nature chemistry

SUPPLEMENTARY INFORMATION

DOI: 10.1038/NCHEM.1180

Combining Acid–Base, Redox and Substrate Binding Functionalities to Give a Complete Model for the [FeFe]-Hydrogenase

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Supplementary Figure 7: Plot of $1/\chi_M$ vs temperature for $[\mathbf{1}]^{2+}$.

Supplementary Figure 8: NMR stack plot of reaction of $[\mathbf{1}]^{2+}$ and P(*o*-tol)$_3$ with H_2 and D_2.

Supplementary Figure 9:Kinetic plot for the reaction of $[\mathbf{1}]^{2+}$ with H_2 in the presence of P(*o*-tol)$_3$ fit to a first order exponential. *Inset:* Linearized kinetic plot illustrating first-order kinetics.

Supplementary Figure 10: ^{31}P NMR stack plot showing catalytic oxidation of H_2 by $[\mathbf{1}]^{2+}$ in the presence of excess $FcBAr^F{}_4$ and excess base.

I. Supplementary Methods

All procedures were carried out using standard Schlenk Techniques. All solvents were dried and degassed using by passage through activated alumina and sparging with argon respectively. IR spectra were recorded on a Perkin Elmer Spectrum 100. NMR spectra were recorded on a Varian Unity 500Mhz NMR Spectrometer. X-band EPR spectra were collected on a Varian E-122 spectrometer equipped with an E-257 variable-temperature accessory. Magnetic fields were calibrated using a Varian NMR Gauss meter. The microwave frequency was measured with an EIP frequency meter. EPR simulations were carried out using the program SIMPOW6.

Generation of $[Fe_2(adt^{Bn})(CO)_3(dppv)(Me_9FcCH_2PEt_2)][BAr^F{}_4]_2$, ($[1]^{2+}$). *Via titration of $FcBAr^F{}_4$ into **1**.* A solution of **1** (15 mg, 12.5 μmol, in 5 mL dichloromethane) was titrated with a solution of $FcBAr^F{}_4$ (26.15 mg, 25 μmol, in 2 mL dichloromethane) in 0.5 mL aliquots. Upon addition of the oxidant, the solution turned from brown-orange to purple. The reaction was monitored by IR after each 0.5 mL addition of oxidant. After 1.0 equiv of oxidant was added, all starting material was consumed and the IR spectrum (ν_{CO} = 2012 (s), 1961 (s), 1859 (w) cm^{-1}) was assigned to $[\mathbf{1}]^+$. After addition of 2.0 equiv of oxidant, the IR spectrum changed (ν_{CO} = 2015 (s), 1965 (s), 1849 (w) cm^{-1}) and the resulting species was assigned to **$[1]^{2+}$.** An isosbestic point at 1969 cm^{-1} upon conversion of $[1]^+$ to $[1]^{2+}$ was observed (Figure 4).

EPR measurements of $[1]^+$ and $[1]^{2+}$: *$[1]^+$*.A solution of **1** (5 mg, 4.1 μmol) in 2 mL toluene and a solution of $FcBAr^F{}_4$ (4.4 mg, 4.1 μmol) in 2 mL of CH_2Cl_2 were mixed under inert atmosphere. 300 μL of the resulting purple solution was transferred to an EPR tube with J. Young valve. The solution was frozen in liquid nitrogen to form a glass. X-band EPR was collected at 110 K and is shown in Supplementary Figure 3. Simulation shows predominantly rhombic (xy) splitting and an additional small (5 to 20 MHz) third ^{31}P splitting from *Fc*P*.

$[1]^{2+}$. A solution of **1** (5 mg, 4.1 μmol) in 2 mL toluene and a solution of $FcBAr^F{}_4$ (8.8 mg, 8.2 μmol) in 2 mL of CH_2Cl_2 were mixed under inert atmosphere. 300 μL of the resulting purple solution was transferred to an EPR tube with J. Young valve. The solution was frozen in liquid nitrogen to form a glass. X-band EPR was collected at 110 K and showed a small amount of $[\mathbf{1}]^+$ and no signal for $[\mathbf{1}]^+$. Upon cooling to 4.5 K an additional broad signal appears at g ≈1.66 (Supplementary Figure 4). Upon increasing the power from 10 dB to 30dB, the residual signal for $[\mathbf{1}]^+$ saturates, but the signal for $[\mathbf{1}]^{2+}$ does not (Supplementary Figure 5).

