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An insight into the protonation property of a diiron azadithiolate complex pertinent to the active site of Fe-only hydrogenases

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Experimental Section

Instrumentation. Infrared spectra were recorded on a JASCO FT/IR 430 spectrophotometer. ^{1}H NMR spectra were collected on a Varian INOVA 400NMR instrument. Mass spectra were performed by electro-spray ionization (ESI) on an HP1100 MSD instrument and TOF-ESI-MS on an HPLC-Q-TOF MS (Micromass) mass spectrometer. Elemental analyses were performed on a THERMOQUEST-FLASH EA 1112 elemental analyzer.

Synthesis of [{(μ-SCH_2)$_2$N(C_6H_4-*p*-NO_2)}{Fe(CO)$_2$(PMe_3)}$_2$] (2). Trimethylphosphine (4.0 mL, 1.0 M in THF) was dropped to the toluene solution (50 mL) of **1** (0.5 g, 0.98 mmol) under N_2. The mixture was stirred at 60 °C until the reaction was completed (monitored by IR spectra). After removal of solvent in vacuo, the purple brown residue was purified by column chromatography on silicon gel with toluene as eluent. Recrystallization of the crude product from CH_2Cl_2/hexane (1/5, v/v) gave **2** as red brown crystals (0.45 g, 76%). Elemental analysis (%) calcd for $C_{18}H_{26}Fe_2N_2O_6P_2S_2$: C, 35.78, H, 4.34, N, 4.64; found: C, 35.55, H, 4.25, N, 4.78; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (s, P(CH_3)$_3$, 18H), 4.20 (br s, SCH_2, 4H), 6.68 (br s, C_6H_4-*p*-NO_2, 2H), 8.14 ppm (br s, C_6H_4-*p*-NO_2, 2H); ^{31}P{^{1}H} NMR (400 MHz, CH_3CN): δ = 27.19 ppm; IR (CH_3CN): nu(tilde) = 1985 (m), 1949 (s), 1906 (s) cm^{-1} (CO).

[**2**(FeHFe)]$^{+}$[PF_6]$^{-}$: Concentrated HCl (4.0 mL, 12 M) was added dropwise to the solution of **2** (0.5 g, 0.83 mmol) in CH_2Cl_2/EtOH (2 mL/15 mL). The solution turned deep red after stirred for 10 min, to which was added a few drops of saturated aqueous NH_4PF_6 solution. The red orange solid was filtrated, washed with water and ether successively, and dried in vacuo. The μ-hydride diiron complex [**2**(FeHFe)]$^{+}$[PF_6]$^{-}$ was obtained in a yield of 57% (0.42 g). Crystals suitable for an X-ray diffraction studies were obtained by slowly diffusion of Et_2O to the CH_3CN/CH_2Cl_2 (1/15, v/v) solution of [**2**(FeHFe)]$^{+}$[PF_6]$^{-}$. Elemental analysis (%) calcd for $C_{18}H_{27}F_6Fe_2N_2O_6P_3S_2$: C, 28.82, H, 3.63, N, 3.73; found: C, 28.70, H, 3.58, N, 3.82; ^{1}H NMR (400 MHz, CD_3CN): δ = −15.02 (t, J_{PH} = 21.7 Hz, FeHFe, 1H), 1.56 (d, J_{PH} = 10.6 Hz, $P(CH_3)_3$, 18H), 4.64 (m, SCH_2, 4H), 7.06 (d, J_{HH} = 9.2 Hz, C_6H_4-*p*-NO_2, 2H), 8.17 ppm (d, J_{HH} = 9.2 Hz, C_6H_4-*p*-NO_2, 2H); ^{31}P{^{1}H} NMR (400 MHz, CH_3CN): δ = 22.52 (s, $P(CH_3)_3$), −143.54 ppm (m, PF_6^-); IR (CH_3CN): nu(tilde) = 2035 (s), 1995 (s) cm^{-1} (CO); ESI-MS (*m/z*): calcd for [M – PF_6^-]$^{+}$: 604.9; found: 604.9 (100%).

Synthesis of [2(SH)]$^{+}$[OTf]$^{-}$. The addition of 4 equiv of HOTf to the $CHCl_3$ solution (2 mL) of **2** (0.2 g, 0.33 mmol) afforded an orange paste, which was quickly washed with O_2-free $CHCl_3$ and dried in vacuo. [**2**(SH)]$^{+}$[OTf]$^{-}$ was obtained in a yield of ca. 31% (77 mg), contaminated with a small amount of μ-hydride complex (ca. 20% according to the integrations of the signals in the ^{1}H NMR spectrum). ^{1}H NMR (400 MHz, CD_3CN): δ = 1.50 (d, J_{PH} = 14.0 Hz, $P(CH_3)_3$, 18H), 3.05 (s, μ-SH, 1H), 5.39 (br s, SCH_2, 2H), 6.66 (br s, SCH_2, 2H), 7.61 (br s, C_6H_4-*p*-NO_2, 2H), 8.31 ppm (br s, C_6H_4-*p*-NO_2, 2H); ^{31}P{^{1}H} NMR (400 MHz, CH_3CN): δ = −1.09 ppm; IR (CH_3CN): nu(tilde) = 2112 (s), 2075 (s) cm^{-1} (CO); HR-ESI-MS (*m/z*): calcd for [M – OTf^-]$^{+}$: 604.9485; found: 604.9496 (100%).

