Supplementary Matewrials: New Phosphorous-Based [FeFe]-Hydrogenase Models

Florian Wittkamp¹, Esma Birsen Boydas², Michael Roemelt² and Ulf-Peter Apfel^{1,3,*}

- ¹ Lehrstuhl für Anorganische Chemie I, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany; florian.wittkamp@rub.de
- ² Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany; esma.boydas@theochem.ruhr-uni-bochum.de (E.B.B.); michael.roemelt@theochem.rub.de (M.R.)
- ³ Department of Electrosynthesis, Fraunhofer UMSICHT, Osterfelder Str. 3, 46047 Oberhausen, Germany
- * Correspondence: ulf.apfel@rub.de Tel.: +49-(0)234-32-21831

Computational Methodology

All calculations were carried out with ORCA software in its version 4.2 [1]. The global hybrid density functional B3LYP [2,3] was used in the optimizations along with def2-TZVP(-f) basis set [4]. Dispersion effects were incorporated using Grimme's semiempirical van der Waals corrections with the Becke-Johnson damping (D3BJ) [5,6]. Accuracy in numerical integration was established by a dense integration grid (ORCA Grid 7). The generation of Coulomb and exchange integrals was accelerated with the resolution of identity (RI) and the chain-of-spheres (COSX) approximations [7–11] together with the SARC/J basis set [12,13]. Scalar relativistic effects were approximated by means of zeroth orde regular approximation (ZORA) [14,15]. Solvent effects were modeled by conductor-like PCM (C-PCM)[16] in acetonitrile (ε = 36.6). The nature of the optimized structures was verified by numerical Hessian calculations, in which the stable intermediates have a positive definite Hessian.

IR frequencies for CO stretching and bending modes were reported by harmonic frequencies. Due to the shortcomings of the current level of theory which introduces an overestimation of the vibrational frequencies [17], a scaling factor of f = 0.9816 was applied to achieve better numberical agreement with the measured spectra [18].



Figure S1. Complete asymmetric unit of compound 12-OMe, showing two individual molecules, one with a coordinated toluene moiety. Ellipsoids drawn at 50% probability.



Figure S2. Molecular structure of 12-Me.



Figure S3. IR spectra of compounds 12-R in presence of 0-50 equiv. HBF₄ (33 % in H₂O) in acetonitrile at room temperature. A) Spectra of phosphinate 12-OEt. B) Spectra of phosphine oxide 12-Me.



Figure S4. DFT derived IR spectra of 12-Me in its neutral and protonated forms. Protonation sites are highlighted in green for better readability.



Figure S5. Cyclic voltammograms of 12-OMe in absence and presence of HBF₄ (33% in H₂O). Upon addition of HBF₄, the hydrogenase model gets protonated that results in a shift of the reduction potential to more positive values.



Figure S6. IR-differencespectrum of the reduction of 12-OEt.



Figure S7. Comparison of IR-Spectra of 12-OEt, [12-OEt]⁻ and [12-OEt]⁻ after addition of 2 equivalents HOAc.

NMR- and Mass spectra

Bis(hydroxymethyl)phosphinic acid (1)



150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100-110 chem. shift [ppm]

Figure S9. ³¹P-NMR spectrum of 1.



Figure S10. ESI-MS mass spectrum of 1.



10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 chem. shift [ppm]

Figure S11. ¹H-MNR spectrum of 2.



180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 chem. shift [ppm]

Figure S13. ³¹P-NMR spectrum of 2.



Figure S14. ESI-MS mass spectrum of 2.

Bis(chloromethyl)phosphinic acid (5)



Figure S15. ¹H-MNR spectrum of 5.





Ethyl bis(chloromethyl)phosphinate (3-Et)

$$\begin{array}{c} O \\ \hline P \\ CI \\ CI \\ CI \\ \end{array} + N(Et)_3 + EtOH \xrightarrow{THF} O \\ \hline r.t. \\ CI \\ CI \\ CI \\ \end{array}$$



Figure S18. ¹H-NMR spectrum of 3-Et.



Figure S19. ¹³C-NMR spectrum of 3-Et.



Figure S20. ³¹P NMR of 3-Et.

















Figure S27. ESI-MS mass spectrum of 3-Ph.

Bis(chloromethyl)methyl phoshine oxide (4)





Figure S28. ¹H-MNR spectrum of 4.



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 chem. shift [ppm]





Figure S30. ³¹P-NMR spectrum of 4.



Figure S31. ESI-MS mass spectrum of 4.









