to Fc$^+$/Fc				
BP86-D3/TZP				-4.53
B3LYP-D3/TZP				-2.06

Table S5. Calculated absolute and relative redox potentials of **1**$^{-}$**/1**$^{2-}$.

Energies in kcal/mol	ΔG^0(gas)	ΔG^0(solv, **1**$^{2-}$)	ΔG^0(solv, **1**)	ΔG^0(soln.)
BP86-D3/TZP	+2.37	–153.87	–15.51	–136.00
B3LYP-D3/TZP	+5.9	–155.05	–16.9	–132.25
Redox potentials (**1/1**$^{2-}$) in V				
Absolute				
BP86-D3/TZP				–2.95
B3LYP-D3/TZP				–2.87
Relative to Fc$^+$/Fc				
BP86-D3/TZP				–3.67
B3LYP-D3/TZP				–1.43

Analysis of the HOMO of complex **1**$^{-}$ shows that it is a linear combination of Fe orbitals (22% d_{xy}, 7 % $3d_{z2}$, 6% $3d_{x2\text{-}y2}$) and the elongated Fe-S bond (S 16% 3py).
The second one-electron reduction is thus also metal-based to yield a formal (Fe(0) species.

Table S6. Calculated absolute and relative redox potentials of **1**$^{-}$/**1**$^{2-}$.

Energies in kcal/mol	ΔG^0(gas)	ΔG^0(solv, **1**$^{2-}$)	ΔG^0(solv, **1**$^{-}$)	ΔG^0(soln.)
BP86-D3/TZP	+35.42	–153.87	–30.70	–87.75
B3LYP-D3/TZP	+36.69	–155.05	–35.01	–83.35
Redox potential **1**$^{-}$**/1**$^{2-}$ in V				
Absolute				
BP86-D3/TZP				–3.81
B3LYP-D3/TZP				–3.61
Relative to Fc^{+}/Fc				
BP86-D3/TZP				–2.81
B3LYP-D3/TZP				–0.69

Table S7. Calculated absolute and relative redox potentials of **1**SH **->** **1**SH-.

Energies in kcal/mol	ΔG^0(gas)	ΔG^0(solv, **1SH**$^{-}$)	ΔG^0(solv, **1SH**)	ΔG^0(soln.)
BP86-D3/TZP	–47.13	–51.03	–15.48	–82.68
B3LYP-D3/TZP	–30.62	–52.82	–17.61	–65.83
Redox potential **1SH/1SH**$^{-}$ in V				
Absolute				
BP86-D3/TZP				–3.59
B3LYP-D3/TZP				–2.85
Relative to Fc^{+}/Fc				
BP86-D3/TZP				–3.03
B3LYP-D3/TZP				–1.45

Computational Details

Structural optimizations were performed *in vacuo* and in solution with a COSMO implicit solvation model [A. Klamt and G. Schüürmann, COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient, Journal of the Chemical Society: Perkin Transactions 2, 799 (1993); C.C. Pye and T. Ziegler, An implementation of the conductor-like screening model of solvation within the Amsterdam density functional package, Theoretical Chemistry Accounts 101, 396 (1999)] with ADF2014 [ADF2016, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.; Chemistry with ADF, Journal of Computational Chemistry 22, 931 (2001)] using the BP86 functional and B3LYP hybrid exchange-correlation functional with the D3 dispersion correction from Grimme and Becke-Johnson damping.

Analytical frequencies were computed for the *in vacuo* for BP86 structures and those thermochemical corrections and ZPE were used for all subsequent calculations.

Solvation was considered with a COSMO in acetonitrile (eps=37.5), using the solvent-excluding-surface (SES) to set up the cavity and adjusted Allinger atomic radii [N.L. Allinger, X. Zhou, J. Bergsma, Molecular mechanics parameters, Journal of Molecular Structure: THEOCHEM 312, 69 (1994)].