

A Sterically Stabilized Fe^I-Fe^I Semi-Rotated Conformation of [FeFe] Hydrogenase Subsite Model

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General Procedures: All reactions were performed under a dry nitrogen or argon atmosphere with standard Schlenk techniques. All solvents were dried and distilled according to standard methods prior to use. Infrared spectra were recorded with a Bruker Vertex 70 spectrometer. Preparative column chromatography was performed with silica gel (Fluka, Kieselgel 60). ¹H, ¹³C, ³¹P and ²⁹Si NMR spectra were obtained with either a BRUKER Avance 200, Avance 400 spectrometer or a Bruker AMX 400 spectrometer. Elemental analyses were performed with a Vario EL III CHNS analyzer from Elementar Analysensysteme GmbH. Mass spectra were measured with a FINNIGAN MAT SSQ710 instrument.

Structure Determinations: The intensity data for the compounds **2**, **3**, **4** and **5** were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans¹⁻³ Measurements for compound **6** were carried out on an Oxford Diffraction X-Calibur-2 CDD diffractometer equipped with a jet cooler device. Graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$) was used in this experiment. The structure was solved and refined by standard procedures.⁴⁻⁶

The structures were solved by direct methods (SHELXS⁷) and refined by full-matrix least squares techniques against Fo² (SHELXL-97^[26]). The hydrogen atoms bounded to the thiole-groups of **2** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically.⁷ Crystallographic data as well as structure solution and refinement details are summarized in Table S1.

Supporting Information available: Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1028097 for **2**, CCDC-1028098 for **3**, CCDC-1028099 for **4**, CCDC-1028100 for **5** and CCDC-1028773 for **6**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].

Electrochemical Procedures: The electrochemical experiments were conducted under an inert atmosphere of nitrogen or argon. The preparation and purification of the supporting electrolyte ($[\text{NBu}_4][\text{PF}_6]$) was performed as described previously.^[34] Cyclic voltammetry was performed in a three-electrode cell by using a radiometer potentiostat (PGSTAT 128N or μ -Autolab III) driven by the GPES software. The working electrode consisted of a vitreous carbon disk, which was polished on a felt tissue with alumina, thoroughly rinsed with water, and dried before each CV scan. The Ag/Ag^+ reference electrode was separated from the analyte by a $\text{CH}_2\text{Cl}_2 - [\text{NBu}_4][\text{PF}_6]$ bridge. All the potentials are reported against the ferrocenium-ferrocene-couple; ferrocene was added as an internal standard at the end of the experiments.

Synthesis of Bis(benzylthio)diphenylsilane (**2**)

Benzylmercaptane (10 g, 0.08 mol) was dissolved in 100 mL THF and cooled to 0°C. Subsequently, 32.2 ml (0.08 mol) *n*-butyllithium (2.5 mol/L in hexane) were added dropwise. To this mixture, 10.1 g (0.04 mol) diphenyldichlorsilan were added slowly and the solution was stirred for additional 24 hours at room temperature, whereupon a white precipitate was formed. Afterwards the solution was cooled to -78°C and 50 mL (0.08 mol) *tert*-butyllithium (1.6 mol/L in pentane) was added. After 24 hours, the orange suspension was cooled to 0°C and acidified with 2N HCl to pH = 4. The organic solvents were removed under reduced pressure and the residue extracted three times with 100 mL of dichloromethane. The combined organic fractions were extracted with water, dried with sodium sulfate and evaporated to dryness. Crystallization from hexane afforded 10.5 g (61%) of **2** as white solid. Anal. calc. for $\text{C}_{26}\text{H}_{24}\text{S}_2\text{Si}$: C, 72.9 %; H, 5.6 %; S, 14.9 %. Found: C, 72.4 %; H, 5.7 %; S, 14.6 %. ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.58\text{--}6.98$ (20H, m, $\text{CH}_{\text{aromatic}}$), 3.89 (2H, d, $J = 9.6$ Hz, CH), 1.87 (2H, d, $J = 9.6$ Hz, SH). ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 141.7, 137.6, 130.6, 130.3, 128.7, 127.9, 127.7, 127.2, 126.1$ ($\text{CH}_{\text{aromatic}}$), 26.4 (CH). m/z (DEI): 428 (M^+).

