This journal is © The Royal Society of Chemistry 2011

Electronic Supporting Information

Bio-inspired hydrogenase models: Mixed-valence triion complexes as proton reduction catalysts

Shishir Ghosh,[b] Graeme Hogarth,[*a] Katherine B. Holt,[*a] Shariff E. Kabir,[*b] Ahibur Rahaman[b] and David G. Unwin[a]

1. Synthesis and characterisation data of complexes

*Synthesis of [$Fe_3(CO)_7(\mu$-edt)$_2$] (**1**)* - To a suspension of $Na_2[Fe(CO)_4]$, (*ca*. 2.183 g, 10.20 mmol) in THF (30 mL) was added dropwise a solution of 1,2-ethanedithiol (0.479 g, 5.10 mmol) in THF (30 mL). After stirring for 24 h at room temperature, the solvent was removed *in vacuo* and the residue extracted with hexane and filtered on Kieselguhr. The filtrate was concentrated under reduced pressure to give a reddish-yellow gummy mass, which was chromatographed by TLC on silica gel. Elution with hexane developed to bands. The faster moving reddish-yellow band gave [$Fe_2(CO)_6$(μ-edt)] (512 mg, 27 %) as red crystals while the slower moving band afforded [$Fe_3(CO)_7$(μ-edt)$_2$] (**1**) (90 mg, 5 %) as deep red crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C. IR (ν(CO), CH_2Cl_2): 2073 s, 2040 vs, 2008 s, 1974 s, 1904 w cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.53 (m, 4 H), 2.26 (m, 4H). ^{13}C{^{1}H} NMR (CD_2Cl_2): 221.5 (s, 1CO), 211.6 (s, 2CO), 207.3 (s, 1CO), 206.7 (s, 1CO), 206.0 (s, 2CO), 37.8 (s, CH_2), 36.2 (s, CH_2).

*Reaction of [$Fe_3(CO)_7(\mu$-edt)$_2$] (**1**) with PPh_3* - A benzene solution (20 mL) of **1** (75 mg, 0.137 mmol) and PPh_3 (36 mg, 0.137 mmol) was heated to reflux for 15 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (v/v 9:1) developed five bands. The first and last band was unreacted **1** (trace). The second to fifth band afforded the following compounds in order of elution: [$Fe_2(CO)_5(PPh_3)$(μ-edt)] (**4**) (18 mg, 22 %) as red crystals, [$Fe_3(CO)_6(PPh_3)$(μ-edt)$_2$] (**2**) (25 mg, 23 %) as orange crystals, [$Fe_3(CO)_5(PPh_3)_2$(μ-edt)$_2$] (**3**) (16 mg, 12 %) as red crystals and Ph_3PS, (15 mg, 30 %) as white crystals after recrystallization from hexane/CH_2Cl_2 at –20 °C. Spectral data for **2**: Anal. Calcd for $C_{28}H_{23}Fe_3O_6PS_4$: C, 42.99; H, 2.96. Found: C, 43.44; H, 3.07%. IR (ν(CO), CH_2Cl_2): 2035 s, 2012 vs, 1963 vs, 1882 w cm^{-1}. ^{1}H NMR ($CDCl_3$): both isomers: δ 7.65 (m, 4H), 7.58 (m, 2H), 7.44 (m, 9H), 2.49 (m, 2H), 2.18 (m, 2H), 1.81 (m, 2H), 1.04 (m, 2H). ^{31}P{^{1}H} NMR ($CDCl_3$): major isomer: δ 65.0 (s); minor isomer: δ 52.7 (s). Spectral data

