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Synthesis, protonation and electrochemical properties of trinuclear NiFe₂ complexes $Fe_2(CO)_6(\mu_3-S)_2[Ni(Ph_2PCH_2)_2NR]$ (R = *n*-Bu, Ph) with an internal pendant nitrogen base as a proton relay

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ABSTRACT

Two trinuclear NiFe₂ complexes $Fe_2(CO)_6(\mu_3-S)_2[Ni(Ph_2PCH_2)_2NR]$ (R = *n*-Bu, **1**; Ph, **2**) containing an internal base were prepared as biomimetic models for the active sites of FeFe and NiFe hydrogenases. Treatment of complex $Fe_2(CO)_6(\mu_3-S)_2[Ni(Ph_2PCH_2)_2N(n-Bu)]$ (**1**) with HOTf gave an N-protonated complex $[Fe_2(CO)_6(\mu_3-S)_2[Ni(Ph_2PCH_2)_2N(n-Bu)]]$ (**1**) with HOTf gave an N-protonated complex $[Fe_2(CO)_6(\mu_3-S)_2[Ni(Ph_2PCH_2)_2N(n-Bu)]]$ (**1**H][OTf]). The structures of complexes **1**, **2** and **[1H]**[OTf] were determined by X-ray crystallography, which shows that the proton held by the N atom of **[1H]**[OTf] lies in an equatorial position. Cyclic voltammograms of complexes **1** and **[1H]**[OTf] were studied and compared with that of $Fe_2(CO)_6(\mu_3-S)_2[Ni(dppe)]$.

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1. Introduction

Hydrogenases can catalyze the reduction of protons and the oxidation of molecular hydrogen. According to the metals contained in the enzymes, hydrogenases can be classified into two major families: FeFe hydrogenases and NiFe hydrogenases. The structures of both FeFe and NiFe hydrogenases have been determined by X-ray crystallography with high resolution. Fig. 1a depicts the active site of the FeFe hydrogenase from *Desulfovibrio desulfuricans* and Fig. 1b shows the active site of NiFe hydrogenase from *Desulfovibrio gigas* in the oxidized form [1–4]. Density functional calculations relevant to the theoretical models of FeFe and NiFe hydrogenase active sites suggest that an internal base near the catalytically active metal centers in both FeFe and NiFe hydrogenases could facilitate the enzymatic H–H bond formation or the heterolytic cleavage of molecular hydrogen in an intramolecular proton–hydride form [5–7].

The synthesis and crystallographic structure of trinuclear complex $Fe_2(CO)_6(\mu_3-S)_2[Ni(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) have been reported by Seyferth et al. and Lozano et al. [8,9], but the redox property of the trinuclear complex was not reported. This complex, containing a butterfly Fe_2S_2 center and a thiolate-bridged NiFe center, possesses the characteristics of the structural features of both

FeFe and NiFe hydrogenases. Considering the important role of the internal base in enzymatic hydrogen uptake and production, we tried to introduce an internal basic site to such an interesting trinuclear NiFe₂ complex. Dubois et al. described the important role of the bridging-N atom of the Et₂PCH₂N(Me)CH₂PEt₂ (PNP) ligand in the reaction of $[Ni(PNP)_2](BF_4)_2$ with molecular hydrogen to form [HNi(PNP)(PNHP)](BF₄)₂, in which a hydride is bound to the Ni center and a proton is bound to the pendant N atom of a PNP ligand [10]. This result motivated us to introduce the ligands (Ph₂PCH₂)₂NR (R = n-Bu, Ph) as a proton relay to the nickel center of the trinuclear complex, aiming at preparing biomimetic models for the active site of FeFe and NiFe hydrogenases. Herein, we report the synthesis and molecular structures of trinuclear complexes $Fe_2(CO)_6(\mu_3 S_{2}[Ni(Ph_{2}PCH_{2})_{2}NR]$ (R = n-Bu, 1; Ph, 2) and an N-protonated complex $[Fe_2(CO)_6(\mu_3-S)_2[Ni(Ph_2PCH_2)_2NH(n-Bu)]][OTf] ([1H][OTf]).$ In addition, the electrochemical properties of complexes 1, [1H][OTf] and $Fe_2(CO)_6(\mu_3-S)_2[Ni(dppe)]$ were investigated.