Synthesis of $[\text{Fe}_2(\text{CO})_6]\{\mu\text{-(SCHPh)}_2\text{SiPh}_2\}$ (**3**)

Bis(benzylthio)diphenylsilane (**2**) (200 mg, 0.47 mmol) and $\text{Fe}_3(\text{CO})_{12}$ (239 mg, 0.47 mmol) were dissolved in 50 mL of toluene and stirred under reflux for one hour. Evaporation, purification via column chromatography (dichloromethane: hexane = 1:8) afforded 97 mg (64%) of a red crystalline solid. Anal. calc. for $\text{C}_{32}\text{H}_{22}\text{S}_2\text{SiFe}_2\text{O}_6 + 0.9$ hexane: C, 57.3 %; H, 4.4 %; S, 8.2 %. Found: C, 57.7 %; H, 4.0 %; S, 8.3 %. ^1H NMR (200 MHz, CDCl_3 , ppm): $\delta = 7.35$ (20H, m, $\text{CH}_{\text{aromatic}}$), 3.59 (2H, s, CH). ^{13}C NMR (50 MHz, CDCl_3 , ppm): $\delta = 207.5, 206.7$ (CO), 50 139.7, 139.0, 135.3, 133.7, 130.6, 130.2, 128.4, 128.1, 127.4, 126.4, 125.6 ($\text{CH}_{\text{aromatic}}$), 34.4 (CH). m/z (DEI): 706 (M^+), 650 (M-2CO), 622 (M-3CO), 594 (M-4CO), 566 (M-5CO), 538 (M-6CO). $\nu_{\text{max}}/\text{cm}^{-1}$ (CH_2Cl_2): 2073 (s), 2035 (s), 1999 (s), 1978 (s).

Synthesis of $[\text{Fe}_2(\text{CO})_5\{\mu\text{-(SCHPh)}_2\text{SiPh}_2\}_2(\mu\text{-dmpe})]$ (**4**), $[\text{Fe}_2(\text{CO})_5(\kappa^2\text{-dmpe})\{\mu\text{-(SCHPh)}_2\text{SiPh}_2\}]$ (**5**), $[\text{Fe}_2(\text{CO})_5(\mu\text{-dmpe})\{\mu\text{-(SCHPh)}_2\text{SiPh}_2\}]$ (**6**).

Method A: A solution of $[\text{Fe}_2(\text{CO})_6\{\mu\text{-(SCHPh)}_2\text{SiPh}_2\}]$ **3** (0.2 g, 0.28 mmol) and dmpe (0,049 mL, 0.283 mmol) in 50 mL of THF was refluxed for 25 min. After evaporation of the solvent, the residue was purified by column chromatography with a dichloromethane/hexane mixture, which afforded a red solution of **4** as first phase and a deep red solution of **6** as second phase. Compound **4** (40 mg, 19%) and **6** (7 mg, 3%) were obtained as red solids.

Method B: In a known procedure, a solution of $[\text{Fe}_2(\text{CO})_6\{\mu\text{-(SCHPh)}_2\text{SiPh}_2\}]$ **3** (0.5 g, 0.71 mmol) and dmpe (0,24 mL, 1.42 mmol) in 100 mL of THF was refluxed for 25 min. After evaporation of the solvent, the residue was purified by column chromatography with dichloromethane/hexane mixture, which afforded red-purple solution of **5** as first phase and a deep red solution of **6** as second phase. Compound **5** (40 mg, 7%) was obtained as purple solid and **6** (199 mg, 35%) as red solid.