Magnetic Succeptibility of $[1]^+$: Magnetic susceptibility measurements were carried out using Evans' Method.[1-3] A melting point capillary was sealed with pure CD_2Cl_2. A J. Young tube was charged with a solution of **1** (7 mg, 5.8 μmol) and $FcBAr^F{}_4$ (6.1mg, 5.8 μmol) in 0.7 mL CD_2Cl_2. The capillary was inserted into the tube, and the solution analyzed by ^1H NMR at various temperatures. The temperature of the NMR probe was calibrated using a 100% methanol standard. The difference in the chemical shift of the residual solvent resonance in the capillary and the residual solvent resonance in the solution was measured from the center of the corresponding 1:1:1 triplets. The following formula yields the magnetic susceptibility where Δν

is the peak separation in Hz, ν_I is the spectrometer frequency in Hz, and *c* is the solute concentration in mol/L:

$$\chi_M = (477)\frac{\Delta\nu}{2\nu_I c}$$

The data are in Table 1. The slope of a plot of $1/\chi_m$ vs temperature (Supplementary Figure 6) yields the Curie constant, C, from which the number of unpaired electrons (*n*) may be calculated using the following formula:

$$C = \frac{1}{8}n(n+2)$$

The magnetic moment may also be calculated from the following:

$$\mu_{eff} = \sqrt{8\chi_M T}$$

The magnetic moments calculated for $[1]^+$ and $[1]^{2+}$ match those expected for species with 1 and 2 unpaired electrons (1.73 BM and 2.83 BM respectively).

Magnetic Susceptibility of $[2]^+$: Magnetic susceptibility measurements were carried out as above using a solution of **1** (7 mg, 5.8 μmol) and $FcBAr^F_4$ (12.2 mg, 11.6 μmol) in 0.7 mL CD_2Cl_2. A plot of $1/\chi_m$ vs temperature is in Supplementary Figure 7.

Reaction of $[1]^{2+}$ with D_2: A J. Young tube was charged with a solution of **1** (4.2mg, 3.5 μmol), P(*o*-tol)$_3$ (1 mg, 3.5 μmol), and $FcBAr^F_4$ (7.3 mg, 7.0 μmol) in 0.7 mL CH_2Cl_2. The tube was then evacuated, pressurized with 14.5 psig D_2, shaken, and allowed to react at 0 °C overnight. ^{2}H NMR (97 MHz, CD_2Cl_2) δ = 8.4 ppm (d, $J_{P\text{-}D}$ = 74 Hz, 1D), -15.4 (bs, 1D). The spectrum is in Supplementary Figure 8.

Rate of H_2 oxidation by $[1]^{2+}$: A J. Young tube was charged with a solution of **1** (4.2mg, 3.5 μmol), P(o-tol)$_3$ (1 mg, 3.5 μmol), $FcBAr^F_4$ (7.3 mg, 7.0 μmol) and $HFe_2(adt^{Bn})(PMe_3)_2(CO)_4][PF_6]$ (2.1 mg, 4.0 μmol) as internal standard in 0.7 mL CD_2Cl_2. The tube was then evacuated, pressurized with 14.5 psig H_2, shaken, and cooled to 0 °C. The reaction was monitored by appearance of the product hydride peak at -15.33 ppm in the ^{1}H NMR. Under the reaction conditions, H_2 dissolved more quickly than it was consumed, and was present in large excess. The appearance of product hydride $[\mathbf{1}H]^+$ was strictly first order with observed pseudo-first order rate constant $k_{obs} = 8.3(4)\times10^{-5}$ s^{-1} (Supplementary Figure 9).

Catalytic oxidation of H_2 using $[1]^{2+}$: A J. Young tube was charged with a solution of **1** (4.2 mg, 3.5 μmol), P(o-tol)$_3$ (6.4 mg, 21 μmol), $FcBAr^F_4$ (22 mg, 21 μmol) and $HFe_2(adt^{Bn})(PMe_3)_2(CO)_4][PF_6]$ (2.1 mg, 4.0 μmol) as internal standard in 0.7 mL CD_2Cl_2. The tube was then evacuated, and pressurized with 14.5 psig H_2. The reaction was monitored by observing the disappearance of P(o-tol)$_3$ and appearance of $[HP(o\text{-}tol)_3][BAr^F_4]$ in the ^{31}P NMR spectrum (δ = -12.3(s) and -28.9(s) respectively). During the course of the reaction the solution changed from purple to orange. After 5h, complete conversion of P(o-tol)$_3$ to $[HP(o\text{-}tol)_3][BAr^F_4]$ was observed (Supplementary Figure 10).

