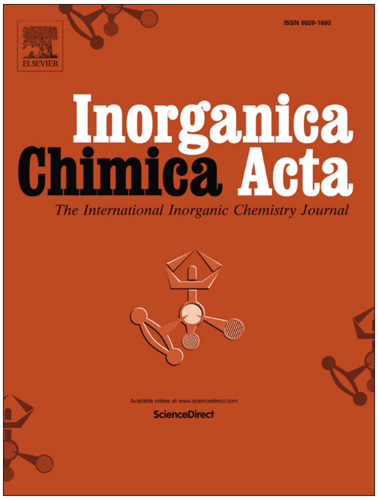

Structural and HER Studies of Diphosphine-Monothiolate Complexes $[Fe_2(CO)_4(\mu\text{-naphthalene-2-thiolate})_2(\mu\text{-dppe})]$ and $[Fe_2(CO)_4(\mu\text{-naphthalene-2-thiolate})_2(\mu\text{-DPEPhos})]$

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Structural and HER Studies of Diphosphine-Monothiolate Complexes [$Fe_2(CO)_4$(μ-naphthalene-2-thiolate)$_2$(μ-dppe)] and [$Fe_2(CO)_4$(μ-naphthalene-2-thiolate)$_2$(μ-DPEPhos)]

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Abstract

Two new compounds [$Fe_2(CO)_4$(μ-naphthalene-2-thiolate)$_2$(μ-dppe)] **1** and [$Fe_2(CO)_4$(μ-naphthalene-2-thiolate)$_2$(μ-DPEPhos)] **2** with chelating phosphine ligands were synthesized and characterized {dppe = 1,2-Bis(diphenylphosphino)ethane and DPEPhos = (Oxydi-2, 1-phenylene)bis(diphenylphosphine)}. The bridging coordination mode of the diphosphine ligand in complex **1** was confirmed by X-ray crystallography. Complexes **1** and **2** were further evaluated as catalysts for the hydrogen evolution reaction (HER) by electrochemical investigations. Complex **1** showed better stability whereas complex **2** degraded in presence of acids.

Keywords: Diphosphine • Electrocatalysis • Hydrogenases • Iron • Proton reduction

1. Introduction

The reversible processes between protons/electrons and molecular hydrogen are known to be catalyzed by the hydrogenase (H_2ase) enzymes [1]. Among the hydrogenase enzymes known ([NiFe], [FeFe] and Hmd hydrogenase), the hydrogen production capability of the [FeFe]-H_2ase enzyme is 6000-9000 molecules of hydrogen per second at 30 °C and this is greater than the other two hydrogenases [2, 3]. Inspired by the [Fe_2S_2] core known to be present in the structure of the [FeFe]-H_2ase active site [4−8], chemists have carried out intensive studies on aliphatic and aromatic dithiolate-bridged complexes over the past few decades [9]. Examples reported so far include all carbonyl iron complexes and complexes in which one or more of the CO ligands have been replaced with electron-donating ligands. Substitution with basic ligand(s) has been related to the creation of an electron-rich site for the coordination of the proton(s), which is considered to be an essential step in the electrocatalytic reduction of protons to H_2. Among the electron-donating ligands, the phosphines have received special attention as they are considered to be good substitutes for the CN^- ligands present in the enzyme active site [10].

A number of diiron complexes with bidentate phosphines have been studied as structural and/or functional mimics [10, 11, 12] since the pioneering work by Tye, Hall and Darensbourg suggesting that creating asymmetry at the diiron centers in the models was preferable [11b]. The bidentate phosphines can however, bind in the chelating or bridging mode depending on the nature of the diphosphine backbone and reaction conditions [11d]. The chelate coordination mode of the phosphines can lead to the formation of different isomers (dibasal and apical-basal) for the [FeFe] complexes while the bridging mode is known to form only the cisoid-dibasal isomer [13].

Though examples of complexes with dithiolates are known for the bridging coordination mode of the diphosphines [10, 14], complexes [$Fe_2(\mu\text{-}SC_6F_5)_2(\mu\text{-}dppm)(CO)_4$] **a′** [15], [$Fe_2(\mu\text{-}SR)_2(\mu\text{-}dppm)(CO)_4$] (R= $(CH_2)_3OH$, **b'**; = SMe, **c'**; = Ph, **d'**; = *p*-tol, **e'**) (dppm = bis(diphenylphosphino)methane) [12a, 16] with monothiolate ligands have been reported only as structural mimics (Figure 1). The solely studied complexes are either the all carbonyl or the monodentate phosphine substituted bis(monothiolate) Fe complexes [15,17].