4: Anal. calc. for $\text{C}_{68}\text{H}_{60}\text{S}_2\text{Si}_2\text{Fe}_4\text{O}_{10}\text{P}_2 + 1.0$ hexane: C, 55.79 %; H, 4.68 %; S, 8.05 %. Found: C, 55.74 %; H, 4.46 %; S, 8.06 %. $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): $\delta = 7.34\text{-}7.06$ (40H, m, $\text{CH}_{\text{aromatic}}$), 3.63 (4H, m, CH), 1.99 (4H, s, CH_2), 1.48 (12H, m, CH_3). $^{31}\text{P NMR}$ (161.9 MHz, CDCl_3 , ppm): $\delta = 36.87$. $\nu_{\text{max}}/\text{cm}^{-1}$ (CH_2Cl_2): 2039 (m), 1984 (s), 1964 (m), 1929 (w).

5: Anal. calc. for $\text{C}_{36}\text{H}_{38}\text{S}_2\text{SiFe}_2\text{O}_4\text{P}_2$: C, 54.01 %; H, 4.78 %; S, 8.01 %. Found: C, 53.42 %; H, 4.87 %; S, 7.96 %. $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): $\delta = 7.36\text{-}7.00$ (20H, m, $\text{CH}_{\text{aromatic}}$), 3.80 (2H, m, CH), 1.98 (2H, m, CH_2), 1.86 (2H, m, CH_2), 1.57 (6H, m, CH_3), 1.27 (6H, m, CH_3). $^{31}\text{P NMR}$ (161.9 MHz, CDCl_3 , ppm): $\delta = 63.87$. m/z (DEI) 800 (M^+), 744 (M-2CO), 716 (M-3CO), 688 (M-4CO). m/z (DEI): 800 (M^+), 744 (M-2CO), 688 (M-4CO). $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$: 2007, 1937, 1903. $\nu_{\text{max}}(\text{solid state})/\text{cm}^{-1}$: 2002 (s), 1974 (s), 1911 (s), 1899 (s), 1801 (w).

6: Anal. calc. for $\text{C}_{36}\text{H}_{38}\text{S}_2\text{SiFe}_2\text{O}_4\text{P}_2 + 0.33$ hexane: C, 55.02 %; H, 5.22 %; S, 7.73 %. Found: C, 55.04 %; H, 5.19 %; S, 7.73 %. $^1\text{H NMR}$ (400 MHz, CD_2Cl_2 , ppm): $\delta = 7.25\text{-}7.03$ (20H, m, $\text{CH}_{\text{aromatic}}$), 3.68 (1H, s, CH), 3.47 (1H, m, CH) 1.93 (4H, m, CH_2), 1.57 (12H, m, CH_3). $^{31}\text{P NMR}$ (161.9 MHz, CD_2Cl_2 , ppm): $\delta = 38.69, 32.58$. m/z (DEI): 800 (M^+), 744 (M-2CO). $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$: 1984 (m), 1950 (s), 1917 (m), 1899 (w).

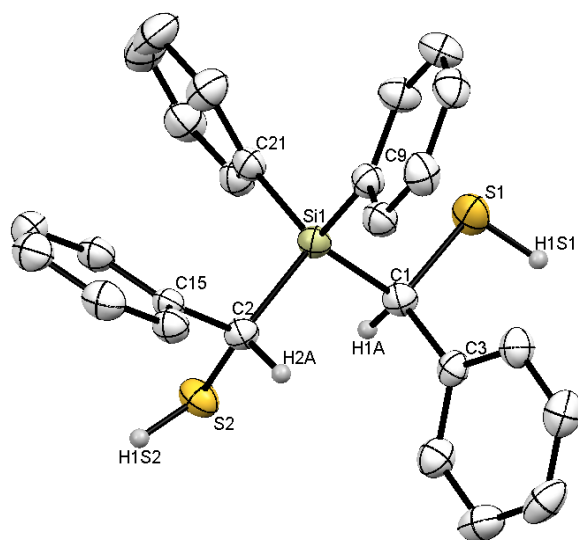


Fig. S1: Molecular structure of compound **2**. Aromatic hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2**: Si1-C1 1.899(2), Si1-C2 1.910(2), Si1-C9 1.867(2), Si1-C21 1.870(2), C1-S1 1.840(2), C2-S2 1.837(2), C1-Si1-C2 105.85(9), C1-Si1-C9 111.35(9), C2-Si1-C9 109.13(9), C2-Si1-C21 111.59(9).