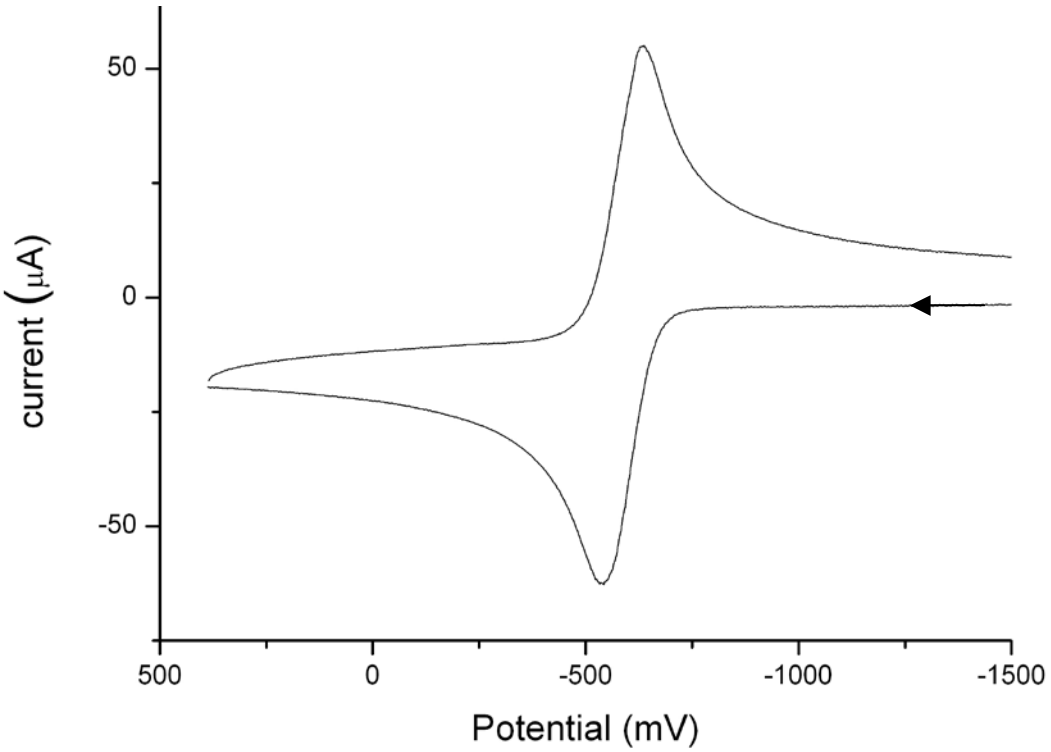
II. Tables

Table 1: Magnetic Susceptibility Data

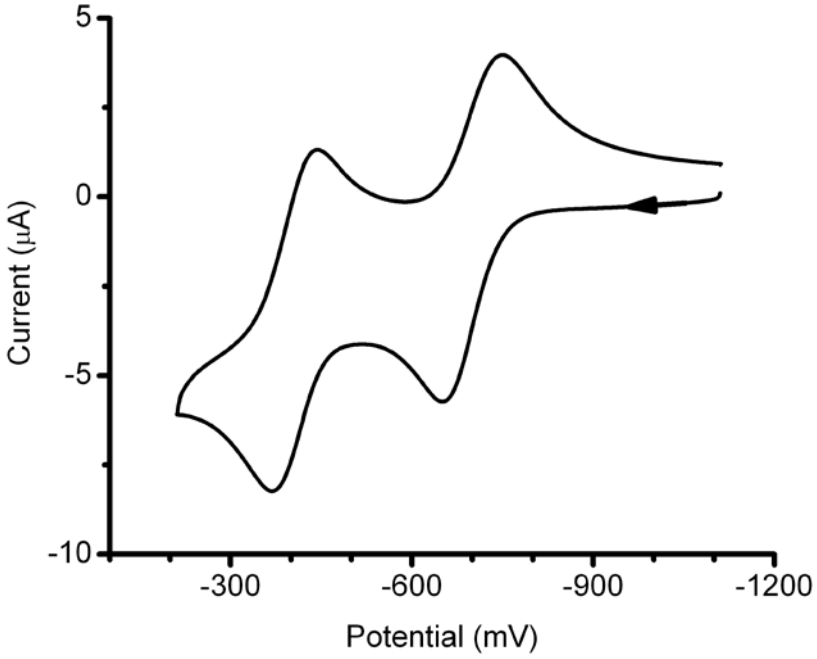
	$[\mathbf{1}]^+$				$[\mathbf{2}]^+$			
Temp	Δδ (Hz)	χ_m	# electrons	μ_{eff}	Δδ (Hz)	χ_m	# electrons	μ_{eff} (BM)
298.5	21.86	.00126	0.9(2)	1.8(1)	60.61	.00348	1.8(2)	2.9(1)
272.1	25.40	.00146			69.57	.00400		
255.0	26.60	.00153			74.07	.00423		