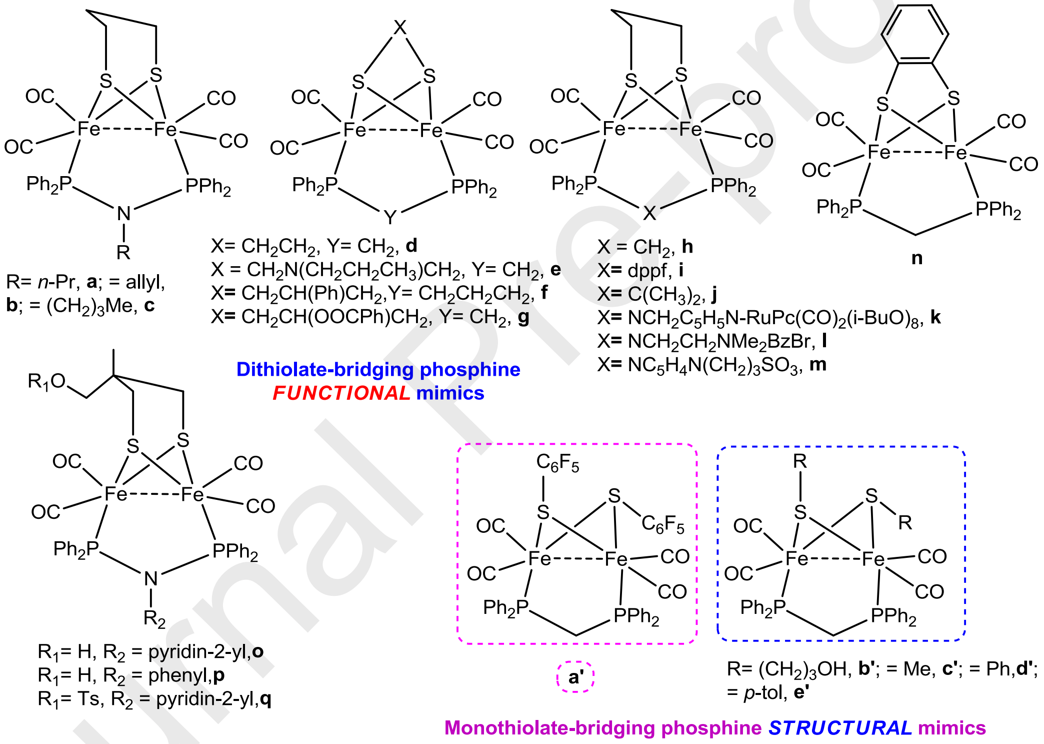


Figure 1. Selected thiolate-bridged complexes reported with bridging coordination mode of diphosphines (**a-q** studied for HER; **a′-e′** are only structural mimics).

Hence, we were interested in studying the reaction of the monothiolate-bridged starting complex [$Fe_2(CO)_6(\mu\text{-naphthalene-2-thiolate})_2$] **A** with two different diphosphine ligands dppe [1,2-bis(diphenylphosphino)ethane] and DPEPhos [(Oxydi-2, 1-phenylene)bis(diphenylphosphine)]. The purpose was to study the influence of two different diphosphines (with different bite angles) in forming chelating or bridging phosphine complexes with monothiolates. Also, complex **2** was designed to explore the possibility of the ‘O’ heteroatom in the DPEPhos ligand to act as a pendant site for proton attachment during the catalytic process. Though a number of examples of dithiolate-bridged complexes are known with ligands (mostly -NR) acting as proton relay there is hardly any report with Fe-monothiolates [13, 18]. The two new complexes $[Fe_2(CO)_4(\mu\text{-naphthalene-2-thiolate})_2(\mu\text{-dppe})]$ **1** and $[Fe_2(CO)_4(\mu\text{-naphthalene-2-thiolate})_2(\mu\text{-DPEPhos})]$ **2** thus, obtained were further studied as catalysts for the reduction of protons to hydrogen using acetic acid (AA) and trifluoroacetic acid (TFA).