Figure S33: ¹³C-NMR spectrum of 7-Et



Figure S34: ³¹P-NMR spectrum of 7-Et













210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 chem. shift [ppm]

Figure S39: ¹³C-NMR spectrum of 9



Figure S40: ³¹P-NMR spectrum of 9



Figure S41: ESI-MS mass spectrum of 9

Ethyl bis(mercaptomethyl)phosphinate (8-Et)





Figure S43: ¹³C-NMR spectrum of 8-Et





Figure S45: ESI-MS mass spectrum of 8-Et





Figure S47: ¹³C-NMR spectrum of 8-Ph



240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 chem. shift [ppm]





Bis(mercaptomethyl)methyl phosphine oxide (10)



Figure S50: 1H-MNR spectrum of 10



Figure S51: ³¹P-NMR spectrum of 10



Figure S52: ESI-MS mass spectrum of 10

Cable S1: Crystallographic data and refinement parameters of compounds 12-R.	

Property	Value				
Identification code	12-OMe	12-OEt	12-Me	4	
Empirical formula	$C_{24}H_{20}Fe_4O_{17}P_2S_4$	$C_{10}H_9Fe_2O_8PS_2$	C9H7Fe2O7PS2	C ₃ H ₇ Cl ₂ OP	
Formula weight	993.98	463.96	433.94	160.96	
Temperature/K	108(12)	114(2)	100.0(2)	293(2)	
Crystal system	triclinic	triclinic	orthorhombic	orthorhombic	
Space group	P-1	P-1	Pca21	Pna21	
a/Å	7.3694(2)	7.11406(19)	22.1755(15)	5.8835(9)	
b/Å	15.3319(4)	9.4564(3)	6.9433(8)	17.677(2)	
c/Å	17.5708(3)	12.8023(4)	20.1450(16)	6.7983(18)	
$\alpha/^{\circ}$	110.813(2)	84.927(3)	90	90	
β/°	92.797(2)	74.521(3)	90	90	
γ/°	98.585(2)	87.660(2)	90	90	
Volume/Å ³	1823.76(8)	826.63(5)	3101.7(5)	707.0(2)	
Z	2	2	8	6	
Qcalcg/cm ³	1.810	1.864	1.858	2.268	
µ/mm ⁻¹	1.946	17.700	18.767	14.374	
F(000)	996.0	464.0	1728.0	492.0	
Crystal size/mm ³	0.329 × 0.066 × 0.026	0.2737 ×	0.02 x 0.02 x 0.02	0.02 x 0.02 x 0.02	
		0.2174 ×			
		0.0959			
Dediction	Mo K α (λ =	$CuK\alpha$ (λ =	$CuK\alpha$ (λ =	$CuK\alpha$ (λ =	
Kaulation	0.71073)	1.54184)	1.54184)	1.54184)	
2Θ range for data	2 101 to E2 E19	7.188 to	7.974 to 145.702	10.008 to 144.94	
collection/°	2.494 10 55.546	152.468			
	8chc0 10ck	$-8 \le h \le 8, -11$	-20 \leq h \leq 27, -5 \leq	$-7 \leq h \leq 7, -21 \leq k$	
Index ranges	$-0 \le 11 \le 9, -19 \le K$	$\leq k \leq 11, -15 \leq l$	$k \le 8, -24 \le l \le 19$	\leq 18, -7 \leq l \leq 8	
	≤ 19, -22 ≤ 1 ≤ 22	≤16			
Reflections collected	24372	14320	8025	1465	
	7570 [R _{int} =	3386 [R _{int} =	4462 [R _{int} =	948 [Rint =	
Independent reflections	0.1095, R _{sigma} =	0.0521, R _{sigma} =	0.1237, R _{sigma} =	0.0328, Rsigma =	
	0.0696]	0.0251]	0.1583]	0.0424]	
Data/restraints/parameters	7570/0/463	3386/0/209	4462/1/192	948/1/65	
Goodness-of-fit on F ²	1.066	1.048	1.182	1.666	
Final P indexes [I>-2g (I)]	$R_1 = 0.0827, wR_2$	$R_1 = 0.0297,$	$R_1 = 0.1634, wR_2$	$R_1 = 0.0945, wR_2$	
Final K indexes [I>= 2σ (I)]	= 0.2124	$wR_2 = 0.0757$	= 0.3642	= 0.2353	
Final R indexes [all data]	$R_1 = 0.0946, wR_2$	$R_1 = 0.0311,$	$R_1 = 0.2272, wR_2$	$R_1 = 0.1032, wR_2$	
rmai k indexes [all data]	= 0.2210	$wR_2 = 0.0766$	= 0.4231	= 0.2445	
Largest diff. peak/hole / e Å- 3	1.19/-1.15	0.35/-0.52	5.63/-1.54	0.61/-0.80	

CCDC reference	1996968	1996967	-	-

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