2. Results and discussion

2.1. Preparation and spectroscopic characterization of complexes 1, 2 and [1H][OTf]

Ligands $(Ph_2PCH_2)_2NR$ (R = *n*-Bu, Ph) were prepared according to the literature procedure [11,12]. Compound $(Ph_2PCH_2)_2NPh$



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Fig. 1. Structures of the hydrogenase active sites from (a) Desulfovibrio desulfuricans (X¹ = NH or CH₂), (b) Desulfovibrio gigas in the oxidized form (X² = OH⁻ or O²⁻), as well as complexes 1, 2 and [1H]⁺.

is a solid at room temperature and can be easily purified by recrystallization, while $(Ph_2PCH_2)_2N(n-Bu)$ is an oil. Complex $NiCl_2(Ph_2PCH_2)_2NR$ (R = n-Bu, Ph) could be readily obtained by the reaction of $NiCl_2 \cdot 2H_2O$ with the corresponding diphosphine ligands. Complexes **1** and **2** were prepared from the reactions of $(\mu-LiS)_2Fe_2(CO)_6$ and $NiCl_2(Ph_2PCH_2)_2NR$ (R = n-Bu, Ph) in moderate yields. Treatment of a dark red solution of complex **1** in dichloromethane with HOTf gave a light red solution. Protonated species **1**H][OTf] of **1** was precipitated upon addition of hexane. Complex **1** is scarcely soluble in acetonitrile, while its protonated species **1**H][OTf] has a good solubility in acetonitrile. Therefore it is easy to distinguish complex **1** from its protonated species according to their solubility in acetonitrile. The in situ IR spectra show there is no reaction between complex **1** and molecular hydrogen under H₂ atmosphere.

Complexes **1**, **2** and [**1**H][OTf] were characterized by IR, ¹H and ³¹P NMR spectroscopy and elemental analysis. Four strong v(CO) bands in the region of 2045–1940 cm⁻¹ were observed in the IR spectra of complexes **1** and **2** (Table 1). A quite broad resonance was detected in the ³¹P NMR spectra of **1** and **2** in CDCl₃. Compared with complex **1**, the average value of the v(CO) absorptions for [**1**H][OTf] is shifted to higher energy by ca. 7 cm⁻¹. When complex **1** was protonated, the methylene resonances in ¹H NMR spectra

Table 1The v(CO) bands of complexes 1, 2, and [1H][OTf]

Complex	v(CO) (KBr, cm ⁻¹)
1 2	2044 s, 2004 s, 1975 s, 1940 s 2045 s, 2005 s, 1977 s, 1940 s
[1 H][OTf]	2051 s, 2010 s, 1982 s, 1950 s, 1932

were shifted to lower field by ca. 0.74 and 0.36 ppm for the NCH₂P and NCH₂C groups, respectively. These results strongly support the protonation of the bridging-N atom. The 8.4 ppm upfield shift in the ³¹P NMR spectrum of [1H][OTf] was possibly caused by the steric effect. The similar phenomena can be observed in other bridg-ing-N protonated diiron complexes containing phosphine ligands [13,14]. In terms of different ³¹P chemical shifts for complex 1 and [1H][OTf], the reversibility of protonation/deprotonation process was explored in dichloromethane. Upon addition of an equiv of aniline to the solution of [1H][OTf], the signal at δ 1.9 for the N-protonated species quickly disappeared, and at the same time the signal at δ 10.2 for complex 1 appeared as only one in the ³¹P NMR spectrum, indicating a reversible protonation/deprotonation process between 1 and [1H]⁺.