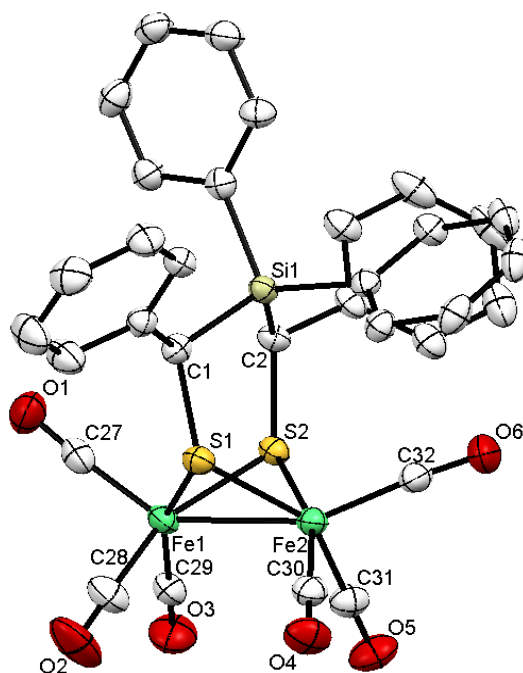


Fig. S2: Molecular structure of complex **3**. Aromatic hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: **3**: Fe1-Fe2 2.5123(6), Si1-C1-S1 113.06(15), Si1-C2-S2 120.21(14), C1-Si1-C2 105.63(12).