III. Supplementary Figures

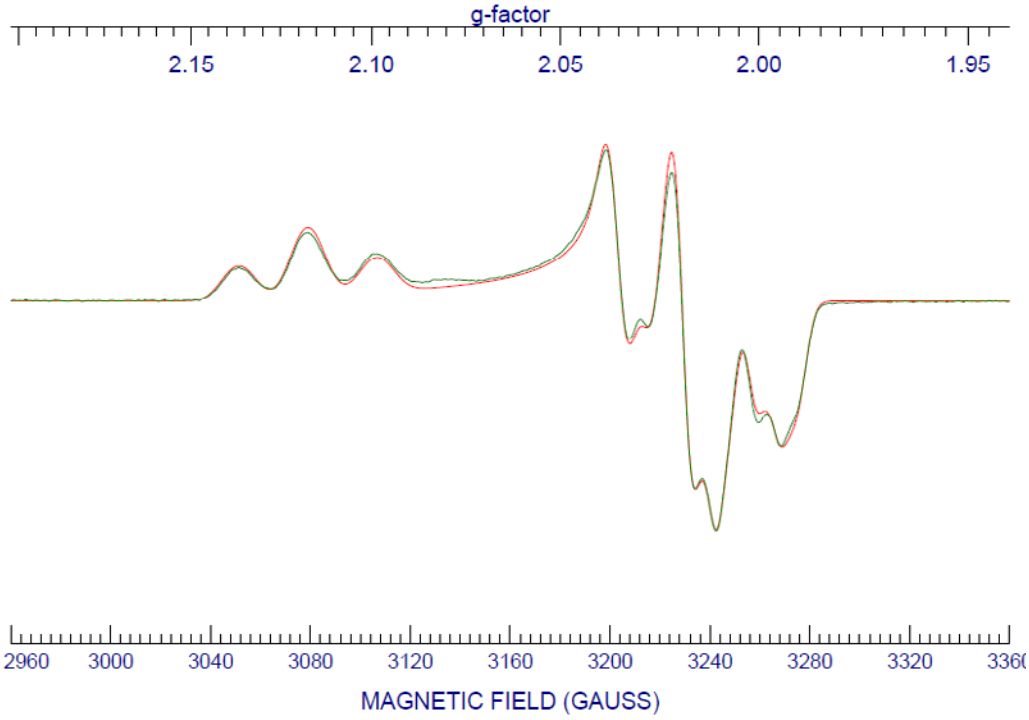
Supplementary Figure 1. Cyclic voltammogram of (Diethylphosphinomethyl)nonamethylferrocene (*Fc*P*) in CH_2Cl_2 referenced to Fc/Fc^+. [*Fc*P*] = 1 mM, [TBA][BAr^F_4] = 100 mM, scan rate = 300 mV/s, IR compensation at -950 mv, $E_{1/2}$ = -591 mV (I_{pa}/I_{pc} = 0.95)



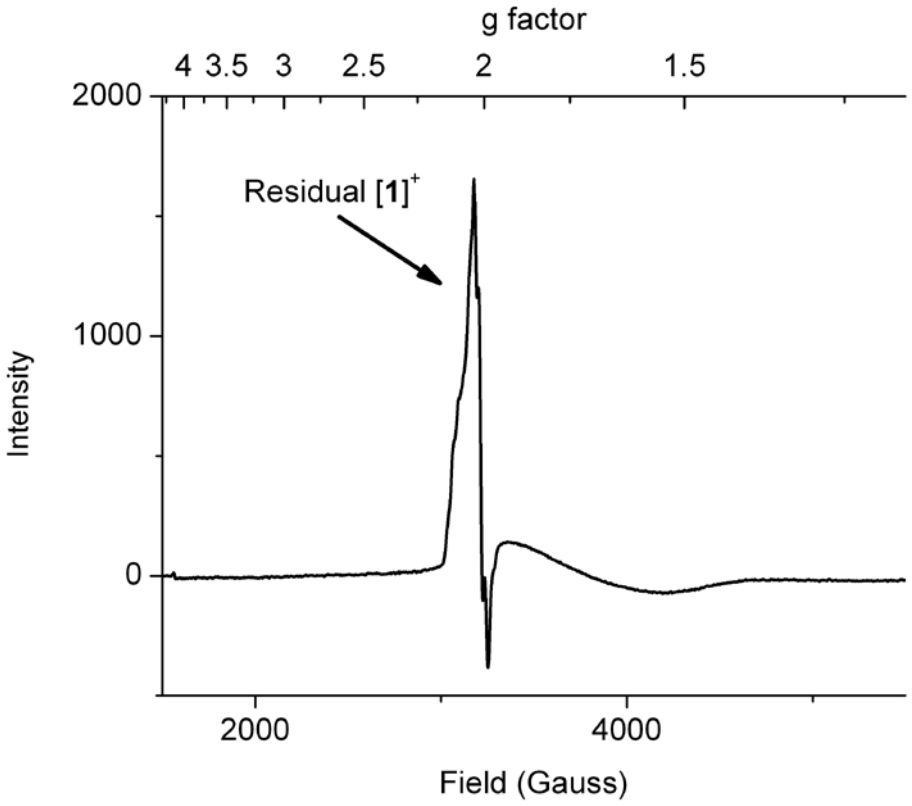
Supplementary Figure 2: Cyclic voltammogram of **1** in CH_2Cl_2 referenced to Fc/Fc^+. [**1**] = 1 mM, [TBA][BAr^F_4] = 100 mM, scan rate = 100 mV/s, IR compensation at -950 mV, $E_{1/2}$ = -393 mV (I_{pa}/I_{pc} = 0.90), $E_{1/2}$ = -700 mV (I_{pa}/I_{pc} = 0.85).