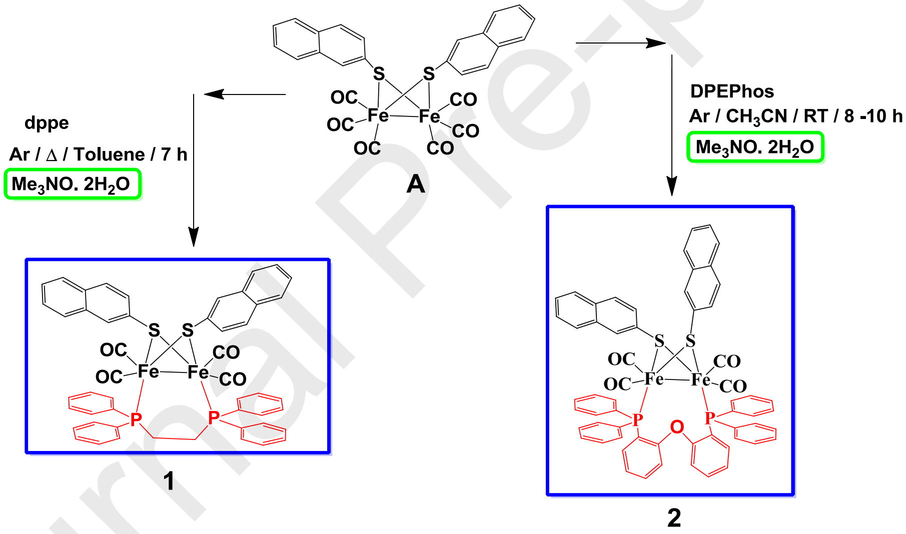
2. Results and Discussion

2.1. Preparation and structural characterization

Complex $[Fe_2(CO)_6(\mu\text{-naphthalene-2-thiolate})_2]$ **A** was prepared as reported in the literature [17f]. During the synthesis of **A**, a violet-colored triiron cluster $[Fe_3(\mu_3\text{–}S)_2(CO)_9]$ was obtained as a byproduct, also reported earlier [19]. The byproduct formed in higher yields when the reaction was carried out in tetrahydrofuran (THF) but in toluene only **A** was obtained. Reaction of complex **A** under argon atmosphere with the chelating diphosphine ligands, dppe in toluene (reflux, 7-8 h) and DPEPhos in acetonitrile (stirring at room temperature, 8-10 h) led to the production of two new compounds **1** and **2**, respectively (Scheme 1).The complexes were purified by column/flash chromatography and re-crystallized from dichloromethane-hexane solution leading to orange-red and red products, respectively. Complex **1** was obtained in low yields when the reaction was carried out in refluxing toluene without $Me_3NO.2H_2O$ or in acetonitrile with

$Me_3NO.2H_2O$. In contrast, the yields for complex **2** were low on carrying out the reaction in refluxing toluene. The bridging phosphine complex was always the product irrespective of the reaction conditions used.

Characterization of the new complexes **1** and **2** was carried out by Mass, NMR, FTIR and UV-Vis spectroscopic techniques. The FTIR spectra in CH_2Cl_2 for complexes **1** and **2** displayed ν_{CO} absorption vibrations (corresponding to terminal carbonyls) in the range 1990-1880 cm^{-1} (see supporting information). The values are shifted towards lower wavenumbers (~85 and 90 cm^{-1}) in comparison to complex **A** (2070-2000 cm^{-1}) (Table 1).



Scheme 1. Schematic diagram for the synthesis of targeted complexes **1** and **2**.

Moreover, the ν_{CO} bands are within the range reported for comparable complexes (Table 1) [10]. The greater shift in the ν_{CO} frequencies in comparison to complex **A** or other reported complexes with monodentate phosphines [15,17a-i] is due to the attachment of the diphosphine ligands in the bridging coordination mode.

Table 1. FTIR data for complexes **1** and **2** in CH_2Cl_2.

	Wavenumber [cm^{-1}]	Ref
[$Fe_2(CO)_4$(μ-naphthalene-2-thiolate)$_2$(μ-dppe)] **1**	1990, 1948, 1912	Present work
[$Fe_2(CO)_4$(μ-naphthalene-2-thiolate)$_2$(μ-DPEPhos)] **2**	1985, 1945, 1921, 1887	Present work
[$Fe_2(CO)_6$(μ-naphthalene-2-thiolate)$_2$] **A**	2075, 2039, 2001	17f
[$Fe_2(CO)_5$(μ-naphthalene-2-thiolate)$_2$(P(PhOMe-*p*)$_3$)]	2050, 1990, 1960	17h
[$Fe_2(CO)_4$(μ-dppe)(μ-pdt)]	1990, 1953, 1920,1902	10
[$Fe_2(CO)_4$(μ-dppm)(μ-bdt)] **n**	1995, 1965, 1932, 1915	14a
[Fe_2(μ-SC_6F_5)$_2$(μ-dppm)$(CO)_4$] **a′**	2007, 1981, 1948, 1926	15
[Fe_2(μ-$S(CH_2)_3OH$)$_2$(μ-dppm)$(CO)_4$] **b′**	1985, 1955, 1920, 1903	16a

The ^{1}H NMR spectrum of **1** in $CDCl_3$ displayed peaks in the aromatic region (7.2−8.3 ppm) for the phenyl rings of dppe and naphthyl ring protons, in addition to peaks between 2.4−2.5 ppm for -CH_2- protons of dppe (see supporting information). A singlet at 62.3 ppm in the ^{31}P {^{1}H} NMR spectrum of **1**, similar to that observed for the dithiolate-bridged complex [$Fe_2(CO)_4$(μ-dppe)(μ-pdt)] (60.5 ppm) [10] further confirmed the binding of dppe ligand in the bridging mode. The ^{1}H NMR spectrum of **2** displayed peaks between 6.3–8.5 ppm for the protons of naphthalene thiol and DPEPhos ligand (see supporting information). Complex **2** displayed two peaks at 62.2 and 60.3 ppm in the ^{31}P {^{1}H} NMR spectrum, which could be due to the inequivalence of the two phosphorus nuclei in solution resulting from the highly flexible diphosphine allowing the two ends to have slightly different orientations with respect to the two thiolate ligands (see supporting information) [14h, 17g] .