2.2. Molecular structures of complexes 1, 2, and [1H][OTf]

The molecular structures of complexes **1**, **2** and **[1H]**[OTf] were determined by X-ray diffraction of single crystals (Fig. 2). Selected bond lengths and angles are listed in Table 2. The [2Fe2S] skeleton of these three complexes has a well-known butterfly configuration, and each iron atom is approximately coordinated in a square-pyramidal geometry. The nickel atom is coordinated in an almost planar geometry by two P and two S atoms. The dihedral angles defined by the planes of the S–Ni–S and the P–Ni–P are 8.14°, 8.86° and 3.57° for complexes **1**, **2** and **[1H]**[OTf], respectively, which are similar to the 3.74° reported for Fe₂(CO)₆(μ ₃-S)₂[Ni(dppe)] [9]. The six-membered rings formed by nickel and diphosphine ligand in complexes **1**, **2** and **[1H]**[OTf] are all in the chair conformation. After protonation of **1**, the Ni–Fe distance is shortened by ca. 0.06 Å. The P–Ni–P angle increases from 81.22(3)° for **1** to 98.63(5)° for **[1H]**[OTf]. On the contrary, the



Fig. 2. Molecular structures of 1 (left), 2 (middle) and [1H]⁺ (right). Hydrogen atoms are omitted for clarity except for the one on the N atom in [1H]⁺.

Table 2	
Selected bond lengths (Å) and angles (°) for complexes 1, 2 and [1H][OTf]	

Complex	1	2	[1 H][OTf]
Ni(1)···Fe(1)	3.1206(10)	3.1102(14)	3.0608(9)
$Ni(1) \cdots Fe(2)$	3.2209(6)	3.2476(15)	3.2621(9)
Fe(1)-Fe(2)	2.5009(6)	2.5072(15)	2.5190(11)
Ni(1)-P(1)	2.1542(7)	2.1577(19)	2.1622(13)
Ni(1)-P(2)	2.1612(7)	2.165(2)	2.1734(12)
Ni(1)-S(1)	2.1804(7)	2.1916(19)	2.1776(12)
Ni(1)-S(2)	2.1902(7)	2.183(2)	2.1800(12)
Fe(1)-S(1)	2.2722(8)	2.277(2)	2.2758(15)
Fe(1)-S(2)	2.2745(8)	2.278(2)	2.2750(14)
Fe(2)-S(1)	2.2704(9)	2.275(2)	2.2767(14)
Fe(2)–S(2)	2.2759(8)	2.281(2)	2.2768(13)
S(1)–Ni(1)–S(2)	93.81(3)	81.04(7)	81.00(4)
P(1)-Ni(1)-P(2)	81.22(3)	94.62(7)	98.63(5)

S-Ni-S angle decreases from 93.81(3)° to 81.00(4)°. Compared with the structural data reported for the hydrogenase from Desulfovibrio gigas in the oxidized form (Fe–S(68), 2.2 Å; Ni–S(68), 2.6 Å; Ni…Fe, 2.9 Å) [4], complexes 1, 2 and [1H][OTf] possess similar Fe-S bond lengths (2.27–2.28 Å), significantly shorter Ni–S bonds (2.18-2.19 Å), and somewhat longer Ni…Fe distances (3.06-3.12 Å). The Fe-Fe bond lengths are 2.5009(6), 2.5072(15) and 2.5190(11) Å for 1, 2 and [1H][OTf], respectively, which are shorter than the Fe-Fe bond length reported for the [2Fe2S] H-cluster in the enzyme structure (ca. 2.6 Å) [1,2]. The X-ray studies show that protonation of 1 has almost no influence on the framework of the molecule except for the spatial orientation of the *n*-Bu on the N atom of the NCPNiPC chair conformation. The position of the n-Bu group changes from equatorial in **1** to axial in **[1**H][OTf]. In the structure of [1H][OTf], the proton on the bridging-N atom lies in an equatorial position. The result indicates that the bridging-N atom of the ligand $(Ph_2PCH_2)_2N(n-Bu)$ in complex 1 can play a role of the proton relay.