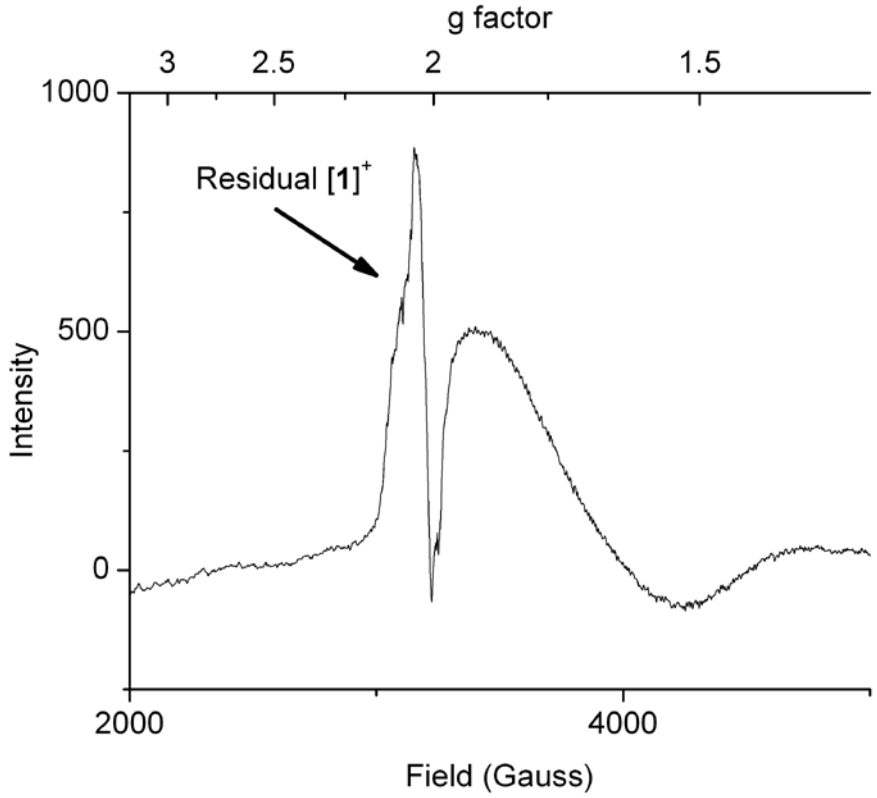
Supplementary Figure 3: Experimental (red) and Simulated (green) X-band EPR spectrum of $[\mathbf{1}]^+$ at 110 K in a 50/50 CH_2Cl_2/toluene glass. $g_z = 2.1174$ with $A_z(^{31}P) = 79.9$ MHz, $g_x \approx g_y = 2.0190$ with $A_x(^{31}P) \approx A_y(^{31}P) = 67.7$ MHz.