The UV-Vis spectra of complexes **1** and **2** were recorded in acetonitrile (see supporting information). The bands for **1** and **2** were further red-shifted in comparison to complex **A** and the previously reported complex [$Fe_2(CO)_5$(μ-naphthalene-2-thiolate)$_2$(P(PhOMe-*p*)$_3$)] [17h] because of greater electron densities at both the Fe centres (Table S1).

The low stability of complex **2** in solution was confirmed by UV measurements (see supporting information). Further, attempts to obtain single crystals for complex **2** were not successful.

*2.2. X-ray crystal structure analysis of complex**1***

Single crystals for complex **1** were obtained from hexane-dichloromethane solution at low temperature. The molecular structure of complex **1** is illustrated in Figure 2. The crystallographic details of the complex are given in Table 2. For selected bond distances (Å) and angles (°) see supporting information.

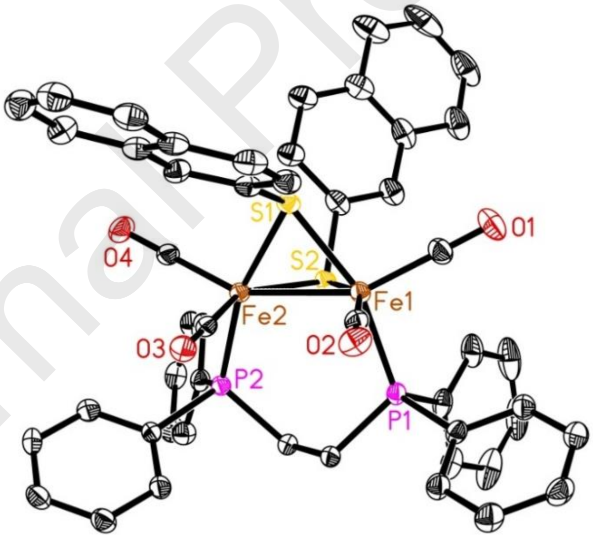


Figure 2. Molecular structure of complex [$Fe_2(CO)_4$(μ-naphthalene-2-thiolate)$_2$(μ-dppe)] **1**. Displacement ellipsoids correspond to 30% probability and hydrogen atoms have been omitted for clarity.

Complex **1** crystallized in the monoclinic space group $P2_1/c$ with a butterfly structure of the Fe_2S_2 core and the naphthyl groups in anti-position. The diphosphine ligand occupied the cisoid basal/basal position and bridged the two Fe fragments. A torsion angle P1-Fe1-Fe2-P2 of -4.29(4)° was observed. The distance between the two Fe centers in complex **1** was 2.5435(7) Å which is in range of the value known for the [FeFe] hydrogenase enzyme (2.6 Å) [6] and similar to the values reported for analogous complexes (Table S3) [10, 14f, 14g].

Table 2. Crystallographic details of complex **1**.

	1
Formula sum	$C_{50}H_{38}Fe_2O_4P_2S_2$
Formula weight	940.56
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	18.9602(4)
b (Å)	11.0683(3)
c (Å)	20.8501(5)
α (°)	90
β (°)	95.1797(15)
γ (°)	90
V (Å^3)	4357.67(18)
T (K)	150 (2)
Z	4
F_{000}	1936
GOF on F^2	1.007
ρ_{calcd} (g cm^{-3})	1.434
No. of reflections measured	32848
No. of independent reflections (R_{int})	7566 (R_{int} = 0.085)
No. of observed reflections [$I > 2\sigma(I)$]	5867
No. of parameters	493
R_1 [$I > 2\sigma(I)$]	0.0450
wR_2 [all data]	0.1149

The two Fe–P bond distances (Fe1–P1 = 2.2187(10) and Fe2-P2 = 2.2098(9) Å) and the P-Fe-Fe bond angles (P1–Fe1–Fe2 = 104.19(3) and P2–Fe2–Fe1 = 108.79(3)^o). However, the slight difference in the Fe-S/Fe-P bond distances and Fe-Fe-P bond angles in complex **1** compared to reported dppe-dithiolate complexes [$Fe_2(CO)_4$(μ-$SCH_2N(C_6H_4CO_2Me$-*p*)CH_2S)(μ-dppe)] [14f], [$Fe_2(CO)_4$(μ-$SCH_2N(^iPr)CH_2S$)(μ-dppe)] [14g] and [$Fe_2(CO)_4$(μ-pdt)(μ-dppe] [10] could be due to less steric hindrance in the monothiolate complex **1** (Table S3).