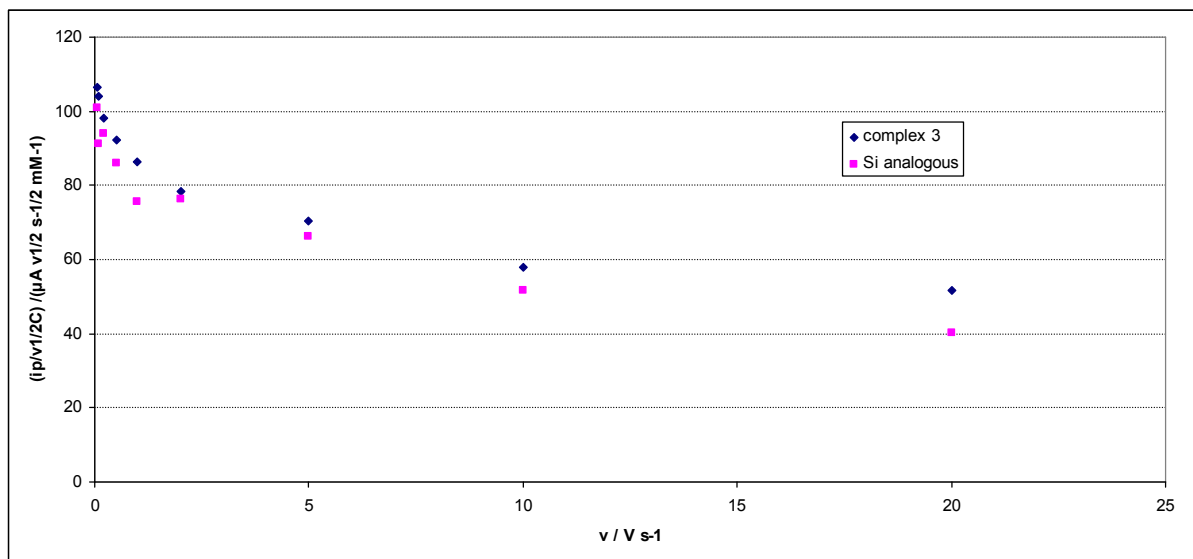


Figure S3 : Scan rate dependence of the current function ($i_p^{\text{red}}/ v^{1/2} C$) for the reduction of $[\text{Fe}_2(\text{CO})_6\{\mu\text{-(SCH}_2)_2\text{R}\}]$ (R = 1-silafluorenyl, $\text{C}_{12}\text{H}_8\text{Si}$) (0.34 mM, \ominus) and for the reduction of **3** (0.91 mM, \oplus) in $\text{CH}_2\text{Cl}_2\text{-[NBu}_4\text{][PF}_6\text{]}$ (potentials are in V vs Fc^+/Fc).

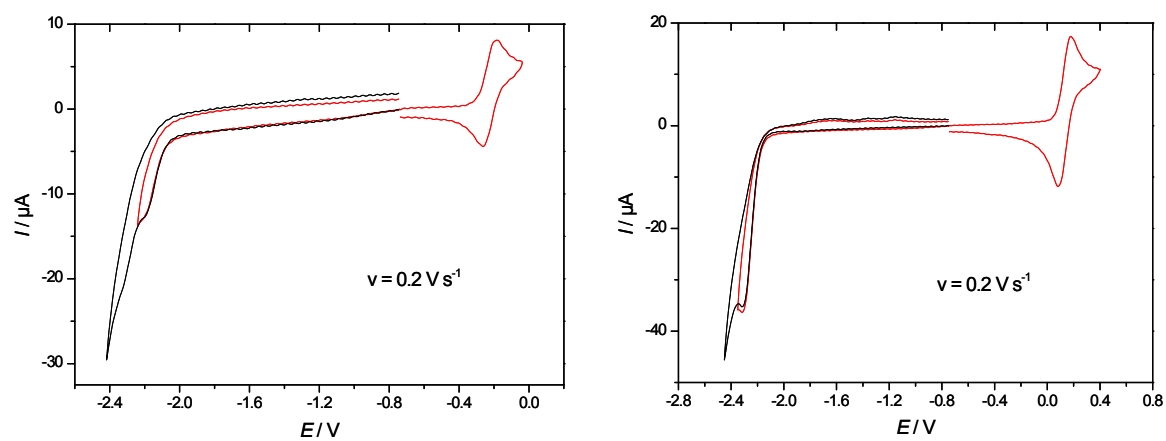


Figure S4: Cyclic voltammetry of **5**, 0.52 mM (left) and **6**, 0.71 mM (right) in CH₂Cl₂-[NBu₄][PF₆] ($\nu = 0.2 \text{ V s}^{-1}$; potentials are in V vs Fc⁺/Fc).