2.3. Electrochemistry of complexes **1**, [**1**H][OTf] and $Fe_2(CO)_6(\mu_3-S)_2$ -[Ni(dppe)]

The cyclic voltammograms (CV) of complexes **1**, [**1**H][OTf] and $Fe_2(CO)_6(\mu_3-S)_2[Ni(dppe)]$ are shown in Fig. 3. To compare the electrochemical property of **1** with other [2Fe2S] complexes that were detected in acetonitrile [15], the CV of complex **1** was also performed in acetonitrile even though complex **1** is not very soluble



Fig. 3. CVs of complexes **1** (0.5 mM), [**1**H][OTf] (0.5 mM) and Fe₂(CO)₆(μ ₃-S)₂[Ni(-dppe)] (1.0 mM) in CH₃CN under Ar at a scan rate of 0.1 V s⁻¹.



Fig. 4. CVs of 1 (0.5 mM) under Ar and CO in CH_3CN at a scan rate of 0.1 V s⁻¹.

in acetonitrile. A good CV of complex **2** could not be obtained because of the poor solubility of **2** in acetonitrile.

The redox potentials of three trinuclear complexes are summarized in Table 3. Under Ar atmosphere, complex 1 displays two oxidation peaks and two reduction peaks. The oxidation peaks are assigned to the iron centers as the nickel(II) in complex 1 cannot be further oxidized. Compared with the electrochemical data of other reported diiron dithiolate complexes [15,16], the first oxidation peak at +0.18 V is attributed to the Fe^IFe^I/Fe^{II}Fe^I process and the second one at +0.52 V is assigned to the further oxidation process of Fe^{II}Fe^{II} to Fe^{II}Fe^{II}. Nickel complexes with P₂S₂ or N₂S₂ coordination modes reported previously did not show redox potentials within the window of CH₃CN [17]. In the light of this experimental fact, the first reduction peak is ascribed to the Fe^IFe^I/Fe⁰Fe^I process instead of the Ni^{II}/Ni^I process. A typical phenomenon for multi-carbonyl diiron dithiolate complexes is that the second reduction peak close to the first one disappears when CV is measured in CH₃CN under a CO atmosphere [15,16,18], due to the depression of the CO-displacement by solvent. The CV control study of complex 1 showed that the second reduction peak of 1 at -2.00 V disappeared (Fig. 4) when the measurement was carried out under CO. Therefore, the second reduction peak is attributed to the reduction process of Fe¹Fe¹ to Fe⁰Fe¹ for a CH₃CN substituted species of complex **1**. Similarly, the first oxidation peak at +0.19 V and the first reduction peak at -1.68 V for Fe₂(CO)₆(μ_3 -S)₂[Ni(dppe)] are attributed to the Fe^IFe^I/Fe^{II}Fe^I process and the Fe^IFe^I/Fe⁰Fe^I process, respectively. When the bridging-N atom of complex 1 is protonated, the electron density of the iron centers is somewhat decreased. Upon addition of two equivalent acid (HOTf) to the solution of **1** in CH₃CN, a new reduction peak was observed at ca. -1.42 V, resulting from the formation of [1H][OTf] in situ. The first reduction peak of the isolated [1H][OTf] salt appeared at -1.40 V, shifted to anodic direction by ca. 330 mV as compared to that of 1. It is noticeable that the intensity of the peaks at +0.36 and -1.40 V for [1H][OTf] is relatively weak, and in addition to the

Table 3	
Redox potentials of 1, [1H][OTf] and Fe_2(CO)_6(μ_3 -S)_2[Ni(dppe)] vs. Ag/Ag	,+

Complex	$E_{\rm pa}\left(V\right)$	$E_{\rm pa}\left({\sf V}\right)$	$E_{\rm pc}\left({\sf V}\right)$
	Fe ^{II} Fe ^{II} Fe ^{II} Fe ^{II}	Fe ^I Fe ^I /Fe ^{II} Fe ^I	Fe ^I Fe ^I /Fe ⁰ Fe ^I
1	+0.52	+0.18	-1.73
[1 H][OTf]		+0.36	-1.40
$Fe_2(CO)_6(\mu_3-S)_2[Ni(dppe)]$		+0.19	-1.68

peaks of [1H][OTf], weak redox peaks for complex 1 at +0.18 and -1.73 V were also observed. It indicates the partial deprotonation of [1H][OTf] in acetonitrile. In the presence of aniline, the peaks at +0.36 and -1.40 V quickly disappeared and the peaks at +0.18 and -1.73 V for 1 was quantitatively recovered.