*2.3. Electrochemical and electrocatalytic studies of complexes **1** and **2***

The cyclic voltammograms (CVs) for complexes **1** and **2** were studied in acetonitrile under argon with $^nBu_4NPF_6$as the supporting electrolyte (Table 3). The CVs for **1** and **2** exhibited two irreversible one-electron reduction waves at E_{pc} = –1.96, –2.33 and –1.74, –1.94 V, respectively (see Figure 3 and supporting information). Oxidations peaks were observed at 0.35, 0.73 (**1**) and 0.36, 1.13 V (**2**). The reductions for complex **1** and **2** occurred at more negative potentials than **A** [17f] or the monodentate phosphine substituted complexes due to removal of two CO ligands [15, 17a, 17f-i]. Chemical steps or rearrangements might be involved as the reductions in the absence of acid were irreversible. CVs for complex **1** were also recorded at different scan rates (0.025–1 Vs^{-1}). Linear plots for i_p (current of the reduction peak) *vs*. square root of scan rate indicate that the reduction processes were diffusion-controlled (see supporting information) [20, 21]. Complexes **1** and **2** were further probed as electrocatalysts for the reduction of protons to molecular hydrogen in the presence of acids of varying strengths acetic acid (AA) and trifluoroacetic acid (TFA) (Figures 4 and 5) (Table 3).

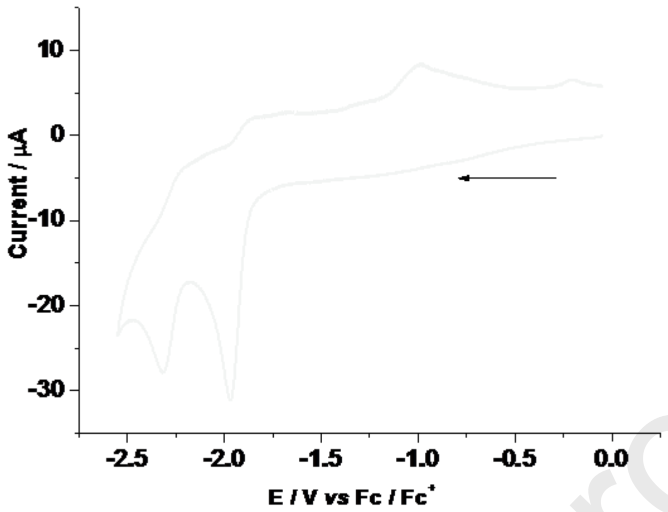


Figure 3. Cyclic voltammogram for complex **1** (0.638 mM) in acetonitrile (scan rate 0.1 Vs^{-1}).

With the addition of AA complex **1** showed two new peaks at –1.88 and –2.28 Vat lower acid concentrations (Figure 4). The first peak is anodically shifted while the second peak shifted cathodically with increase in current height on subsequent addition of acid. The current height for the first peak at -1.88 V did not increase on further acid additions indicating the formation of an intermediate. The currents stabilized with the addition of upto101 mM of acetic acid (AA). Electrochemical investigations for complex **1** with TFA showed different results (Figures S9 and 5). On initial addition of acid (1.2 mM) a new peak appeared at -1.74 V (Figure S9). With further acid additions, the complex reduction peaks disappeared with two new peaks (–1.82 and –2.05 V) on addition of 17 mM of acid (Figure 5). At higher acid concentrations, the peaks shifted cathodically, and levelled off with 78.26 mM of acid. Furthermore, the peak-type catalytic currents and the appearance of two catalytic peaks have been associated with disturbances in the diffusion layer and homoconjugation processes involving TFA [22].

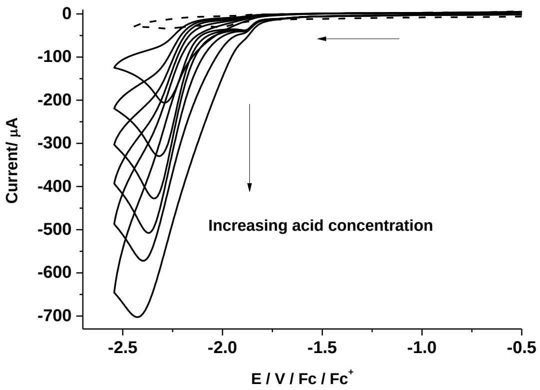


Figure 4. Cyclic voltammograms for complex **1** (0.638 mM) (- - -) and complex **1** with AA (—) (6.95, 13.86, 20.75, 27.62, 34.45, 48.05 mM) at 0.1 Vs^{-1}.

In comparison to complex **1**, complex **2** did not show catalysis with AA but showed small current increase on adding upto ~23 mM TFA. Hence, detailed catalytic studies were not performed for complex **2**.

Table 3. Electrochemical data of complexes **1**, **2** and similar reported complexes in CH_3CN (scan rate, 0.1 Vs^{-1}).