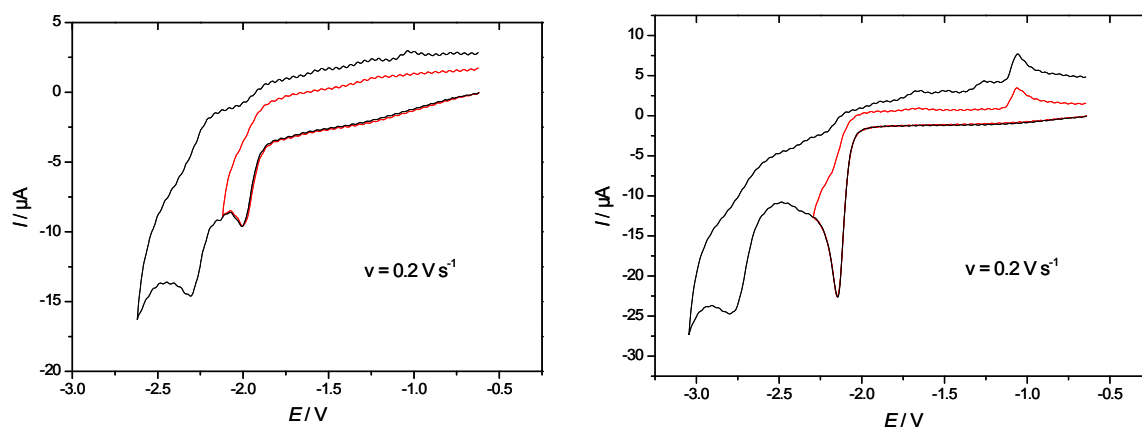


Figure S5 Cyclic voltammetry of **5**, 0.40 mM (left) and **6**, 0.44 mM (right) in MeCN-[NBu₄][PF₆] ($v = 0.2 \text{ V s}^{-1}$; potentials are in V vs Fc⁺/Fc).

Table S1: Crystal data and refinement details for the X-ray structure determinations of the compounds **2 - 6**.

Compound	2	3	4	5	6
formula	C ₂₆ H ₂₄ S ₂ Si	C ₃₂ H ₂₂ Fe ₂ O ₆ S ₂ Si	C ₆₈ H ₆₀ Fe ₄ O ₁₀ P ₂ SSi ₂ ·2H ₂ O	C ₃₆ H ₃₈ Fe ₂ O ₄ P ₂ S ₂ Si	C ₃₆ H ₃₈ Fe ₂ O ₄ P ₂ S ₂ Si
fw (g·mol ⁻¹)	428.66	706.41	1542.95	800.51	800.51
T/°C	-90(2)	-90(2)	-140(2)	-140(2)	-103(2)
crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	P 2 ₁ /n	P 2 ₁	P $\bar{1}$	P 2 ₁ /n	P 2 ₁ /c
a/ Å	12.5725(7)	8.9705(2)	11.1625(2)	9.4944(5)	11.4702(5)
b/ Å	10.0053(3)	13.1314(5)	17.4213(5)	28.8784(16)	11.9426(5)
c/ Å	18.5969(9)	12.9610(5)	19.7848(5)	13.4812(7)	29.2444(14)
α /°	90	90	98.998(2)	90	90
β /°	105.747(2)	92.088(2)	100.977(2)	91.570(3)	94.382(4)
γ /°	90	90	102.728(2)	90	90
V/Å ³	2251.54(18)	1525.73(9)	3604.34(15)	3694.9(3)	3994.3(3)
Z	4	2	2	4	4
ρ (g·cm ⁻³)	1.265	1.538	1.422	1.439	1.472
μ (cm ⁻¹)	3	11.71	10.4	10.55	11.13
measured data	14761	10977	21863	27814	30116
data with I > 2 σ (I)	3153	5518	12708	4716	8162
unique data (R _{int})	5130/0.0732	6369/0.0316	15488/0.0293	6956/0.0898	8162/0.0604
wR ₂ (all data, on F ²) ^{a)}	0.1074	0.0714	0.1582	0.1849	0.1068
R ₁ (I > 2 σ (I)) ^{a)}	0.0455	0.0328	0.0776	0.0919	0.0482
S ^{b)}	0.973	1.017	1.281	1.116	0.938
Res. dens./e·Å ⁻³	0.540/-0.252	0.296/-0.248	1.393/-0.490	0.703/-0.518	0.858/-0.630
Flack-parameter	-	-0.030(11)	-	-	-
absorpt method	multi-scan	multi-scan	multi-scan	multi-scan	Multi-scan
absorpt corr T _{min} /T _{max}	0.7235/0.7640	0.6892/0.7464	0.6270/0.7456	0.5927/0.7456	0.8509/0.8969
CCDC No.	1028097	1028098	1028099	1028100	1028773

^{a)} Definition of the R indices: $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$; $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \text{Max}(F_o^2)]/3$;

^{b)} $S = \{\sum [w(F_o^2 - F_c^2)^2] / (N_o - N_p)\}^{1/2}$

Notes and references

1. COLLECT, Data Collection Software; Nonius B.V., Netherlands, **1998**.
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