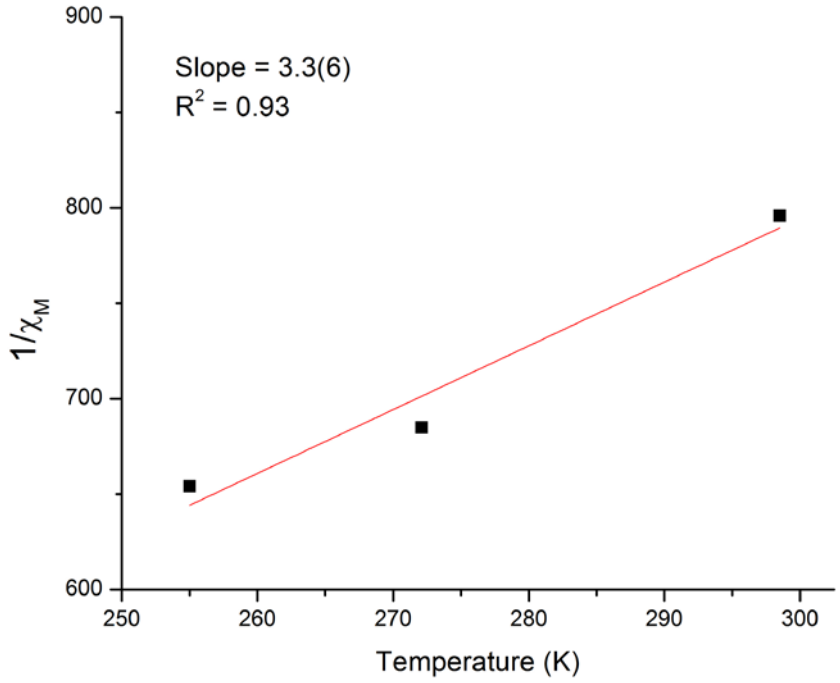
Supplementary Figure 4: X-band EPR spectrum of $[\mathbf{1}]^{2+}$ at 4.5 K and 10 dB power in a 50/50 CH_2Cl_2/toluene glass.



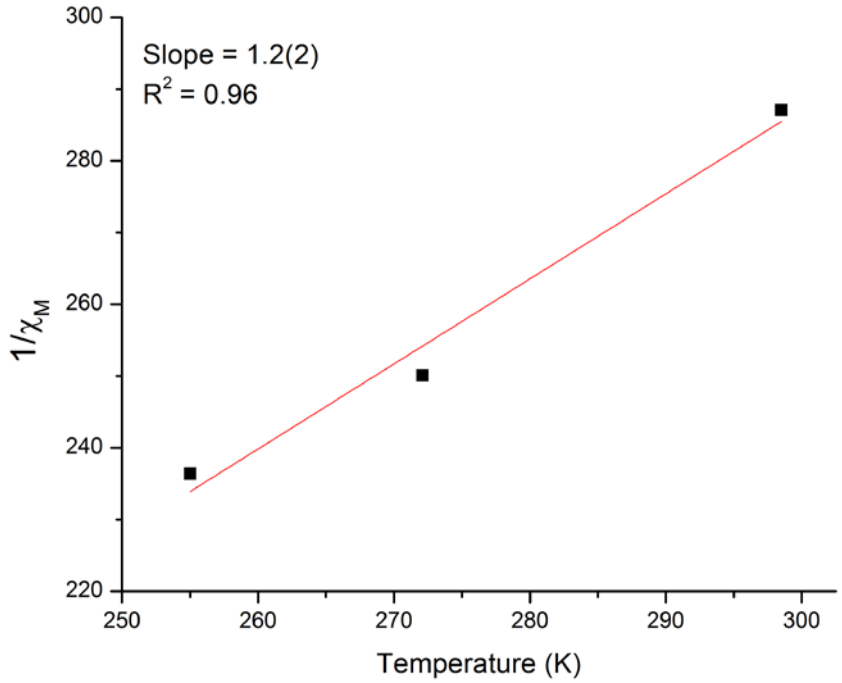
Supplementary Figure 5: X-band EPR spectrum of $[\mathbf{1}]^{2+}$ at 4.5 K and 30 dB power in a 50/50 CH_2Cl_2/toluene glass.