Complex	*HER*	E_{pc}/ V	E_{pa}/ V	Acid	E_{cat}/ V	OP^a / V	Ref
$[Fe_2(CO)_4$(μ-naphthalene-2-thiolate)$_2$(μ-dppe)] **1**	Active	-1.96 -2.33	0.35 0.73	AA	-2.28	-0.82	Present work
	Active	-	-	TFA	-1.98	-1.09	Present work
$[Fe_2(CO)_4$(μ-naphthalene-2-thiolate)$_2$(μ-DPEPhos)] **2**	-	-1.74 -1.94	0.36 1.13	-	-	-	Present work
$[Fe_2(CO)_6$(μ-naphthalene-2-thiolate)$_2$] **A**	Active	- 1.33	0.61	AA	- 2.00	-0.54	17f
$[Fe_2(CO)_5$(μ-naphthalene-2-thiolate)$_2$(P(PhOMe-*p*)$_3$)]	Active	-1.66 -2.37	0.29 1.00	AA	-2.02	-0.56	17h

[a]Overpotential (η)

Also curve crossing was seen for the reverse scans that can be related to plausible electrodeposition and nucleation of the complex on the glassy carbon surface, however, it may not always be the case [23]. CVs measured for only solvent, solvent with acid and solvent with acid and complexes indicate that the enhanced currents were due to catalysis (see supporting information).

The plots of i_{cat}/i_p *vs*. [acid] for complex **1** with AA and TFA are shown in supporting information. For the i_{cat} *vs*. [acid] and i_{cat} *vs*. scan rate plots see supporting information. The linear i_{cat} *vs.* [catalyst] plot indicates first order reaction with respect to [catalyst] (see supporting information). The catalytic efficiency (C.E.) for complex **1** in AA (0.55 to 0.21) and TFA (0.58 to 0.34) was determined using the formula described by Lichtenberger *et. al*. [24]. *TOF*s (s^{-1}) for complex **1** were calculated using the i_{cat}/i_p values at the maximum [acid] used (78 mM TFA, $i_{cat}/i_p = 42.6$, *TOF* = 352 and 101 mM AA, $i_{cat}/i_p = 35.7$, *TOF* = 247) [25].

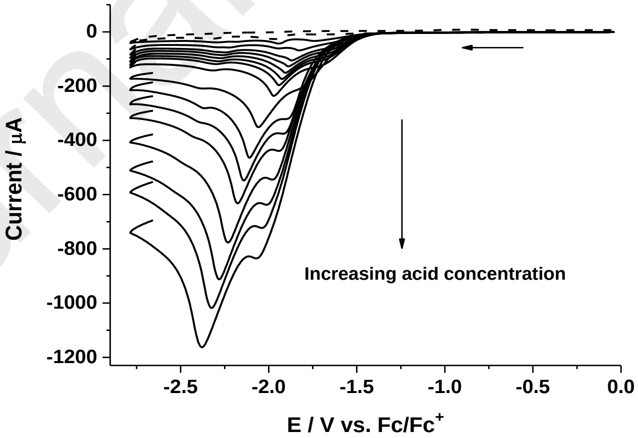


Figure 5. Cyclic voltammograms for complex **1** (0.638 mM) (- - -) and complex **1** with TFA (—) (1.2, 2.39, 3.58, 4.76, 5.94, 7.11, 8.28, 10.61, 17.48, 23.08, 28.57, 33.96, 44.44, 54.54, 64.28, 78.26 mM) at 0.1 Vs^{-1}. For clarity the reverse scans have been neglected.

Since the catalytic peaks with acetic acid are more negative than the neutral complex reduction peaks, the first step in the catalytic cycle is assumed to be reduction (electrochemical, E) of the neutral complex. This is followed by the protonation step (chemical, C) leading to a Fe–H intermediate. The second subsequent reduction (electrochemical, E) and protonation (chemical, C) is followed by hydrogen elimination [14k]. With TFA, the initial anodic shift of the peaks in comparison to the complex reduction peaks indicates a chemical first step (formation of hydride) [9c, 14c]. Also, since the current becomes independent after addition of certain amounts of acid, it can be assumed that elimination of hydrogen is the rate-limiting step [26]. The mechanism for HER has been speculated based on previously reported systems [9c, 14c]. The catalytic currents observed for complex **1** were higher than known examples [14b, 14m, 17h], indicating that the bridging dppe ligand provided additional stability to the complex.

3. Experimental Section

3.1. General Procedure

All the reactions were carried out under an oxygen-free argon environment using Schlenk techniques unless otherwise specified. Complex [$Fe_2(CO)_6$(μ-naphthalene-2-thiolate)$_2$] **A** was prepared according to the procedure reported in literature[17f]. All the anhydrous solvents (dichloromethane, acetonitrile, toluene), deuterated solvent ($CDCl_3$), *n*-Bu_4NPF_6 and starting materials were obtained from Sigma–Aldrich and used without further purification. The ^{1}H and ^{31}P NMR spectra were recorded on a JEOL 400 MHz NMR Spectrometer at room temperature in $CDCl_3$. The FTIR spectra of the samples were recorded on a Perkin-Elmer FTIR Spectrometer in CH_2Cl_2 over the range 400-4000 cm^{-1}, the UV-Vis spectra on an Avantes spectrometer system (diode-array spectrometer) and the elemental analysis was carried out with a Perkin-Elmer 240 C elemental analyzer.