3. Conclusion

An internal base was introduced to the NiFe₂ trinuclear complexes, which possess structural characters of the active sites of FeFe and NiFe hydrogenases. The N atom in Fe₂(CO)₆(μ_3 -S)₂[Ni(Ph₂PCH₂)₂N(*n*-Bu)](1) can readily catch a proton from acid to form N-protonated species [1H]⁺, which quickly and quantitatively regenerates 1 in the presence of aniline. The X-ray studies show that the *n*-Bu group of the (Ph₂PCH₂)₂N(*n*-Bu) ligand changes from the equatorial position in 1 to the axial position in [1H]⁺, resulting in an equatorial position for the proton held by the N atom of [1H]⁺. Complex 1 displays similar IR and CV data to those of the reported [2Fe2S] complexes [15,16,18], indicating that the nickel unit gives rise to no significant influence on the redox property of the [2Fe2S] complex.

4. Experimental

All reactions and operations related to organometallic complexes were carried out under an atmosphere of dinitrogen using standard Schlenk techniques. The solvent THF was pre-dried with KOH and distilled prior to use over sodium/benzophenone ketyl under a nitrogen atmosphere. Compounds $Fe_2(CO)_6(\mu_3-S)_2-$ [Ni(dppe)] [9], (μ -S)₂Fe₂(CO)₆ [8], (Ph₂PCH₂)₂N(*n*-Bu) [11], and (Ph₂PCH₂)₂NPh [12] were prepared according to literature methods. All other commercially available reagents were used as received.

Infrared spectra were recorded on a JASCO FT/IR 430 spectrophotometer using KBr discs. ¹H and ³¹P NMR spectra were recorded on a Varian INOVA 400 NMR spectrometer. Elemental analyses were performed with a Thermoquest-Flash EA 1112 apparatus.

4.1. Synthesis of $NiCl_2[(Ph_2PCH_2)_2NR]$ (R = n-Bu, Ph)

A solution of $(Ph_2PCH_2)_2N(n-Bu)$ (1.5 g, 3.19 mmol) in CH_2CI_2 (30 mL) was added dropwise to a solution of $NiCI_2 \cdot 2H_2O$ (0.53 g, 3.20 mmol) in ethanol (20 mL). The solution became dark red immediately. The mixture was stirred for 30 min and the orange precipitate was isolated by filtration, washed with diethyl ether, and then recrystallized from ethanol to give complex $NiCI_2[(Ph_2PCH_2)_2N(n-Bu)]$. Yield: 1.53 g (80%). ¹H NMR (CDCI₃): δ 7.92 (d, 8H, PPh), 7.53 (t, 8H, PPh), 7.38 (t, 4H, PPh), 4.2–3.8 (s br, 4H, NCH_2P), 2.48 (t, 2H, NCH_2C), 1.25 (m, 2H, $CH_2CH_2CH_2$), 1.05 (m, 2H, CH_2CH_3), 0.78 (t, 3H, CH_2CH_3). ³¹P{¹H} NMR (CDCI₃): δ 1.4 (very br).

Starting complex NiCl₂[(Ph₂PCH₂)₂NPh] was prepared in 85% yield with the similar procedure aforementioned. ¹H NMR (CDCl₃): δ 7.94 (d, 8H, PPh), 7.56 (t, 8H, PPh), 7.42 (t, 4H, PPh), 7.18 (t, 2H, NPh), 6.96 (t, 1H, NPh), 6.61 (d, 2H, NPh). 4.9-4.2 (s br, 4H, NCH₂P). ³¹P{¹H} NMR (CDCl₃): δ 1.2 (very br).