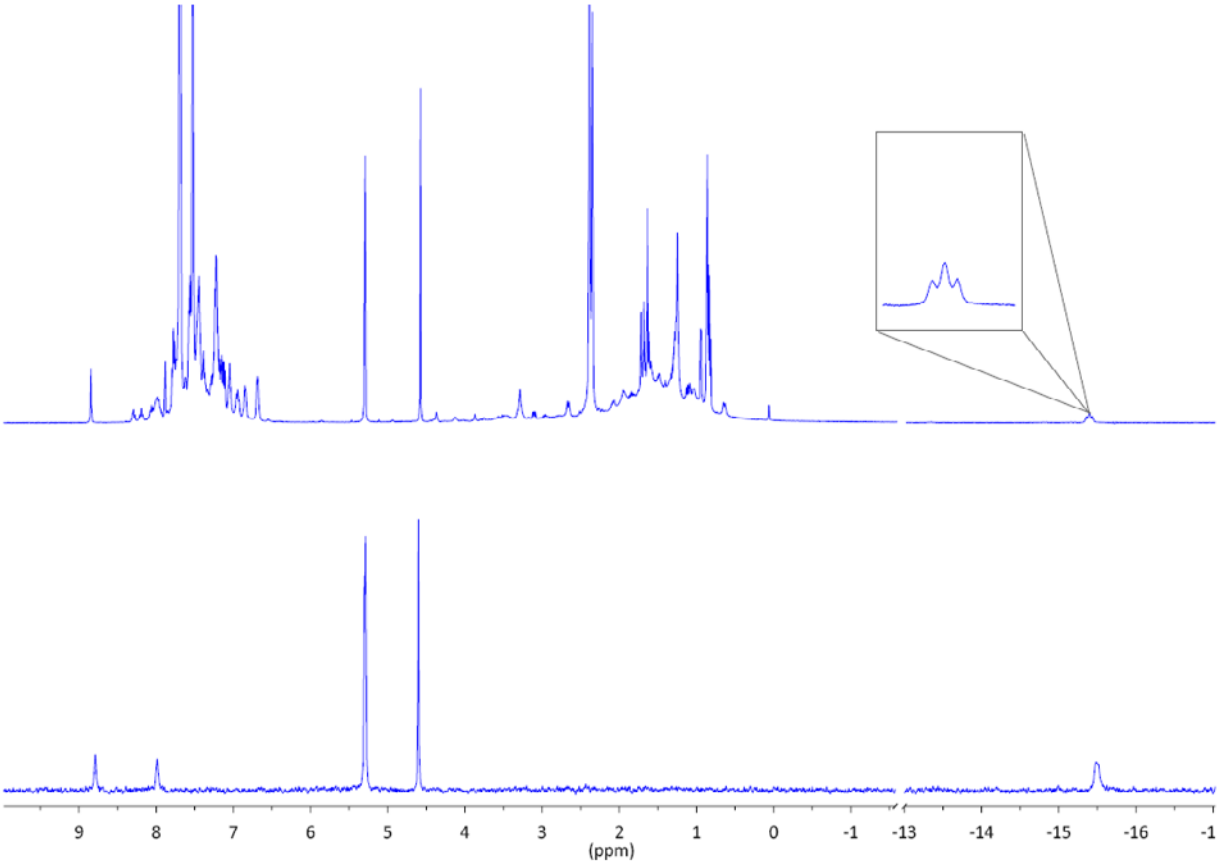
Supplementary Figure 6: Plot of $1/\chi_M$ vs temperature for $[\mathbf{1}]^{+}$.



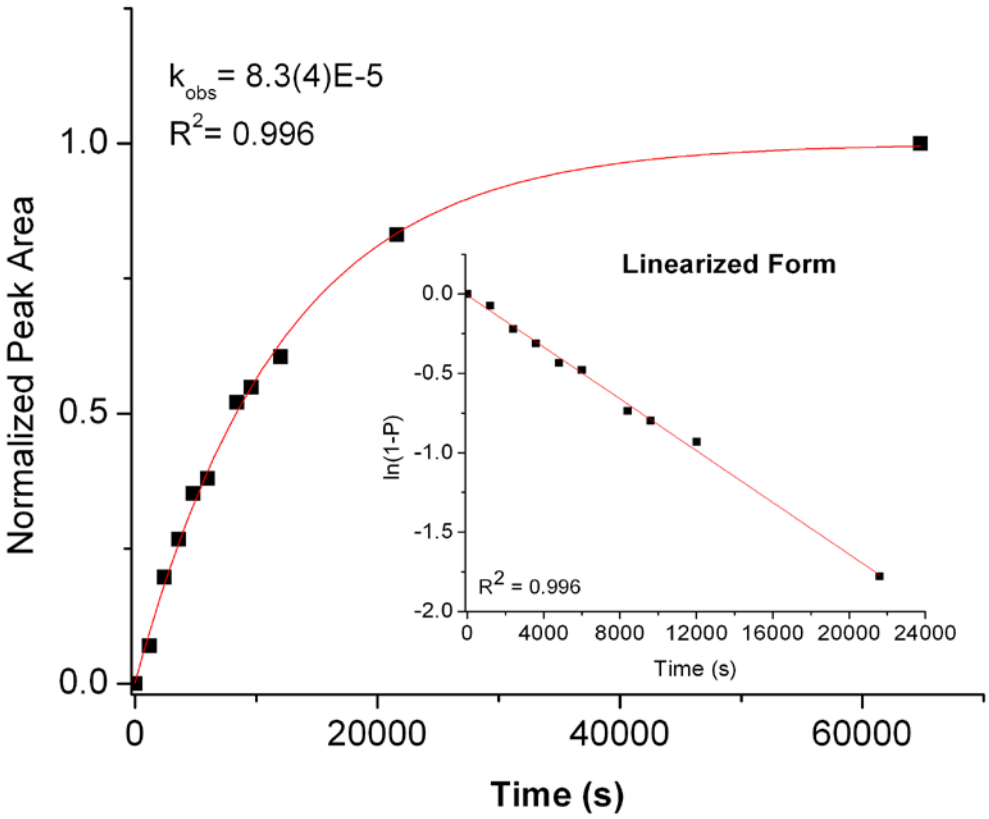
Supplementary Figure 7: Plot of $1/\chi_M$ vs temperature for $[\mathbf{1}]^{2+}$.