for **3**: Anal. Calcd for $C_{45}H_{38}Fe_3O_5P_2S_4$: C, 53.17; H, 3.77. Found: C, 53.69; H, 3.91%. IR (ν(CO), CH_2Cl_2): 2008 s, 1965 vs, 1953 sh, 1912 m, 1869 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.66 (m, 10H), 7.39 (m, 20H), 1.98 (m, 4H), 1.01 (m, 2H), 0.77 (m, 2H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.8 (s), 61.5 (s), 53.1 (s). Spectral data for **4**: Anal. Calcd for $C_{25}H_{19}Fe_2O_5PS_2$: C, 49.53; H, 3.16. Found: C, 50.03; H, 3.23%. IR (ν(CO), CH_2Cl_2): 2048 vs, 1984 vs, 1936 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.57 (m, 6H), 7.42 (m, 9H), 1.86 (m, 2H), 1.13 (m, 2H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 64.2 (s). Spectral data for **Ph_3PS**: Anal. Calcd for $C_{18}H_{15}PS$: C, 73.45; H, 5.14. Found: C, 74.18; H, 5.26%. ^1H NMR ($CDCl_3$): δ 7.71 (m, 6H), 7.51 (m, 3H), 7.43 (m, 6H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 44.8 (s). TOF (MS): *m/z* 295.08 (calc. 294.35).

Actually there are three resonances in the $^{31}P\{^1H\}$ NMR spectrum of **3** which appear at δ 63.8, 61.5, 53.1 with the relative intensity of **2.5:3.5:1**. I think the molecule is fluxional in solution. The singlet at δ 63.8 (integrated to 2.5P) is for the major isomer while that at δ 53.1 (integrated to 1P) is for the minor isomer. The resonance at δ 61.5 (integrated to 3.5 P) is the sum of other two resonance of the major and minor isomer (2.5+1 = 3.5).

2. X-ray Crystallography

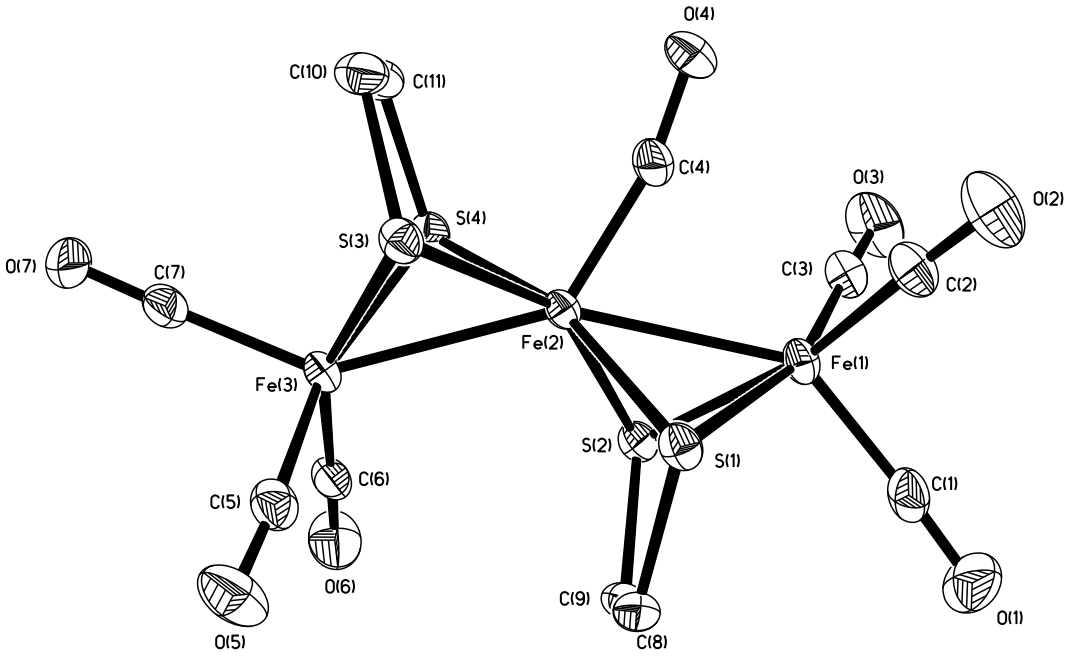
Single crystals were mounted on fibres and diffraction data collected at 150 K on a Bruker SMART APEX diffractometer using Mo-Kα radiation (λ = 0.71073 Å). Data collection, indexing and initial cell refinements were all done using SMART software [ESI**1**]. Data reduction was accomplished with SAINT [ESI**2**] software and SADABS [ESI**3**] programs were used to apply empirical absorption corrections. The structures were solved by direct methods or Patterson methods and refined by full matrix least-squares (SHELXTL, V6.12) [ESI**4**]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included using a riding model. Scattering factors were taken from International Tables for X-ray Crystallography. Crystals of **3** showed significant decomposition during the data collection. They contained some solvent which were modelled as a highly disordered molecule of pentane and also a molecule of methanol. The protons on these molecules were not calculated. It is likely that the poor quality of the overall data reflects the loss of one or both of these solvents during the experiment. This does not adversely affect the overall structure of the organometallic complex but is reflected in the relatively poor esds. Additional details of data collection and structure refinement are given in Table 1. Selected bond lengths and angles are given in Table 2.

Table 1 Crystallographic Data and Structure Refinement for **1-3**

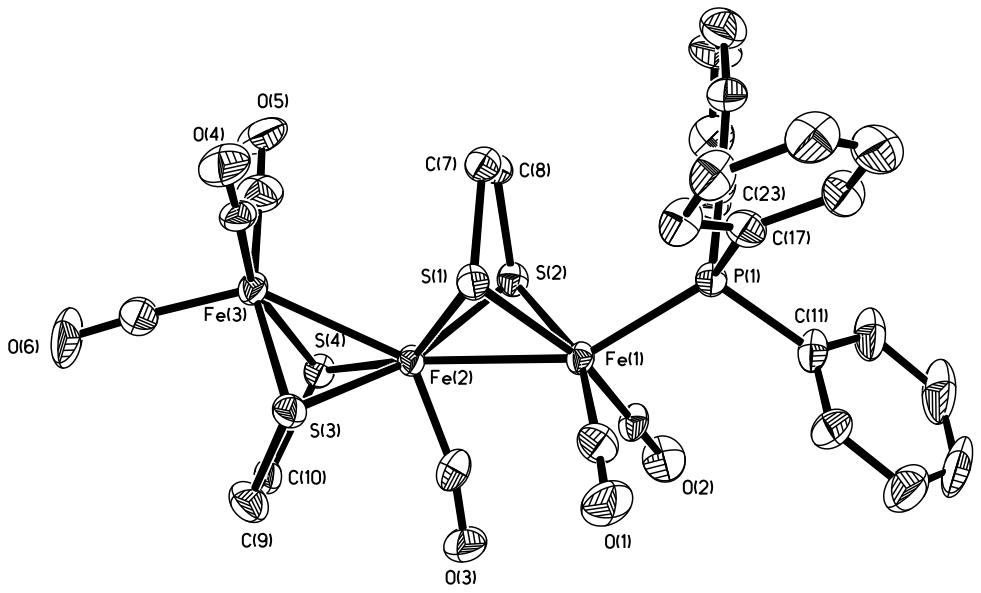
Compound	**1**	**2**	**3**
empirical formula	$C_{11}H_8O_7Fe_3S_4$	$C_{28}H_{23}O_6Fe_3S_4P$	$C_{50}H_{38}O_{5.50}Fe_3S_4P_2$
formula weight	547.96	782.22	1084.53
temp (K)	150(2)	150(2)	150(2)
wavelength (Å)	0.71073	0.71073	0.71073
crystal system	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	C_2/c
a (Å)	6.423(1)	8.799(5)	25.52(2)
b (Å)	8.291(2)	11.268(6)	13.484(9)
c (Å)	18.331(4)	16.543(9)	30.21(2)
α (°)	77.541(3)	90.571(7)	90
β (°)	83.384(3)	90.499(1)	83.813(3)
γ (°)	68.854(3)	109.469(8)	90
Volume (Å^3)	888.2(3)	1546.2(1)	10360(1)
Z	2	2	8
D_{calc} (Mg m^{-3})	2.0499	1.680	1.391
μ (Mo Kα) (mm^{-1})	2.918	1.751	1.096
F(000)	544	792	4432
crystal color	red	orange	red
crystal size (mm)	0.14 × 0.14 × 0.03	0.26 × 0.10 × 0.03	0.22 × 0.10 × 0.05
θ range (°)	1.14−28.28	1.92−28.50	2.22−28.31
limiting indices	$-8 \le h \ge 8$	$-11 \le h \ge 11$	$-32 \le h \ge 33$
	$-10 \le k \ge 10$	$-14 \le k \ge 14$	$-17 \le k \ge 17$
	$-13 \le l \ge 24$	$-21 \le l \ge 20$	$-39 \le l \ge 39$
structure solution	Patterson	direct methods	direct methods
reflections collected	7497	12859	41674
independent reflections (R_{int})	3970 (0.0333)	6918 (0.0526)	12131 (0.2646)
max. and min. transmission	0.9176 and 0.6855	0.9493 and 0.6588	0.9472 and 0.7945
data/restraints/parameters	3970 / 0 / 226	69187 / 0 / 379	12131 / 0 / 581
goodness of fit on F^2	1.051	1.052	0.960
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0417	R_1 = 0.0943	R_1 = 0.1027
	wR_2 = 0.1248	wR_2 = 0.2600	wR_2 = 0.2069
R indices (all data)	R_1 = 0.0480	R_1 = 0.1181	R_1 = 0.2394
	wR_2 = 0.1411	wR_2 = 0.2787	wR_2 = 0.2551
largest difference in peak and hole (e Å^{-3})	1.362 and −0.649	1.045 and −1.726	1.051 and −0.631

Table 2. Selected bond lengths and angles (^{o}) for **1**-**3**

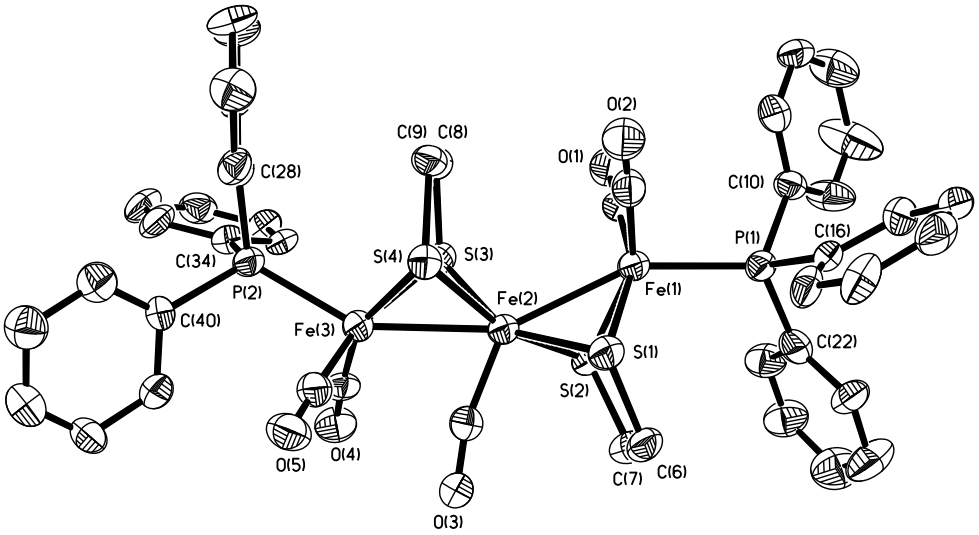
	1	**2**	**3**
Fe(1)-Fe(2)	2.5385(8)	2.546(2)	2.547(2)
Fe(2)-Fe(3)	2.5655(8)	2.584(2)	2.546(2)
Fe(1)-P(1)		2.244(3)	2.250(3)
Fe(3)-P(2)			2.251(3)
Fe(1)-S(1)	2.263(1)	2.249(3)	2.249(3)
Fe(1)-S(2)	2.252(1)	2.261(3)	2.257(3)
Fe(2)-S(1)	2.241(1)	2.258(3)	2.226(3)
Fe(2)-S(2)	2.235(1)	2.256(3)	2.248(3)
Fe(2)-S(3)	2.215(1)	2.210(3)	2.239(3)
Fe(2)-S(4)	2.216(1)	2.198(3)	2.269(3)
Fe(3)-S(3)	2.238(1)	2.238(3)	2.270(3)
Fe(3)-S(4)	2.237(1)	2.238(3)	2.281(3)
Fe(1)-Fe(2)-Fe(3)	151.74(3)	151.83(7)	151.50(6)
Fe(1)-S(1)-Fe(2)	68.62(3)	68.79(8)	69.39(9)
Fe(1)-S(2)-Fe(2)	68.90(3)	68.61(9)	68.87(8)
Fe(2)-S(3)-Fe(3)	70.36(3)	71.05(9)	68.74(8)
Fe(2)-S(4)-Fe(2)	70.37(4)	71.26(8)	68.05(8)
Fe(2)-Fe(1)-P(1)		150.27(9)	154.11(8)
Fe(2)-Fe(3)-P(2)			151.03(8)
Fe(2)-C-O	167.6(4)	167.7(9)	168.2(8)
Fe(2)-C	1.765(4)	1.762(11)	1.751(10)
Fe…C	2.576(4)	2.612(11)	2.566(10)



ORTEP of **1**



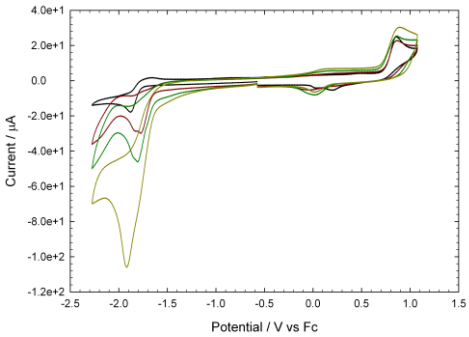
ORTEP of **2**


C(28)
C(34)
P(2)
C(40)
C(9)
C(8)
S(4)
S(3)
Fe(3)
Fe(2)
O(5)
O(4)
O(3)
O(2)
O(1)
Fe(1)
S(1)
S(2)
C(7)
C(6)
C(10)
P(1)
C(16)
C(22)

ORTEP of **3**

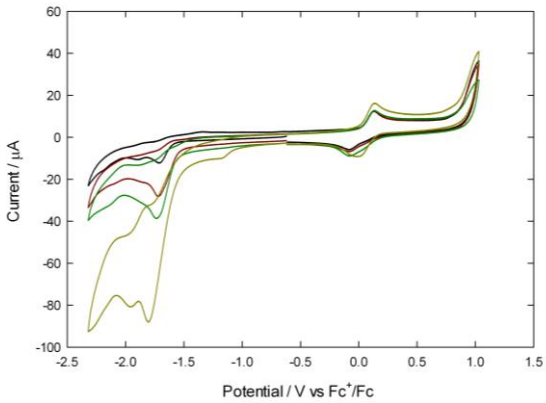
3. Cyclic voltammetry - Electrochemistry was carried out in deoxygenated dichloromethane (DCM) solution with 0.1 M $TBAPF_6$ as supporting electrolyte. The working electrode was a 3 mm diameter glassy carbon electrode which was polished with 0.3 µm alumina slurry prior to each scan. The counter electrode was a Pt wire and the quasi-reference electrode was a silver wire. All CVs were referenced to the Fc/Fc^+ redox couple. An Autolab potentiostat (EcoChemie, Netherlands) was used for all electrochemical measurements. Catalysis studies were carried out by adding equivalents of HBF_4-Et_2O or acetic acid (both from Sigma-Aldrich).