3.2. Synthesis of [Fe$_2$(CO)$_4$(μ-naphthalene-2-thiolate)$_2$(μ-dppe)] **1**

Complex **A** (200 mg, 0.334 mmol), dppe (133.20 mg, 0.334 mmol) and trimethylamine N-oxide dihydrate ($Me_3NO.2H_2O$) (74.24 mg, 0.668 mmol) were refluxed in toluene (argon) for 7-8 h. The solvent was then removed by rotary evaporation. The residue was purified using a silica gel column. Elution with a mixture of hexane/dichloromethane (6:4 v/v) gave a light orange-red colored solution. Complex **1** was obtained as an air-stable light orange-red powder (65 mg, ~20 % yield) on removing the solvent. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.2−8.2 (m, 34H, aromatic protons), 2.45 ppm (m, 4H, PCH_2CH_2P). ^{31}P NMR (161.8 MHz, $CDCl_3$, 298 K): δ= 62.3 ppm (s, dppe). FTIR (CH_2Cl_2): $\tilde{v}$ = 1990 (s), 1948 (s) and 1912 (s) cm^{-1}. $C_{50}H_{38}Fe_2O_4P_2S_2$ (940.6 gmol^{-1}): Calcd. C 63.85, H 4.07, S 6.82; found C 63.57, H 4.13, S 6.78.ES-MS: m/z 941 [M+ H] (calcd 941).

3.3. Synthesis of[Fe$_2$(CO)$_4$(μ-naphthalene-2-thiolate)$_2$(μ-DPEPhos)] **2**

Precursor complex **A** (200 mg, 0.334 mmol), phosphine ligand DPEPhos (180.05 mg, 0.334 mmol) and decarbonylating agent trimethylamine N-oxide dihydrate ($Me_3NO.2H_2O$) (74.24 mg, 0.668 mmol) were stirredin acetonitrile at room temperature(argon) for 8-10 h. The solvent was then removed by rotary evaporation and the residue was purified using a silica gel column by flash chromatography. Elution with a mixture of hexane/dichloromethane (3:7 v/v) gave a red-colored solution. Complex **2** was obtained as a light-red powder (60 mg, ~17 % yield) after removal of solvent. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.3-8.5 (m, 42H, aromatic protons) ppm. ^{31}P NMR (161.8 MHz, $CDCl_3$, 298 K): δ = 62.2 and 60.3 ppm (DPEPhos). FTIR (CH_2Cl_2): $\tilde{\nu}$ = 1985 (s), 1945 (s), 1921 (s) and 1887 (s) cm^{-1}.$C_{60}H_{42}Fe_2O_5P_2S_2$ (1080.74 gmol^{-1}): Calcd. C 66.68, H 3.92, S 5.93; found C 66.52, H 4.25, S 5.87.

3.4. X-ray crystallography

Slow evaporation of hexane/dichloromethane solutions at low temperature resulted in single crystals for**1**. Diffraction data were collected on a Bruker Kappa APEX II Duo diffractometer using CuKα radiation. The structure was solved by direct methods (SHELXS-97) [27a] and refined by full-matrix least-squares procedures on F^2 (SHELXL-2014) [27b]. XP (Bruker AXS) was used for graphical representation. CCDC 1904985 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

3.5. Electrochemistry

All the electrochemical measurements were carried out in CH_3CN. Tetrabutylammoniumhexafluorophosphate (0.1 M) (n-Bu_4NPF_6) was used as the supporting electrolyte. Cyclic voltammetry was performed using an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie). A three–electrode cell was used with glassy carbon disc (diameter 3 mm, freshly polished) as working electrode, platinum wire as the counter electrode and a non-aqueous Ag/Ag$^+$ electrode for reference (CH Instruments, 0.010 M $AgNO_3$ in acetonitrile). All the potentials were calibrated with the ferrocene-ferrocenium couple (Fc/Fc$^+$); ferrocene was added as an internal standard at the end of the experiments.