4.2. Synthesis of $Fe_2(CO)_6(\mu_3-S)_2[Ni(Ph_2PCH_2)_2NR]$ (*R* = *n*-Bu, **1**; Ph, **2**)

A solution of LiHBEt₃ (6 mL, 1 M in THF) was added to the solution of $(\mu$ -S)₂Fe₂(CO)₆ (1.0 g, 2.90 mmol) in THF (15 mL) at -78 °C within 15 min. The green solution was stirred for another 10 min at -78 °C, and then NiCl₂[(Ph₂PCH₂)₂N(*n*-Bu)] (1.74 g, 2.90 mmol) was added. The mixture was warmed to room temperature and the dark red solution was stirred for 2 h. After removal of solvent

on a rotary evaporator, the crude product was purified by column chromatography on silica gel using dichloromethane/hexane (2/1, v/v) as eluent. Complex **1** was obtained as brown solid. Yield: 1.56 g (62%). IR (KBr): v(CO) 2044 s, 2004 s, 1975 s, 1940 s cm⁻¹. ¹H NMR (CDCl₃): δ 7.77 (s br, 8H, PPh), 7.42 (s br, 12H, PPh), 3.16 (s br, 4H, NCH₂P), 2.48 (s br, 2H, NCH₂C), 1.25 (s br, 2H, CH₂CH₂CH₂). 1.04 (s br, 2H, CH₂CH₃), 0.78 (s br, 3H, CH₂CH₃). ³¹P{¹H} NMR (CDCl₃): δ 10.2. *Anal.* Calc. for C₃₆H₃₃Fe₂NNiO₆P₂S₂ (M_r = 872.11): C, 49.58; H, 3.81; N, 1.61. Found: C, 49.51; H, 3.76; N, 1.60%.

Complex Fe₂(CO)₆(μ_3 -S)₂[Ni(Ph₂PCH₂)₂NPh] (**2**) was prepared in 70 % yield with the essentially identical procedure for complex **1**. IR (KBr): ν (CO) 2045 s, 2005 s, 1977 s, 1940 s cm⁻¹. ¹H NMR (CDCl₃): δ 7.80 (m, 8H, PPh), 7.50 (t, 4H, PPh), 7.44 (t, 8H, PPh), 7.16 (t, 2H, NPh), 6.96 (t, 1H, NPh), 6.61 (d, 2H, NPh). 3.80 (s, 4H, NCH₂P). ³¹P{¹H} NMR (CDCl₃): δ 11.0. *Anal.* Calc. for C₃₈H₂₉Fe₂N-NiO₆P₂S₂ (M_r = 892.10): C, 51.16; H, 3.28; N, 1.57. Found: C, 51.11; H, 3.26; N, 1.55%.

4.3. Synthesis of $Fe_2(CO)_6(\mu_3-S)_2[Ni(Ph_2PCH_2)_2NH(n-Bu)](OTf)$ ([1H][OTf])

The acid HOTf (12 µL) was added to the solution of $Fe_2(CO)_6(\mu_3-S)_2[Ni(Ph_2PCH_2)_2N(n-Bu)]$ (100 mg, 0.11 mmol) in CH_2CI_2 (5 mL) with stirring. Hexane (15 mL) was added to the solution after 5 min, and a brown solid was precipitated, which was isolated by filtration, washed with hexane, and dried in vacuo to give the pure product. Yield: 0.11 g (89%). IR (KBr): v(CO) 2051 s, 2010 s, 1982 s, 1950 s, 1932 s cm⁻¹. ¹H NMR (CD₃CN): δ 7.89, 7.58 (2s br, 20H, PPh), 5.43 (s, 1H, NH), 3.90 (s br, 4H, NCH₂P), 2.84 (s br, 2H, NCH₂C), 1.38 (s br, 2H, CH₂CH₂CH₂). 1.04 (s br, 2H, CH₂CH₃), 0.76 (t, 3H, CH₂CH₃). ³¹P{¹H} NMR (CD₃CN): δ 1.9. Anal. Calc. for C₃₇H₃₄F₃Fe₂N-NiO₉P₂S₃ (M_r = 1022.19): C, 43.47; H, 3.35; N, 1.37. Found: C, 43.41; H, 3.34; N, 1.32%.

4.4. Crystal structure determination of complexes 1, 2 and [1H][OTf]

Single crystals of $Fe_2(CO)_6(\mu_3-S)_2[Ni(Ph_2PCH_2)_2NR]$ (R = *n*-Bu, **1**; Ph, **2**) and Fe₂(CO)₆(μ_3 -S)₂[Ni(Ph₂PCH₂)₂NH(*n*-Bu)](OTf)([**1**H][OTf]) were obtained from saturated CH₂Cl₂ solutions of complexes by diffusion of hexane. Crystallographic data were collected on a Bruker Smart APEXII diffractometer for 1 and [1H][OTf], and on a Bruker P4 diffractometer for 2 with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Data processing was accomplished with the SAINT processing program [19]. Intensity data were corrected for absorption by the sadabs program [20]. The structures were solved by direct methods and refined on F^2 against full-matrix least-squares methods using the SHELXTL97 program package [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed by geometrical calculation and refined in a riding model, and the proton on the N atom of [1H][OTf] was located by the difference Fourier map. Crystal data and parameters for data collections and refinements of complexes 1, 2, and [1H][OTf] are listed in Table 4.

4.5. Electrochemistry studies of complexes **1**, [**1**H][OTf] and $Fe_2(CO)_{6^-}(\mu_3-S)_2[Ni(dppe)]$

Electrochemical measurements were recorded using a BAS-100W electrochemical potentiostat as previously reported [15]. Cyclic voltammograms were obtained in a three-electrode cell under argon. A glassy carbon disc was used as working electrode, a non-aqueous Ag/Ag⁺ electrode (0.01 M AgNO₃ in CH₃CN) as reference electrode, and a platinum wire as auxiliary electrode. A solution of 0.05 M *n*-Bu₄NPF₆ (Fluka, electrochemical grade) in CH₃CN was used as a supporting electrolyte.

Table 4

Crystallographic data and processing parameters for 1, 2, and [1H][OTf]

	1	2	[1 H][OTf]
Formula	$C_{36}H_{33}Fe_2NNiO_6P_2S_2$	$C_{38}H_{29}Fe_2NNiO_6P_2S_2$	$C_{37}H_{34}F_{3}Fe_{2}NNiO_{9}P_{2}S_{3} \cdot 0.5H_{2}O$
M _w	872.10	892.09	1031.19
Crystal system	monoclinic	monoclinic	triclinic
Space group	P21/c	P2 ₁ /c	PĪ
a (Å)	11.692(2)	11.896(4)	11.2601(2)
b (Å)	16.581(3)	16.261(5)	12.2963(2)
<i>c</i> (Å)	20.084(4)	20.163(6)	17.0799(3)
α (°)	90.00	90.00	93.388(1)
β (°)	92.17(3)	92.887(7)	93.580(1)
γ (°)	90.00	90.00	104.409(1)
$V(Å^3)$	3890.8(12)	3895(2)	2279.16(7)
Ζ	4	4	2
$D_{\text{calcd}} (\text{g cm}^{-3})$	1.489	1.521	1.503
$\mu ({\rm mm^{-1}})$	1.448	1.448	1.307
F(000)	1784	1816	1050
Crystal size (mm)	$0.22\times0.15\times0.12$	$0.45\times0.32\times0.20$	$0.26\times0.25\times0.09$
θ Range (°)	2.03-27.00	1.61-26.10	2.51-27.56
Reflections collected	28244	21 543	21402
Independent reflections	8379	7719	10429
R _{int}	0.0279	0.1222	0.0387
Reflections with $[I > 2\sigma(I)]$	6412	3594	6137
Parameters refined	479	469	536
Goodness-of-fit on F ²	1.038	0.969	1.015
$R_1^{a} [I > 2\sigma(I)] / w R_2^{b}$	0.0370/0.0963	0.0734/0.1018	0.0582/0.1599
Residue electron density (e $Å^{-3}$)	0.467/-0.644	0.405/-0.362	1.128/-0.641

$$_{a}^{a} R_{1} = \sum ||F_{0}| - |F_{c}||.$$

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Appendix A. Supplementary material

CCDC 647078, 647079 and 647077 contain the supplementary crystallographic data for 1, 2 and ([1H][OTf]). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.04.011.

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