Cyclic voltammetry of (µ-edt)$Fe_2(CO)_6$



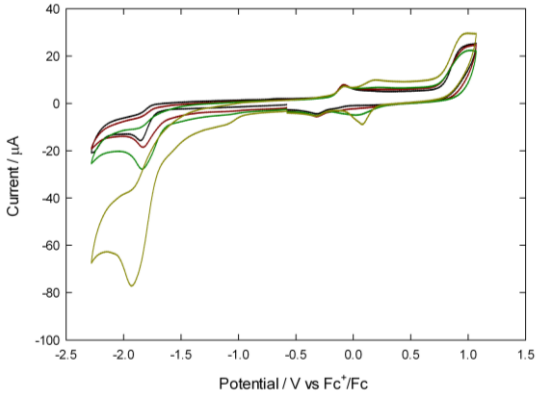
CV of 0.5 mM di-iron hexacarbonyl complex, (µ-edt)$Fe_2(CO)_6$ in 0.1 M $TBAPF_6$ in DCM under Ar, GC electrode, scan rate 100 mV s^{-1}. Black = neutral complex (no protons); brown = 1 equivalent HBF_4; green = 2 equivalents HBF_4; light green = 10 equivalent HBF_4.

Cyclic voltammetry of Fe_3(µ-edt)$_2(CO)_5PPh_3$ (2)



CV of 0.5 mM Fe_3(µ-edt)$_2(CO)_5PPh_3$ in 0.1 M $TBAPF_6$ in DCM under Ar, GC electrode, scan rate 100 mV s^{-1}. Black = neutral complex (no protons); brown = 1 equivalent HBF_4; green = 2 equivalents HBF_4; light green = 10 equivalent HBF_4.

Cyclic voltammetry of $Fe_3(\mu\text{-edt})_2(CO)_4(PPh_3)_2$ (3)



CV of 0.5 mM $Fe_3(\mu\text{-edt})_2(CO)_4(PPh_3)_2$ in 0.1 M $TBAPF_6$ in DCM under Ar, GC electrode, scan rate 100 mV s^{-1}. Black = neutral complex (no protons); brown = 1 equivalent HBF_4; green = 2 equivalents HBF_4; light green = 10 equivalent HBF_4.

4. Parameters for DigiSim Simulation

Simulation of the first catalytic response of complex **1** in the presence of HBF_4 was carried out using DigiSim version 3.0. The reaction scheme is shown in the main document. The specific parameters used are listed below:

Charge transfer reactions:

$\mathbf{1} + e^- = \mathbf{1}^-$	$E^0 = -1.5$ V	$\alpha = 0.5$	k = 1 cm/s
$\mathbf{1}H + e^- = \mathbf{1}H^-$	$E^0 = -1.4$ V	$\alpha = 0.5$	k = 1 cm/s

Homogeneous chemical reactions:

$\mathbf{1}^- + H^+ = \mathbf{1}H$	$K = 1 \times 10^{10}$	$k_f = 1 \times 10^5$
$\mathbf{1}H^- + H^+ = \mathbf{1} + H_2$	$K = 1 \times 10^{10}$	$k_f = 3000$
$\mathbf{1}^-$ = product (electroinactive)	$K = 1 \times 10^4$	$k_f = 50$

Experimental parameters:

$\nu = 0.1$ V/s T = 298 K $R_u = 0\ \Omega$ $C_{dl} = 0$ F Electrode area = 0.07 cm^2

Species parameters:

All D = 1×10^{-5} cm^2/s

[**1**] = 0.5 mM

The value of $k_f = 10^5$ for the protonation of the anion was taken from reference [ESI5] for a similar system and the value of K for the protonation was estimated based on the relative pK_a of the proton source and the complex. The value of k_f for the elimination of H_2 was varied to fit the data.

References

[ESI1] *SMART Version 5.628*, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373, 2003.

[ESI2] *SAINT Version 6.36A*, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373, 2002.

[ESI3] G. M. Sheldrick, *SADABS Version 2.10*, University of Göttingen, 2003.

[ESI4] “A short history of SHELX". G. M. Sheldrick, Acta Cryst. A64, 112 (2008).

[ESI5] J. F. Capon, S. Ezzaher, F. Gloaguen, F. Y. Petillon, P. Schollhammer, J. Talarmin, Chem. Eur. J., 2008, 14, 1954.