Table 1. Crystallographic data and processing parameters for complexes **2** and [**2**(FeHFe)]$^+$

Complex	**2**	[**2**(FeHFe)]$^+$
Empirical formula	$C_{18}H_{26}Fe_2N_2O_6P_2S_2$	$C_{18}H_{27}F_6Fe_2N_2O_6P_3S_2$
M_w	604.17	750.2
T (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P2(1)/n$
a (Å)	13.248(3)	11.3070(6)
b (Å)	14.676(3)	14.1755(5)
c (Å)	15.028(3)	18.9123(9)
α (°)	64.96(3)	90.00
β (°)	82.40(3)	104.846(3)
γ (°)	82.83(3)	90.00
V (Å^3)	2616.4(9)	2930.1(2)
Z	4	4
ρ_{calc} (g cm^{-3})	1.534	1.700
$F(000)$	1240	1520
Crystal size (mm^3)	0.25 x 0.20 x 0.20	0.25 x 0.20 x 0.20
$\theta_{min/max}$ (°)	3.0/27.46	1.82/28.28
Reflns collected/unique	11823 / 7847	7212 / 4388
Parameters refined	577	356
Goodness-of-fit on F^2	1.061	0.990
Final $R1$ [$I > \sigma(I)$]	0.0485	0.0531
Final $wR2$	0.1174	0.1382
Residual electron density (e Å^{-3})	0.680, -0.401	1.536, -0.944

Table 2. Selected bond lengths (Å) and angles (°) for complex **2**

Bond lengths		Bond angles	
Fe(1)–Fe(2)	2.5671(10)	S(1)–Fe(2)–Fe(1)	55.48(3)
Fe(1)–S(1)	2.2633(11)	S(1)–Fe(1)–Fe(2)	55.38(3)
Fe(1)–S(2)	2.2679(14)	S(2)–Fe(2)–Fe(1)	55.56(4)
Fe(2)–S(1)	2.2606(12)	S(2)–Fe(1)–Fe(2)	55.44(4)
Fe(2)–S(2)	2.2644(12)	Fe(2)–S(1)–Fe(1)	69.15(4)
N(1)–C(11)	1.432(5)	P(1)–Fe(1)–Fe(2)	114.81(5)
N(1)–C(12)	1.423(5)	P(2)–Fe(2)–Fe(1)	112.22(4)
N(1)–C(13)	1.389(5)	C(11)–N(1)–C(13)	121.9(3)
Fe(1)–P(1)	2.2124(15)	C(11)–N(1)–C(12)	113.6(3)
Fe(2)–P(2)	2.2427(12)	C(12)–N(1)–C(13)	122.2(3)
Fe(3)–Fe(4)	2.5280(14)	Fe(3)–S(4)–Fe(4)	67.31(5)
Fe(3)–S(3)	2.2706(14)	Fe(3)–S(3)–Fe(4)	67.66(5)
Fe(3)–S(4)	2.2705(13)	P(3)–Fe(3)–Fe(4)	116.16(5)
Fe(4)–S(3)	2.2704(13)	P(4)–Fe(4)–Fe(3)	151.51(5)
Fe(4)–S(4)	2.2911(14)	C(31)–N(3)–C(30)	120.3(3)
N(3)–C(29)	1.450(5)	C(31)–N(3)–C(29)	122.6(4)
N(3)–C(30)	1.430(5)	C(30)–N(3)–C(29)	114.6(3)
N(3)–C(31)	1.393(5)		
Fe(3)–P(3)	2.2138(14)		
Fe(4)–P(4)	2.2324(16)		

Table 3. Selected bond lengths (Å) and angles (°) for complex [**2**(FeHFe)]$^{+}$[PF_6]$^{-}$

Bond lengths		Bone angles	
Fe(1)–Fe(2)	2.5879(8)	Fe(2)–Fe(1)–H(1)	42.9(15)
Fe(1)–H(1)	1.72(5)	Fe(1)–Fe(2)–H(1)	41.5(16)
Fe(2)–H(1)	1.77(5)	S(1)–Fe(1)–Fe(2)	54.90(3)
Fe(1)–S(1)	2.2845(12)	S(2)–Fe(1)–Fe(2)	55.52(3)
Fe(1)–S(2)	2.2614(11)	S(2)–Fe(2)–Fe(1)	54.95(3)
Fe(2)–S(2)	2.2772(13)	S(1)–Fe(2)–Fe(1)	55.71(3)
Fe(2)–S(1)	2.2622(12)	P(2)–Fe(2)–Fe(1)	111.50(4)
Fe(1)–C(1)	1.784(5)	P(1)–Fe(1)–H(1)	79.8(15)
Fe(1)–C(2)	1.795(5)	S(2)–Fe(1)–H(1)	79.7(15)
Fe(1)–P(1)	2.2428(12)	S(1)–Fe(1)–H(1)	88.5(15)
Fe(2)–C(3)	1.793(5)	C(4)–Fe(2)–H(1)	81.0(15)
Fe(2)–C(4)	1.785(4)	C(3)–Fe(2)–H(1)	174.1(15)
Fe(2)–P(2)	2.2551(13)	P(2)–Fe(2)–H(1)	89.8(15)
N(1)–C(12)	1.434(6)	S(1)–Fe(2)–H(1)	88.1(15)
N(1)–C(11)	1.441(7)	S(2)–Fe(2)–H(1)	78.4(16)
N(1)–C(13)	1.382(6)	C(13)–N(1)–C(12)	124.2(4)
		C(13)–N(1)–C(11)	121.4(4)
		C(11)–N(1)–C(12)	114.3(4)