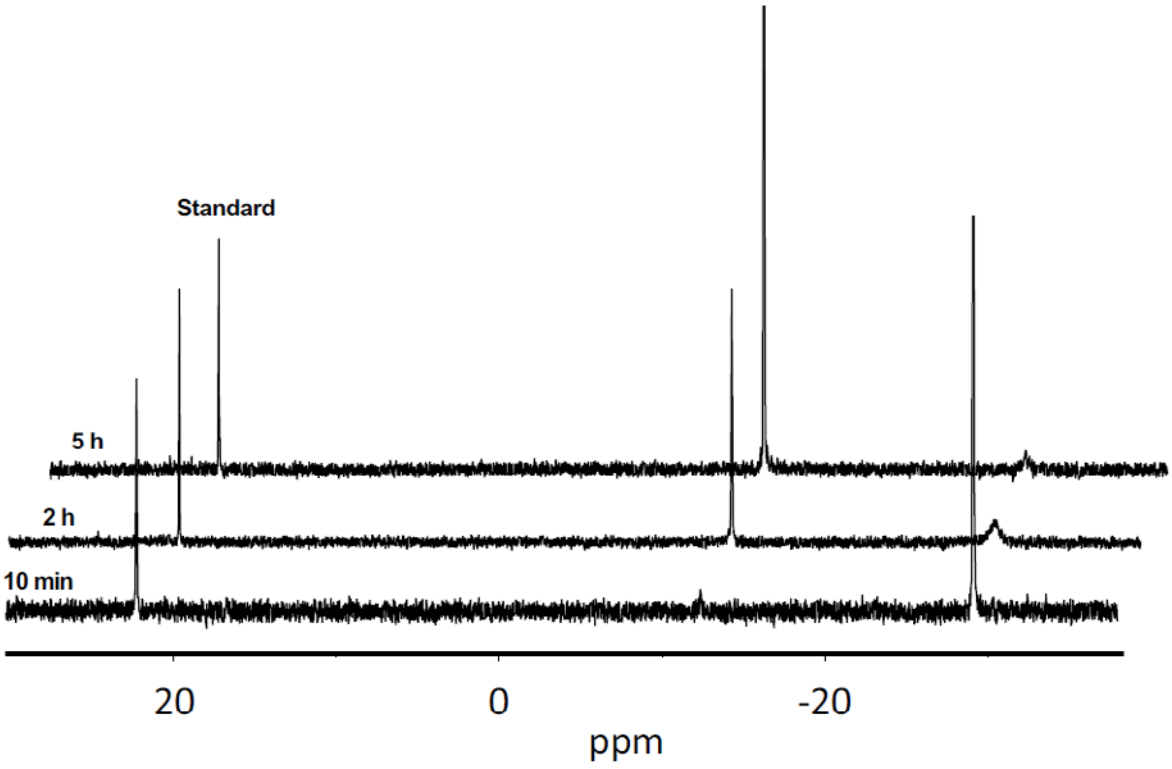
Supplementary Figure 8: NMR stack plot of reaction of $[\mathbf{1}]^{2+}$ and P(*o*-tol)$_3$ with H_2 and D_2. *Top:* ^{1}H NMR (500 MHz, CD_2Cl_2) of H_2 activation reaction. *Bottom:* ^{2}H NMR (97 MHz, CD_2Cl_2) of D_2 activation reaction. The ^{2}H NMR shows ^{2}H incorporation into the product hydride and phosphonium.



Supplementary Figure 9:Kinetic plot for the reaction of $[1]^{2+}$ with H_2 in the presence of P(*o*-tol)$_3$ fit to a first order exponential. *Inset:* Linearized kinetic plot illustrating first-order kinetics.



Supplementary Figure 10: ^{31}P NMR stack plot showing catalytic oxidation of H_2 by $[\mathbf{1}]^{2+}$ in the presence of excess $FcBAr^F{}_4$ and excess base. δ = -12.3 (s, $[HP(o\text{-tol})_3]^+$) , -28.9 (s, $P(o\text{-tol})_3$).



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