4. Conclusions

The reaction of the monothiolate-bridged precursor [$Fe_2(CO)_6$(μ-naphthalene-2-thiolato)$_2$] **A** has been investigated with diphosphine ligands. Previously, Schollhammer has shown that the chelating phosphine complex [$Fe_2(CO)_4$(κ^2-dppe)(μ-pdt)] is formed upon reaction of [$Fe_2(CO)_6$(μ-pdt)] and dppe in acetonitrile in the presence of decarbonylating agent $Me_3NO.2H_2O$ [11d,f]. On the other hand, Hogarth reported that in refluxing toluene in the absence of Me_3NO. $2H_2O$, the bridging phosphine complex [$Fe_2(CO)_4$(μ-dppe)(μ-pdt)] is the major product [14h, 11f]. However, in the present work, we have shown that the formation of the bridged phosphine complexes **1** and **2** was independent of the reaction conditions used (refluxing toluene with or without $Me_3NO.2H_2O$ or acetonitrile/$Me_3NO.2H_2O$/RT). Complexes with the phosphines binding through one phosphorus atom or in the chelating mode were not obtained contrary to the earlier reported examples with dithiolates [11(d,f),12b,14(a-d, g, l-m, p), 17]. The reduction potentials for neutral **1** and **2** were less negative in comparison to their reported dithiolate counterparts [14a-c, g, i, k-n]. The catalytic properties of both the complexes were studied in acetonitrile in the presence of acids. Complex **1** successfully electro–catalyzed the reduction of acids to dihydrogen with low overpotentials [–0.82 (AA) and –1.09 (TFA) V]. Also, high i_{cat}/i_p values for complex **1** suggest faster catalytic processes [14m, 25, 28]. As **2** is unstable in solution in air we have been unable to access the HER activity. Based on the high catalytic currents and i_{cat}/i_p value obtained for complex **1**, it would be interesting to expand this study in future by designing bis(monothiolate) complexes with PNP-type diphosphine ligands.

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Highlights:

- Design, synthesis and characterization of diphosphine-bridged monothiolate {FeFe}-complexes [$Fe_2(CO)_4$(μ-naphthalene-2-thiolate)$_2$(μ-dppe)] **1** and [$Fe_2(CO)_4$(μ-naphthalene-2-thiolate)$_2$(μ-DPEPhos)] **2**.
- X-ray crystal structure analysis for complex **1**.
- Studies on homogeneous electrocatalysis by the {FeFe}-monothiolate complexes in presence of acids.

Structural and HER Studies of Diphosphine-Monothiolate Complexes $[Fe_2(CO)_4(\mu\text{-naphthalene-2-thiolate})_2(\mu\text{-dppe})]$ and $[Fe_2(CO)_4(\mu\text{-naphthalene-2-thiolate})_2(\mu\text{-DPEPhos})]$

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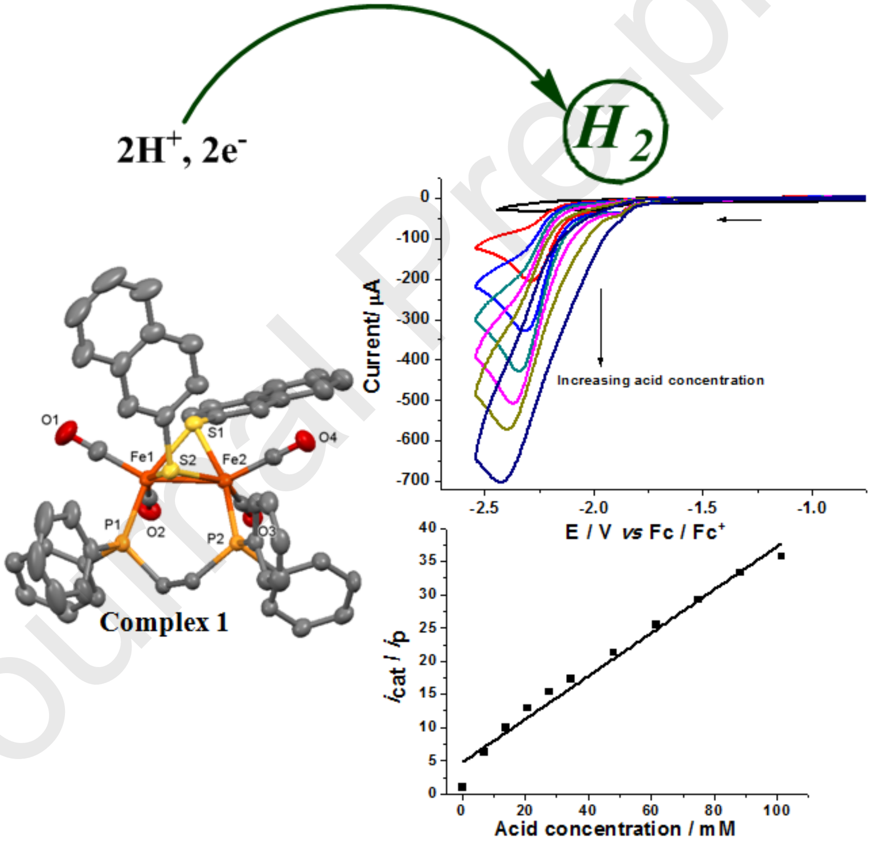

Diphosphine-bridged iron carbonyl complex **1** has been reported as bioinspired mimic of the [FeFe] hydrogenase enzyme. The new complex **1** with bis(monothiolate) linker assisted in electrocatalytic proton reduction with acetic and trifluoroacetic acid in CH_3CN.

Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: