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Mononuclear nickel(II) dithiolate complexes with chelating diphosphines: Insight into protonation and electrochemical proton reduction

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ABSTRACT

Inspired by the metal active sites of [FeFe]- and [NiFe]-hydrogenases, a series of mononuclear Ni(II) ethanedithiolate complexes [$\{(Ph_2PCH_2)_2 \times\}$ Ni(SCH₂CH₂S)] (X = NCH₂C₅H₄N-*p* (2a), NCH₂C₆H₅ (2b), NCH₂CHMe₂ (2c), and CH₂ (2d)) with chelating diphosphines were readily synthesized through the room-temperature treatments of mononuclear Ni(II) dichlorides [{(Ph₂PCH₂)₂×}NiCl₂] (1a-1d) with ethanedithiol (HSCH₂CH₂SH) in the presence of triethylamine (Et₃N) as acid-binding agent. All the as-prepared complexes 1a-1d and 2a-2d are fully characterized through elemental analysis, nuclear magnetic resonance (NMR) spectrum, and by X-ray crystallography for 1b, 2a-2d. To further explore proton-trapping behaviors of this type of mononuclear Ni(II) complexes for catalytic hydrogen (H₂) evolution, the protonation and electrochemical proton reduction of 2a-2c with aminodiphosphines (labeled PCNCP = (Ph₂PCH₂)₂NR) and reference analogue 2d with nitrogen-free diphosphine (dppp = $(Ph_2PCH_2)_2CH_2$) are studied and compared under trifluoroacetic acid (TFA) as a proton source. Interestingly, the treatments of 2a-2d with excess TFA resulted in the unexpected formation of dinuclear Ni(II)-Ni(II) dication complexes [{(Ph₂PCH₂)₂×}₂Ni₂(µ-SCH₂CH₂S)](CF₃CO₂)₂ (**3a-3d**) and mononuclear Ni(II) N-protonated complexes $[{(Ph_2PCH_2)_2N(H)R}Ni(SCH_2CH_2S)](CF_3CO_2)$ (4a-4c), which has been well supported by high-resolution electrospray ionization mass spectroscopy (HRESI-MS), NMR (³¹P, ¹H) as well as fourier transform infrared spectroscopy (FT-IR) techniques, and especially by X-ray crystallography for 3d. Additionally, the electrochemical properties of 2a-2d are investigated in the absence and presence of strong acid (TFA) by using cyclic voltammetry (CV), showing that the complete protonation of 2a-2d gave rise to dinuclear Ni₂S₂ species 3a-3d for electrocatalytic proton reduction to H₂.

1. Introduction

Over the past decades, fossil fuel as limited natural resources is overconsumed, which has led to serious environmental pollution and global energy crisis [1]. Therefore, scientific researchers have generated great interest in developing clean and sustainable alternative energy sources [2,3]. Hydrogen (H₂) has been considered as the most ideal alternative energy carrier due to its high combustion heat and carbonfree elements [4]. In reality, hydrogen evolution reaction (HER) from proton reduction can be reversibly and efficiently catalyzed by a family of metalloenzymes named as hydrogenases (H₂ase) in nature [5]. According to the metal composition in their active sites, native H₂ases are usually classified into two major groups, *i.e.*, [FeFe]- and [NiFe]-H₂ases as catalytically-active enzymes for reversible HER between molecular H₂ and proton [6,7]. For [FeFe]-H₂ases (left in Fig. 1), their active sites contain a butterfly [Fe₂S₂] cluster (*i.e.*, diiron subsite) that are bridged with a cubic [Fe₄S₄] cluster *via* a cysteinyl sulfur atom [8,9]. Specially, this diiron subsite, which is composed of an bridging azadithiolate units and several terminal CO/CN⁻ ligands [10–14], plays the significant roles in the efficient HER catalyzed by [FeFe]-H₂ase. On the one hand, a terminal open coordination site at the distal Fe core (*i.e.*, Fe_d is designated due to its relative far way to the [Fe₄S₄] cluster) serves as hydrogen binding or evolution [15–17]. On the other hand, a pendant nitrogen base (*i.e.*, NH) in the azadithiolate cofactor is thought to mediate proton relay to and from the open coordination site at the Fe_d core [18,19]. For [NiFe]-H₂ases (right in Fig. 1), their active sites feature

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a heterodinuclear Ni/Fe cluster, in which the Ni core is ligated by two terminal cysteine (Cys—S) units and the Fe core is coordinated by three terminal CO/CN⁻ ligands. Two metal cores of [NiFe]-H₂ase active sites are attached *via* two inherent bridging Cys-S ligands and the third variable bridging ligands such as vacant site, oxygenous groups, hydride [20–24]. It is worthy of noting that the Ni core shows an changeable oxidation state from Ni(II) to either Ni(III) or Ni(I) whereas the Fe core remains unchanged at a low-spin Fe(II) state in the catalytic HER by [NiFe]-H₂ase [25,26].

Inspired by these above insights and our current interest in developing mononuclear metal complexes as the structural precursors related to the Fe_d core of [FeFe]-H₂ases and the Ni core of [NiFe]-H₂ases, we recently prepared a new series of mononuclear Ni(II) ethanedithiolate (edt) complexes with aminodiphosphines (labeled PCNCP = (Ph₂PCH₂)₂NR, middle in Fig. 1) although a few mononuclear Ni(II) analogues with PCNCP ligands were so far reported by DuBois and coworkers [27]. This is because that to further explore the catalytic proton reduction steps for HER by [FeFe]- and [NiFe]-H₂ases, these mononuclear Ni(II) complexes have some unique structural features as follows: (i) the pendant base (NR) of their PCNCP ligands is similar to the NH unit of the azadithiolate cofactor in [FeFe]-H₂ases; and (ii) the ligand environment around their Ni cores is comparable to a free coordination site at the Fe_d core of [FeFe]-H₂ases and an almost square-planar coordination geometry at the Ni core of [NiFe]-H₂ases.

As a result, this work reports the synthesis and structural characterization of three new PCNCP-chelate mononuclear Ni(II) complexes $[{(Ph_2PCH_2)_2NR}Ni(SCH_2CH_2S)]$ (R = CH_2C_5H_4N-p (2a), CH_2C_6H_5 (2b), and CH₂CHMe₂ (2c)) and one known dppp-chelate reference analogue [{(Ph₂PCH₂)₂CH₂}Ni(SCH₂CH₂S)] (2d, labeled $(Ph_2PCH_2)_2CH_2 = dppp)$ [28] for comparison, which were readily obtained from treatments of mononuclear Ni(II) dichloride precursors [(diphosphine)NiCl₂] (1a-1d) with ethanedithiol. Further protonation reactions of complexes 2a-2d with excess trifluoroacetic acid (TFA) resulted in the unexpected formation of dinuclear Ni(II)-Ni(II) dication complexes [{(Ph2PCH2)2×}2Ni2(µ-SCH2CH2S)](CF3CO2)2 (3a-3d) and mononuclear Ni(II) N-protonated complexes [{(Ph₂PCH₂)₂N(H)R}Ni (SCH₂CH₂S)](CF₃CO₂) (4a-4c). In addition, the electrochemical properties of 2a-2d are studied and compared in the absence and presence of TFA as a proton source by using cyclic voltammetry (CV).

2. Experimental section

2.1. Materials and methods

All reactions and operations were carried out under a dry, oxygenfree nitrogen atmosphere with standard Schlenkand vacuum-line techniques. Dichloromethane (CH₂Cl₂) was distilled from CaH₂ under N₂. Starting materials NiCl₂·6H₂O, HSCH₂CH₂SH, Et₃N, (Ph₂PCH₂)₂CH₂ (dppp), and CF₃CO₂H (TFA) were commercially available and used as received. Ligands (Ph₂PCH₂)₂NR (R = CH₂C₅H₄N-*p*, CH₂C₆H₅, CH₂CHMe₂ [29]) were prepared as seen in the Supporting Information (Figs. S1-S4). Preparative thin layer chromatography (TLC) was performed on glass plates (25 cm \times 20 cm \times 0.25 cm) coated with silica gel G (10–40 mm). Elemental analyses were performed on a PerkinElmer 240C analyzer. HRESI-MS spectra were measured on a Thermo ScientificTM Exactive plus spectrometer (Thermo Fisher Scientific Inc., USA). NMR (¹H, ³¹P{¹H}) spectra were obtained on a Bruker Avance 600 MHz spectrometer. FT-IR (KBr) spectra were carried out on a Nicolet iS 10 FT-IR spectrometer.

2.2. General procedure for preparation of mononuclear Ni(II) dichloride salts $\{(Ph_2PCH_2)_2 \times\}$ NiCl₂ (1a-1d)

A CH₂Cl₂ (2 mL) solution of diphosphines (Ph₂PCH₂)₂× (X = NCH₂C₅H₄N-*p*, NCH₂C₆H₅, NCH₂CHMe₂, and CH₂, 0.84 mmol) was added dropwise to an EtOH (7 mL) solution of NiCl₂·6H₂O (0.165 g, 0.70 mmol), in which the reaction solution became dark-red immediately. After the reaction mixture was stirred at room temperature for 5 min, the precipitate appeared and the suspension was filtered with a steel pipe. The resulting solid was washed three times with ether to give the target compound as black solid for 1a and golden-yellow solid for 1b-1d.

Complex **1a** (X = NCH₂C₅H₄N-*p*). Yield: 0.340 g (77%). Anal. Calcd. for $C_{32}H_{30}Cl_2N_2NiP_2$: C, 60.61; H, 4.77; N, 4.42%. Found: C, 60.43; H, 5.03; N, 4.21%. ¹H NMR (600 MHz, *d*₆-DMSO, TMS): δ 7.84–7.30 (m, 24H, 2 x P(C₆H₅)₂ and NCH₂C₅H₄N-*p*), 4.33 (s, 2H, NCH₂C₅H₄N-*p*) and 3.37 (d, *J*_{HP} = 67.2 Hz, 4H, 2 x PCH₂N) ppm. ³¹P{¹H} NMR (243 MHz, *d*₆-DMSO, 85% H₃PO₄): δ 28.0 (s) ppm.

Complex **1b** (X = NCH₂C₆H₅). Yield: 0.356 g (80%). Anal. Calcd. for $C_{33}H_{31}Cl_2NNiP_2$ ·CH₂Cl₂: C, 56.87; H, 4.63; N, 1.95%. Found: C, 56.66; H, 4.81; N, 2.21%. ¹H NMR (600 MHz, *d*₆-DMSO, TMS): δ 7.76–6.85 (m, 25H, 2 x P(C₆H₅)₂ and NCH₂C₆H₅) and 4.21–3.32 (m, 6H, 2 x PCH₂N and NCH₂C₆H₅) ppm. ³¹P{¹H} NMR (243 MHz, *d*₆-DMSO, 85% H₃PO₄): δ 27.9 (s) ppm.

Complex **1c** (X = NCH₂CHMe₂). Yield: 0.554 g (62%). Anal. Calcd. for $C_{30}H_{33}Cl_2NNiP_2$: C, 60.14; H, 5.55; N, 2.34%. Found: C, 59.91; H, 5.34; N, 2.61%. ¹H NMR (600 MHz, *d*₆-DMSO, TMS): δ 7.96–7.31 (m, 20H, 2 x P(C₆H₅)₂), 3.79–3.33 (m, 4H, 2 x PCH₂N), 2.10 (d, *J* = 6.0 Hz, 2H, NCH₂), 1.42 (t, *J* = 6.0 Hz, 1H, CH), and 0.34 (d, *J* = 6.0 Hz, 6H, 2 x CH₃) ppm. ³¹P{¹H} NMR (243 MHz, d6-DMSO, 85% H₃PO₄): δ 27.2 (s) ppm.

Complex **1d** (X = CH₂). Yield: 0.339 g (89%). Anal. Calcd. for $C_{27}H_{26}Cl_2NiP_2$: C, 59.83; H, 4.84%. Found: C, 59.54; H,5.21%. ¹H NMR (600 MHz, d_6 -DMSO, TMS): δ 7.76–6.93 (m, 20H, 2 x P(C₆H₅)₂) and 3.98–3.30 (m, 6H, P(CH₂)₃P) ppm. ³¹P{¹H} NMR (243 MHz, d_6 -DMSO, 85% H₃PO₄): δ 27.9 (s) ppm.



Fig. 1. Schematic structures of $[FeFe]-H_2$ as active sites highlighting the Fe_d core in yellow (left), target mononuclear complexes highlighting the Ni core in pink (middle), and $[NiFe]-H_2$ as active sites highlighting the Ni core in blue (right). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3. General procedure for preparation of mononuclear Ni(II) dithiolate complexes { $(Ph_2PCH_2)_2 \times$ }Ni(SCH_2CH_2S) (2a-2d)

To a CH₂Cl₂ (15 mL) solution of the as-prepared salts {(Ph₂PCH₂)₂×} NiCl₂ (**1a-1d**, 0.29 mmol) and dithiol HSCH₂CH₂SH (0.02 mL, 0.24 mmol) was added Et₃N (0.07 mL, 0.48 mmol). The reaction mixture was stirred for 1 h at room temperature and then the solvent was removed under reduced pressure. The crude product was purified by preparative TLC separation using CH₂Cl₂/EtOAc (1:1, ν/ν for **2a**), CH₂Cl₂/EtOAc (15:1, ν/ν for **2b**), and petroleum ether/EtOAc (2:3, ν/ν for **2c**, **2d**) as eluent. The main red band afforded a red solid as the target complex.

Complex **2a** (X = NCH₂C₅H₄N-*p*). Yield: 0.136 g (86%). Anal. Calcd. for $C_{34}H_{34}N_2NiP_2S_2\cdot 0.5CH_2Cl_2$: C, 59.38; H, 5.06; N, 4.01%. Found: C, 59.56; H, 4.93; N, 4.22%. ¹H NMR (600 MHz, CDCl₃, TMS): δ 8.39 (d, $J_{HH} = 4.2$ Hz, 2H, 2 x C_5H_4N-0), 7.68 (dd, $J_{PH} = 12.0$ Hz, $J_{HH} = 6.6$ Hz, 8H, 2 x P(C_6H_5-o)₂), 7.41 (t, $J_{HH} = 7.8$ Hz, 4H, 2 x P(C_6H_5-p)₂), 7.31 (t, $J_{HH} = 7.8$ Hz, 8H, 2 x P(C_6H_5-m)₂), 6.78 (d, $J_{HH} = 4.2$ Hz, 2H, 2 x C_5H_4N-m), 3.58 (s, 2H, NCH₂C₅H₄N-*p*), 3.31 (s, 4H, 2 x PCH₂N), and 2.73 (s, 4H, 2 x SCH₂) ppm. ³¹P{¹H} NMR (243 MHz, CDCl₃, 85% H₃PO₄): δ 9.4 (s) ppm.

Complex **2b** (X = NCH₂C₆H₅). Yield: 0.102 g (65%). Anal. Calcd. for $C_{35}H_{35}NNiP_2S_2$: C, 64.24; H, 5.39; N, 2.14%. Found: C, 64.11; H, 5.60; N, 2.39%. ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.63 (dd, $J_{PH} = 11.4$ Hz, $J_{HH} = 6.6$ Hz, 8H, 2 × P(C₆H₅-o)₂), 7.37 (t, $J_{HH} = 7.2$ Hz, 4H, 2 × P (C₆H₅-p)₂), 7.27 (t, $J_{HH} = 7.2$ Hz, 8H, 2 × P(C₆H₅-m)₂), 7.23 (t, $J_{HH} = 7.2$ Hz, 3H, NCH₂(C₆H₅-o,p)₂), 6.97 (d, $J_{HH} = 7.2$ Hz, 2H, NCH₂(C₆H₅-m)₂), 3.60 (s, 2H, NCH₂C₆H₅), 3.30 (s, 4H, 2 × PCH₂N), and 2.73 (s, 4H, 2 × SCH₂) ppm. ³¹P{¹H} NMR (243 MHz, CDCl₃, 85% H₃PO₄): δ 9.1 (s) ppm.

Complex **2c** (X = NCH₂CHMe₂). Yield: 0.097 g (65%). Anal. Calcd. for $C_{32}H_{37}NNiP_2S_2 \cdot 0.5CH_2Cl_2$: C, 58.89; H, 5.78; N, 2.11%. Found: C, 58.66; H, 6.15; N, 2.29%. ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.75 (dd, $J_{PH} = 12$ Hz, $J_{HH} = 7.8$ Hz, 8H, $2 \times P(C_6H_5 \cdot o)_2$), 7.39 (t, $J_{HH} = 7.8$ Hz, 4H, $2 \times P(C_6H_5 \cdot p)_2$), 7.31 (t, $J_{HH} = 7.8$ Hz, 8H, $2 \times P(C_6H_5 \cdot m)_2$), 3.27 (s, 4H, $2 \times PCH_2N$), 2.73 (s, 4H, $2 \times SCH_2$), 2.21 (d, $J_{HH} = 7.2$ Hz, 2H, NCH₂), 1.65–1.58 (m, 1H, NCH₂CH), and 0.64 (d, $J_{HH} = 6.6$ Hz, 6H, $2 \times CH_3$) ppm. ³¹P{¹H} NMR (243 MHz, CDCl₃, 85% H₃PO₄): δ 8.9 (s) ppm.

Complex **2d** (X = CH₂). Yield: 0.063 g (47%). Anal. Calcd. for C₂₉H₃₀NiP₂S₂: C, 61.83; H, 5.37%. Found: C, 61.98; H, 5.64%. ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.67 (m, 8H, 2 x P(C₆H₅-o)₂), 7.37 (t, J_{HH} = 7.2 Hz, 4H, 2 x P(C₆H₅-p)₂), 7.31 (t, J_{HH} = 7.2 Hz, 8H, 2 x P(C₆H₅-m)₂), 2.73 (s, 4H, 2 x SCH₂), 2.33 (s, 4H, 2 x PCH₂), and 2.00 (s, 2H, CH₂CH₂CH₂) ppm. ³¹P{¹H} NMR (243 MHz, CDCl₃, 85% H₃PO₄): δ 10.26 (s) ppm.

2.4. General procedure for protonation of complexes 2a-2d with excess TFA to form dinuclear Ni(II)-Ni(II) dication complexes $[{(Ph_2PCH_2)_2 \times}_2Ni_2(\mu$ -SCH_2CH_2S)](CF_3CO_2)_2 (3a-3d) and mononuclear Ni(II) N-protonated complexes $[{(Ph_2PCH_2)_2 \times (H)}Ni (SCH_2CH_2S)](CF_3CO_2) (4a-4c)$

A dry CH₂Cl₂ (5 mL) solution of the above-obtained complexes **2a-2d** (0.1 mmol) was treated with 10 equivalents of TFA (74 μ L, 1.0 mmol). The reaction mixture was stirred at room temperature for 1 h to give a solution colour change from orange-red to black-red. After this reaction was completed by TLC monitor, the volume was reduced under vacuum and *n*-hexane was added. Upon the slow diffusion of *n*-hexane into the above-concentrated CH₂Cl₂ solution at -20 °C overnight, a black-red solid was precipitated and dried to afford the protonated products **3a-3d** and **4a-4c** accompanied by a slight amount of neutral precursors **2a-2d**.

Complexes **3a** and **4a** (X = NCH₂C₅H₄N-*p*). HRESI-MS (MeOH, positive mode) for [{(Ph₂PCH₂)₂N(CH₂C₅H₄N-*p*)}₂Ni₂(μ -SCH₂CH₂C)] (CF₃CO₂)₂ (**3a**): *m/z* 608.1094 [(M-2CF₃CO₂)/2]⁺ (highest peak, Calcd. 608.1109) and for [{(Ph₂PCH₂)₂N(*H*)(CH₂C₅H₄N-*p*)}Ni(SCH₂CH₂S)] (CF₃CO₂) (**4a**): *m/z* 655.1038 [M-CF₃CO₂]⁺ (low peak, Calcd.

655.1065). ³¹P{¹H} NMR (243 MHz, CDCl₃, 85% H₃PO₄): δ 9.8 (s, 8%) ppm for **2a**, 8.1 (s, 8%) ppm for **4a**, and 3.1 (s, 84%) ppm for **3a**.

Complexes **3b** and **4b** (X = NCH₂C₆H₅). HRESI-MS (MeOH, positive mode) for [{(Ph₂PCH₂)₂N(CH₂C₆H₅)}₂Ni₂(μ -SCH₂CH₂S)](CF₃CO₂)₂ (**3b**): *m/z* 607.1133 [(M-2CF₃CO₂)/2]⁺ (higher peak, Calcd. 607.1157) and for [{(Ph₂PCH₂)₂N(*H*)(CH₂C₆H₅)}Ni(SCH₂CH₂S)](CF₃CO₂) (**4b**): *m/z* 654.1080 [M-CF₃CO₂]⁺ (highest peak, Calcd. 654.1112). ³¹P{¹H} NMR (243 MHz, CDCl₃, 85% H₃PO₄): δ 9.0 (br s, 7%) ppm for **2b**, 6.5 (s, 56%) ppm for **4b**, and 2.3 (br s, 37%) ppm for **3b**.

Complexes **3c** and **4c** (X = NCH₂CHMe₂). HRESI-MS (MeOH, positive mode) for [{(Ph₂PCH₂)₂N(CH₂CHMe₂)}₂Ni₂(μ -SCH₂CH₂S)](CF₃CO₂)₂ (**3c**): *m*/*z* 573.1281 [(M-2CF₃CO₂)/2]⁺ (low peak, Calcd. 573.1313) and for [{(Ph₂PCH₂)₂N(*H*)(CH₂CHMe₂)}Ni(SCH₂CH₂S)](CF₃CO₂) (**4c**): *m*/*z* 620.1226 [M-CF₃CO₂]⁺ (highest peak, Calcd. 620.1269). ³¹P{¹H} NMR (243 MHz, CDCl₃, 85% H₃PO₄): δ 8.9 (s, 3%) ppm for **2c**, 6.6 (s, 80%) ppm for **4c**, and 1.1 (br s, 17%) ppm for **3c**.

Complexes **3d** (X = CH₂). HRESI-MS (MeOH, positive mode) for [{(Ph₂PCH₂)₂CH₂}₂Ni₂(μ -SCH₂CH₂S)](CF₃CO₂)₂ (**3d**): m/z 516.0709 [(M-2CF₃CO₂)/2]⁺ (highest peak, Calcd. 516.0735). ¹H NMR (600 MHz, CDCl₃, TMS): δ 7.62–7.48 (m, 16H, 4 x P(C₆H₅-o)₂), 7.37–7.34 (m, 24H, 4 x P(C₆H₅-p,m)₂), 3.09 (s, 4H, 2 x SCH₂), 2.79 (s, 8H, 4 x PCH₂), 1.98 (s, 4H, 2 x CH₂CH₂CH₂) ppm. ³¹P{¹H} NMR (243 MHz, CDCl₃, 85% H₃PO₄): δ 10.1 (br s, 15%) ppm for **2d**, 5.8 (s, 85%) ppm for **3d**.

2.5. X-ray crystal structure determination

Single crystals of complexes **1b**, **2a-2d** and **3d** suitable for X-ray diffraction analysis were grown by slow evaporation of the CH₂Cl₂/*n*-hexane or CH₂Cl₂/ petroleum ether solution at -5 °C or -20 °C. The crystals were mounted on a Bruker-CCD diffractometer. Data were collected at 150(2) or 293 K using a graphite monochromator with Mo K σ radiation ($\lambda = 0.71073$ Å) in the ω - φ scanning mode. The structure was solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares techniques (SHELXS-97) on F^2 [30]. Hydrogen atoms were located using the geometric method. Details of crystallographic data and structure refinement for **1b**, **2a-2d** and **3d** are summarized in Table 1.

2.6. Electrochemical tests

Electrochemical and electrocatalytic properties of complexes **2a-2d** and their main protonated products **3a**, **4b**, **4c**, **3d** were studied by cyclic voltammetry (CV) in MeCN solution. As the electrolyte, *n*-Bu₄NPF₆ was recrystallized multiple times from a CH_2Cl_2 solution by the addition of hexane. All the CV measurements were recorded using a Gamry Interface potentiostat which was connected to a glassy carbon working electrode (3 mm diameter), a platinum wire counter electrode, and Ag/AgCl reference electrode. CV measurements were conducted using a three-neck electrochemical cell that was washed and dried in an oven overnight before use. All electrochemical experiments were conducted under a N₂ atmosphere. The potential scale was calibrated against the Fc/Fc⁺ couple and reported *versus* this reference system.

3. Results and discussion

3.1. Synthesis and characterization of mononuclear Ni(II) dichloride precursors [{ $(Ph_2PCH_2)_2 \times$ }NiCl_2] (X = CH_2C_5H_4N-p, 1a; CH_2C_6H_5, 1b; CH_2CHMe_2, 1c; and CH_2, 1d)

The diphosphine-chelate mononuclear Ni(II) precursors **1a-1d** can be readily obtained from the treatments of diphosphines (Ph₂PCH₂)₂× (X = CH₂C₅H₄N-*p*, CH₂C₆H₅, CH₂CHMe₂, and CH₂) with mononickel salt NiCl₂·6H₂O in the mixed CH₂Cl₂/EtOH solvent at room temperature, as displayed in Scheme 1.

The as-prepared precursors **1a-1d** are air-stable solids, in which it is easy for **1b-1d** but is difficult for **1a** to be dissolved in most organic

Table 1

Details of crystallographic data and structure refinement for 1b, 2a-2d, and 3d.

Complex	1b	2a	2b	2c	2d	3d
Empirical formula	$C_{33}H_{31}Cl_2NNiP_2\bullet CH_2Cl_2$	$C_{34}H_{34}N_2NiP_2S_2{\bullet}0.5CH_2Cl_2$	$\mathrm{C}_{35}\mathrm{H}_{35}\mathrm{NNiP}_{2}\mathrm{S}_{2}$	$C_{32}H_{37}NNiP_2S_2{\bullet}CH_2Cl_2$	C29H30NiP2S2	$C_{56}H_{56}Ni_2P_4S_2{\bullet}2CF_3CO_2{\bullet}2CF_3CO_2H$
Formula	718.06	697.86	654.41	705.32	563.30	1488.52
Temperature	150(2)	150(2)	150(2)	150(2)	150(2)	293
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	P212121	P21	P2 ₁ /n	P21/c	$P2_1/n$	P-1
a (Å)	8.0265(5)	13.6242(12)	8.5386(4)	18.6993(16)	10.1801(8)	13.0245(7)
b (Å)	19.9078(15)	13.7786(12)	19.9641(7)	9.3828(7)	24.5226(17)	13.4777(7)
c (Å)	20.9194(17)	17.6737(16)	19.0182(9)	21.9922(17)	11.2237(10)	22.1673(11)
α (°)	90	90	90	90	90	98.063(2)
β(°)	90	103.897(3)	101.970(2)	121.408(6)	106.643(3)	93.394(2)
γ (°)	90	90	90	90	90	117.525(2)
$V(Å^3)$	3342.7(4)	3220.6(5)	3171.5(2)	3293.2(5)	2684.5(4)	3382.4(3)
7.	4	4	4	4	4	2
D_{colo} (g cm ⁻³)	1.427	1.439	1.371	1.423	1.394	1.462
$\mu (\text{mm}^{-1})$	1.021	0.943	0.870	1.000	1.014	0.798
F(000)	1480.0	1452.0	1368.0	1472.0	1176.0	1524.0
Crystal size	$0.24 \times 0.18 \times 0.14$	$0.22 \times 0.16 \times 0.14$	$0.22 \times 0.18 \times$	$0.28 \times 0.22 \times 0.14$	0.32×0.26	$0.40 \times 0.37 \times 0.30$
(mm)			0.16		× 0.24	
$\theta_{\min}, \theta_{\max}$ (°)	4.398, 52.796	4.268, 52.89	4.63, 52.794	4.67, 52.828	4.494, 52.856	4.596, 51.998
collected/ unique	48,734/6794	44,241/131/8	70,020/6499	43,501/6/43	36,373/5487	53,627/13217
R _{int}	0.0748	0.0668	0.0890	0.0920	0.1154	0.0415
hkl Range	$-8 \le h \le 10$	$-17 \leq h \leq 17$	$-10 \leq h \leq 10$	$-23 \le h \le 23$	$-12 \leq h \leq 12$	$-16 \le h \le 16$
Ū	$-24 \le k \le 24$	$-17 \stackrel{-}{\leq} k \stackrel{-}{\leq} 17$	$-24 \leq k \leq 24$	$-11 \stackrel{-}{\leq} k \stackrel{-}{\leq} 11$	$-30\stackrel{-}{\leq}k\stackrel{-}{\leq}30$	$-16 \leq k \leq 16$
	$-26 \le l \le 26$	$-22 \le l \le 22$	$-23 \le 1 \le 23$	$-27 \leq l \leq 27$	$-14 \leq l \leq 14$	$-27 \le l \le 27$
Completeness to θ_{max} (%)	1.76/0.99	1.90/0.99	0.999	0.997	0.993	0.996
Data/ restraints/ parameters	6794/0/380	13,178/7/767	6499/0/370	6743/0/372	5487/0/307	13,217/223/859
Goodness-of- fit (GOF) on <i>F</i> ²	1.032	1.012	1.055	1.197	1.030	1.125
$\begin{array}{c} R_1/wR_2[I > 2\sigma \\ (I)] \end{array}$	0.0415/0.0983	0.0560/0.1421	0.0383/0.0747	0.1101/0.2705	0.0491/ 0.1076	0.0574/0.1595
R ₁ /wR ₂ (all data)	0.0571/0.1066	0.0834/0.1614	0.0615/0.0830	0.1325/ 0.2814	0.0909/ 0.1275	0.0768/0.1742
Largest difference peak/ hole (e A ⁻³)	0.45/-0.35	0.76/-0.83	0.40/-0.30	1.79/-1.72	1.16/-0.71	1.70/-0.65



Scheme 1. Synthesis of mononuclear Ni(II) dichloride precursors 1a-1d

solvents such as CH₂Cl₂, EtOH, *etc.* Although complexes **1c** and **1d** are known [31,32], all the precursors **1a-1d** have been characterized by elemental analysis, NMR (¹H, ³¹P) spectroscopy, and by X-ray crystallography for **1b**. The ¹H NMR spectra of **1a-1d** in *d*₆-DMSO show their phenyl proton signals in the downfield region of δ_H 4.3–3.3 ppm. Furthermore, the ³¹P{¹H} NMR spectra of **1a-1d** in *d*₆-DMSO display a sharp singlet at δ_P *ca.* 28 ppm for two symmetrical phosphorus atoms of the (Ph₂PCH₂)₂× diphosphines chelated to central nickel atom.

Most intuitively, the molecular struture of **1b** is further confirmed by single-crystal X-ray diffraction analysis, as illustrated in Fig. 2 with

selected lengths and angles. It crystallizes in the orthorhombic space group $P2_12_12_1$ with a target molecule and a dichloromethane solvent in the asymmetric unit (Table 1). As presented in Fig. 2, precursor 1b features a mononuclear Ni(II) core with one chelate diphosphine and two terminal chlorides, thus giving rise to a square-planar coordination around Ni center. It is worth noting that a steady six-membered metallocycle NiPCNCP is formed between the PCNCP diphosphine and the Ni core, wherein the P-Ni-P angle (95.19 (6)°) is much lower in contrast to the C-N-C angle (109.1 (5)°). In addition, the Ni—P lengths (*ca.* 2.16 Å) are smaller relative to the Ni—Cl lengths (*ca.* 2.21 Å), probably due to the following observation that two P atoms and two Cl atoms are



Fig. 2. Molecular structure of precursor **1b** with thermal ellipsoids at 40% probability. Hydrogen atoms and solvent molecules are omitted and phenyl groups are represented as sticks for clarity. Selected lengths (Å) and angles (deg): Ni(1)-P(1) 2.1648 (15), Ni(1)-P(2) 2.1607 (15), Ni(1)-Cl(1) 2.2028 (14), Ni(1)-Cl(2) 2.2107 (14); P(1)-Ni(1)-P(2) 95.19 (6), Cl(1)-Ni(1)-Cl(2) 93.11 (5), C(1)-N(1)-C(2) 109.1 (5).

respectively chelated and terminal to the Ni core (Fig. 2).

3.2. Synthesis and characterization of mononuclear Ni(II) dithiolate complexes [$\{(Ph_2PCH_2)_2 \times\}$]Ni(SCH₂CH₂S) ($X = CH_2C_5H_4N$ -p, 2a; CH₂C₆H₅, 2b; CH₂CHMe₂, 2c; and CH₂, 2d)

As shown in Scheme 2, the room-temperature treatments of the above-obtained precursors **1a-1d** with HSCH₂CH₂SH in the presence of Et₃N as acid-binding agent in CH₂Cl₂ gave rise to a series of mononuclear Ni(II) dithiolate complexes **2a-2d** with chelating diphosphines in 47–86% yields.

The new target complexes ${\bf 2a\mathchar`-2c}$ together with a known reference complex 2d are air-stable solids and characterized by elemental analysis, NMR spectroscopy, as well as X-ray crystallography. The ¹H NMR spectra of **2a-2d** all show a doublet of doublet at δ_H ca. 7.7 ppm and two triplets at δ_H *ca*. 7.4, 7.3 ppm for the phenyl protons of the diphosphine ligands in addition to a broad singlet at δ_H ca. 2.7 ppm for methylene protons of the dithiolate bridges. Meanwhile, a broad singlet is observed at δ_H *ca*.3.3 ppm for **2a-2c** but at δ_H 2.33 ppm for **2d**, being attributed to the phosphorus-attached methylene protons of diphosphines in their ¹H NMR spectra. This finding is possibly due to the difference in the central X moieties of the $(Ph_2PCH_2)_2 \times$ diphosphines, *i.e.*, X = NR for **2a-2c** and $X = CH_2$ for 2d. Additionally, the ³¹P{¹H} NMR spectra of 2a-2c with PCNCP ligands exhibit a sharp singlet at δ_P ca. 9 ppm whereas that of 2d with dppp displays a strong singlet at δ_P 10 ppm, being accordant with the ³¹P NMR signals at δ_P 7–10 ppm reported previously for (diphosphine)Ni(dithiolate) [27].

Further, we managed to obtain the crystal structures of mononuclear Ni(II) complexes **2a-2d** with chelating $(Ph_2PCH_2)_2 \times$ diphosphines, since

the molecular structures of the previously reported mononuclear Ni(II) dithiolate analogues are inferred only through spectroscopic studies [27]. The single crystals of **2a-2d** were grown in a mixed CH_2Cl_2/n -hexane solution at low temperature for days before being subjected to the X-ray diffraction analysis as displayed in Fig. 3. The selected lengths and angles of **2a-2d** are listed in Table 2.

All the solid-state structures of 2a-2d contain a mononuclear Ni(II) cluster core ligated by two phosphorus atoms (i.e., P1 and P2) of the $(Ph_2PCH_2)_2 \times$ diphosphines and two sulfur atoms (*i.e.*, S1 and S2) of the edt bridges (Fig. 3). The central Ni(II) cores of 2a-2d all adopt a slightly distorted square-planar coordination geometry, which are similar to those observed previously for some mononuclear Ni(II) analogues of the type {(Ph₂P)₂NR}Ni(dithiolate) with chelating PNP ligands (labeled PNP = (Ph₂P)₂NR) [33–37]. The (Ph₂PCH₂)₂× diphosphines in **2a-2d** all adopt a chair configuration with a six-membered metallocycle of NiP₂C₂N or NiP₂C₃, whereas their edt bridges exhibit a nearly coplanar conformation with a five-membered metallocycle of NiS₂C₂. This is possibly due to the following observation that the P(1)-Ni(1)-P(2) bite angles (ca. 95°) of the PCNCP ligands are a little larger than the S(1)-Ni (1)-S(2) ones (ca. 92°) of the edt bridges except for 2a. It is worth mentioning that the dihedral angles (more than 10°) between the two planes defined by the P-Ni-P and S-Ni-S atoms in 2a-2d with chelating PCNCP ligands are larger than those (3° to 8°) observed in the known mononuclear Ni(II) analogues with chelating PNP ligands [33-37]. This finding implies that the central X groups of the (Ph₂PCH₂)₂× diphosphines in 2a-2d may be closer to the Ni atom relative to those of the (Ph₂P)₂NR diphosphines in the reported mononuclear Ni analogues [33-37].

3.3. Protonation studies of mononuclear Ni(II) complexes 2a-2d with excess TFA

Although a few mononuclear Ni(II) dithiolate/diphosphine complexes have been reported previously [27], protonation studies of these complexes were not pursued and help to understand the catalytic proton reduction steps for efficient HER by them. Thus, the protonation reactions of complexes **2a-2d** with 10 equiv. TFA at room temperature resulted in the unexpected formations of dinuclear Ni(II)-Ni(II) dication complexes [$\{(Ph_2PCH_2)_2 \times\}_2Ni_2(\mu-SCH_2CH_2S)\}(CF_3CO_2)_2$ (**3a-3d**) [27] and mononuclear Ni(II) N-protonated complexes [$\{(Ph_2PCH_2)_2 \times (H)\}$ Ni (SCH₂CH₂S)](CF₃CO₂) (**4a-4c**) as shown in Scheme 3.

The formations of these protonated products **3a-3d** and **4a-4c** are well supported by the HRESI-MS, NMR (³¹P, ¹H) as well as FT-IR spectra, and especially by the X-ray crystallography for **3d**. First of all, the HRESI-MS and ³¹P{¹H} spectra for protonated products of complexes **2a-2c** with PCNCP ligands display similar characteristics as follows. For protonated product of **2a**, its positive-mode HRESI-MS spectrum gives a highest ion peak at m/z = 608.1094 and a low adjacent ion peak at m/z = 655.1038 (Fig. S5), which are respectively ascribed to the half of dication [{(Ph₂PCH₂)₂N(CH₂C₅H₄N-*p*)}₂Ni₂(μ -SCH₂CH₂S)]²⁺ (Calcd. 608.1109 [(M-2CF₃CO₂)/2]⁺) from the main dinuclear Ni(II)-Ni(II) product **3a** and the monocation [{(Ph₂PCH₂)₂N(*H*)(CH₂C₅H₄N-*p*)}Ni (SCH₂CH₂S)]⁺ (Calcd. 655.1065 [M-CF₃CO₂]⁺) from a little mononuclear Ni(II) N-protonated product **4a**. This is well line with the corresponding ³¹P{¹H} NMR spectrum (Fig. 4A) that shows one strong phosphorus signal at δ_P 3.1 ppm for **3a** and another a very weak P signal



Scheme 2. Synthesis of mononuclear Ni(II) dithiolate complexes 2a-2d



Fig. 3. Molecular structures of complexes 2a (A), 2b (B), 2c (C) and 2d (D) with thermal ellipsoids at 50% probability. Hydrogen atoms and solvent molecules are omitted and phenyl groups are represented as sticks for clarity.

Table 2	
Selected lengths and angles for complexes 2a-2d .	
	_

m-11-0

Complex	2a	2b	2c	2d
Ni(1)-P(1)	2.157 (2)	2.1484 (7)	2.162 (2)	2.1787 (10)
Ni(1)-P(2)	2.155 (2)	2.1641 (7)	2.151 (2)	2.1761 (10)
Ni(1)-S(1)	2.177 (2)	2.1760 (7)	2.181 (2)	2.1660 (11)
Ni(1)-S(2)	2.171 (3)	2.1797 (7)	2.178 (3)	2.1839 (10)
P(1)-Ni(1)-P(2)	90.23 (9)	95.03 (3)	95.91 (9)	92.00 (4)
S(1)-Ni(1)-S(2)	92.40 (10)	92.00 (3)	92.01 (10)	91.24 (4)

at δ_P 8.1 ppm for **4a** [38,39] with the percentage contents of 84% and 8%, respectively. In contrast, for protonated products of **2b** and **2c**, their positive-mode HRESI-MS spectra (Figs. S6 and S7) present a highest ion peak at m/z = 654.1080 and 620.1226 for monocation [{(Ph₂PCH₂)₂N (*H*)R}Ni(SCH₂CH₂S)]⁺ (R = CH₂C₆H₅ for Calcd. 654.1112 and CH₂CHMe₂ for Calcd. 620.1269 [M-CF₃CO₂]⁺) from the main N-protonated mononuclear Ni(II) products **4b** and **4c** respectively, together

with a low adjacent ion peak at m/z = 607.1133 and 573.1281 for the half of dication $[{(Ph_2PCH_2)_2NR}_2Ni_2(\mu-SCH_2CH_2S)]^{2+}$ (R = CH₂C₆H₅ for Calcd. 607.1157 and CH₂CHMe₂ for Calcd. 573.1313 [(M-2CF₃CO₂)/ 2]⁺) from the minor dinuclear Ni(II)-Ni(II) products **3b** and **3c**. This is well accordant with their $^{31}P\{^{1}H\}$ NMR spectra (Fig. 4B and C) that all show a strong phosphorus signal at δ_P 6.5 ppm for **4b** and 6.6 ppm for **4c** [38,39] in company with a weak P signal at δ_P 2.3 ppm for **3b** and 1.1 ppm for **3c**, wherein the percentage contents correspond to 56% for **4b**, 80% for 4c, 37% for 3b, and 17% for 3c. However, for protonated product of 2d with nitrogen-free diphosphine (dppp), a highest ion peak at m/z = 516.0709, corresponding to the half of dication [{(Ph₂PCH₂)₂N $(CH_2)_2Ni_2(\mu-SCH_2CH_2S)^{2+}$ (Calcd. 516.0735 $[(M-2CF_3CO_2)/2]^+)$ from the sole dinuclear product 3d, is noticed in its positive-mode HRESI-MS spectrum (Fig. S8). This is in good agreement with only a new phosphorus signal at δ_P 5.8 ppm for **3d** observed in its ³¹P{¹H} NMR spectrum (Fig. 4D). In addition, further analysis of the FT-IR spectral region in the region of $2700-2300 \text{ cm}^{-1}$ shows no specific differences for both neutral precursors 2a-2d and their protonated products (Fig. S9),



Scheme 3. Protonation reactions of 2a-2d with excess TFA (10 equivalents).



Fig. 4. Comparisons for ³¹P{¹H} NMR spectra (A-D) of mononuclear Ni(II) complexes **2a-2d** (down) *versus* the respective protonated products **3a-3d** as well as **4a-4c** (up), respectively.

suggesting that sulfur protonation didn't occur [40]. The high-field region ¹H NMR spectra for protonated products of **2a-2d** all don't show any proton signals (Fig. S10), indicating no formation of the Niprotonated species ($\delta_{Ni^-H} = ca. -13 \sim -16$ ppm) [27,38,39].

More fortunately, the molecular structure of dinuclear Ni(II)-Ni(II) complex 3d discussed above is definitely confirmed by X-ray crystallography, wherein the perspective drawing of its dication $[{(Ph_2PCH_2)_2N(CH_2)}_2Ni_2(\mu-SCH_2CH_2S)]^{2+}$ is illustrated in Fig. 5 with selected distances and angles. This dication of 3d features a butterflyshaped [Ni₂S₂] framework with one bridging ethanedithiolate (edt) and two chelating diphosphines (dppp), as reported for a known dinuclear analogue $[(dppe)_2Ni_2(\mu-SC_3H_6S)]^{2+}$ [27]. Each Ni(II) core lies in an almost square-planar coordination geometry and its dppp ligand displays a chair conformation of the six-membered NiP₂C₃ ring, which is comparable to its mononuclear Ni(II) precursor 2d. Furthermore, the Ni-P and Ni-S distances around Ni(1) are slightly shorter by 0.01 and 0.03 Å relative to those around Ni(2), respectively. This is possibly due to the following fact that the P-Ni-P and S-Ni-S angles around Ni(1) are different from those around Ni(2). Notably, the Ni-Ni distance is 2.9911(6) Å, which is significantly longer than those observed for natural [FeFe]-H₂ases (2.55–2.62 Å) [8,9] but is closer to those found in native [NiFe]-H₂ases (2.5–2.9 Å) [21–23]. This finding implies that dinuclear Ni₂S₂ complex 3d could be structurally considered as an active site model of [NiFe]-H2ases.

Therefore, these aforemetioned results have shown that protonation of the PCNCP-chelate complexes **2a-2c** produced a mixture of dinuclear Ni(II)-Ni(II) dication complexes **3a-3c** and mononuclear Ni(II) N-protonated complexes **4a-4c**, whose main protonated products are assigned to **3a**, **4b**, and **4c**, respectively. By contrast, protonation of the dpppchelate complex **2d** afforded a sole dinuclear Ni₂S₂ analogue **3d**. It is interesting to note that the resulting protonated products of **2a-2d**, *i.e.*, complexes **3a-3d** and **4a-4c**, might be involved in the following electrocatalytic proton reduction by **2a-2d** in the presence of TFA as a proton source.

3.4. Electrochemical and electrocatalytic studies of mononuclear Ni(II) complexes 2a-2d

The electrochemical properties of mononuclear Ni(II) complexes **2a-2d** are studied in 0.1 M *n*-Bu₄NPF₆/MeCN solution at a scan rate of 0.1 V



Fig. 5. Molecular structure of dication $[{(Ph_2PCH_2)_2N(CH_2)}_2Ni_2(\mu-SCH_2CH_2S)]^{2+}$ from dinuclear Ni(II)-Ni(II) complex **3d** with thermal ellipsoids at 35% probability. Hydrogen atoms are omitted and phenyl groups are represented as sticks for clarity. Selected lengths (Å) and angles (deg): Ni(1)-Ni(2) 2.9911(6), Ni(1)-P(1) 2.1989(10), Ni(1)-P(2) 2.1928(11), Ni(2)-P(3) 2.1983 (10), Ni(2)-P(4) 2.1935(10), Ni(1)-S(1) 2.2047(10), Ni(1)-S(2) 2.2049(10), Ni (2)-S(1) 2.2348(10), Ni(2)-S(2) 2.2305(10); P(1)-Ni(1)-P(2) 91.84(4), P(3)-Ni (2)-P(4) 97.25(4), *S*(1)-Ni(1)-S(2) 81.10(4), *S*(1)-Ni(2)-S(2) 79.88(4).

 s^{-1} under N₂ atmosphere by using CV technique (Fig. 6) and their electrochemical data are given in Table 3.

As presented in Fig. 6, the cyclic voltammograms (CVs) of **2a-2d** all display a reversible reduction peak at $E_{pc} = -2.07$ ($i_{pc}/i_{pa} = 1.0$), -2.09 ($i_{pc}/i_{pa} = 1.0$), -2.11 ($i_{pc}/i_{pa} = 1.0$), and -2.10 V ($i_{pc}/i_{pa} = 1.0$), respectively, which are attributed to the Ni(II/I) redox couple [27]. In addition, the CVs of **2a-2d** collected at multiple scan rates from 0.05 to 0.3 V s⁻¹ in 0.1 M *n*-Bu₄NPF₆/MeCN solution can be used to construct Cottrell plots of reduction peak current (i_{pc}) against square root of scan rate ($\nu^{1/2}$) as shown in Fig. S11, wherein there is a linear correlationship between i_{pc} and $\nu^{1/2}$ (insert of Fig. S11). This indicates that the electrochemical Ni(II/I) reduction processes in **2a-2d** are diffusion limited in MeCN solution with the similar diffusion coefficents of $\sim 10^{-5}$ cm²/s [41–45], thus demonstrating they are homogeneous pre-electrocatalyst [44,45].

Further electrocatalytic behaviors of proton reduction to H₂ catalyzed by complexes **2a-2d** are investigated with TFA ($pK_a^{MeCN} = 12.7$) [41] by using CV technique (Fig. 7) and their electrochemical data upon 10 mM TFA are listed in Table 3.

As displayed in Fig. 7, the CVs of 2a-2d upon sequential additions of 0-10 mM TFA all show an almost identical electrocatalytic feature for proton reduction to H₂. First of all, the addition of 2 mM TFA gives rise to a new and more positive reduction peak at $E_{nc} = ca. -1.70$ V for **2a-2c** with PCNCP ligands and at $E_{pc} = -1.65$ V for **2d** with dppp (Fig. 7 and Table 3), which is accompanied by a nearly disppearence of their initial reduction peaks at $E_{pc} = ca.$ -2.10 V. Furthermore, the new reduction peak currents of **2a-2c** at $E_{pc} = ca$. -1.70 V and **2d** at $E_{pc} = -1.65$ V display the dramatical and linear increasement upon the consecutive additions of acid concentration ([TFA], 2-10 mM) as seen for inserts of Fig. 7, indicating that the typical catalytic proton reduction processes take place at new reduction potentials of $E_{pc} = ca.$ -1.70 and -1.65 V observed above [42-51]. It is noted that the aforementioned behaviors of 2a-2d with TFA are analogous to those observed previously for several diphosphine-chelate dinuclear Fe₂S₂ complexes with strong acids such as HOTs, HBF4, TFA [49-51]. However, in contrast to those with excess strong acid (TFA), the CVs of 2a-2d with excess weak acid (HOAc, 0-10 mM) show the distinct electrocatalytic feature for proton reduction to H₂ as follows. The initial reduction peak currents of **2a-2d** $at^{1}E_{pc} = ca.$ -2.10 V do not almost grow but the new reduction peak currents at $E_{pc} = ca.$ -2.25 V (i.e., more negative reduction potential



Fig. 6. CVs of 1.0 mM complexes **2a** (black), **2b** (red), **2c** (blue), and **2d** (pink) recorded in 0.1 M *n*-Bu₄NPF₆/MeCN solution at a scan rate of 0.1 V s⁻¹. All potentials are *versus* the ferrocene/ferrocenium (Fc^{0/+}) couple. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

Relevant electrochemical data for neutral complexes **2a-2d** and their main protonated products **3a**, **4b**, **4c**, **3d** prepared above.

Complex	${}^{a}E_{\rm pc}$ (V vs. Fc ⁺ /Fc)	${}^{b}E_{\rm pc}$ (V vs. Fc ⁺ /Fc)	$^{c}E_{\rm pc}$ (V vs. Fc ⁺ /Fc)
2a	-2.07	-1.69	-1.67
2b	-2.09	-1.73	-1.59
2c	-2.11	-1.70	-1.60
2d	-2.10	-1.65	-1.62

^a E_{pc} is defined as the potential of initial reduction peak for complex **2a-2d** at 0 mM TFA.

 $^{\rm b}$ E_{pc} is defined as the potential of initial reduction peak for complex **2a-2d** at 10 mM TFA.

^c E_{pc} is defined as the potential of initial reduction peak for the main protonated products **3a**, **4b**, **4c**, and **3d** obtained in the above protonation studies.

appeared upon 2 or 4 mM) sharply and linearly increase as the concentrations of HOAc are from 2 to 10 mM (Fig. S12). These observations imply that the complete protonations of **2a-2d** under excess TFA and electrochemical condition gave rise to the new and similar electroactive species **3a-3d** as observed in the chemical protonation studies (Scheme 3), thus affording the new and more positive reduction peak potentials at $E_{pc} = ca$. -1.70 or -1.65 V.

To further support the formation of the electroactive species **3a-3d** proposed during eletrocatalysis of **2a-2d** with excess TFA, we tested the CV curves of the main protonated products **3a**, **4b**, **4c**, and **3d** prepared above, which are compared with those of **2a-2d** upon 10 mM TFA as illustrated in Fig. 8. The relevant electrochemical data of **3a**, **4b**, **4c**, and **3d** are summarized in Table 3. First of all, the main dinuclear Ni(II)-Ni (II) dication products **3a** and **3d** display a similar initial reduction peak at $E_{pc} = -1.67$ and -1.62 V (solid lines of Fig. 8A, D and Table 3) respectively, the potentials of which are closer to those observed for their neutral precursors **2a** and **2d** upon 10 mM TFA at $E_{pc} = -1.69$ and

- 1.65 V (dash lines of Fig. 8A, D and Table 3). In contrast, the main mononuclear Ni(II) N-protonated products 3b and 3c show a nearly identical initial reduction peak at $E_{pc} = ca$. -1.60 V (solid lines of Fig. 8B, C and Table 3), whose potentials are obviously more positive than those observed for their neutral precursors **2b** and **2c** with 10 mM TFA at E_{pc} = ca. -1.70 V (dash lines of Fig. 8B, C and Table 3). It is worth mentioning that the CVs of homologues 2a-2c all present a very similar reduction potential at $E_{pc} = ca$. -1.70 V to that for reference 2d ($E_{pc} =$ -1.65 V) in the presence of 10 mM TFA (dash lines of Figs. 8A-8C and Table 3). Meanwhile, the ³¹P{¹H} spectrum of the electroactive species in situ formed upon addition of 10 mM TFA to 2d shows only a phosphorus signal at δ_P 5.9 ppm assigned to **3d**, being well consistent with that ($\delta_P = 5.8$ ppm) observed above for the as-prepared complex 3d (Fig. S13). Thus, these results strongly suggest the formation of the same electroactive species **3a-3c** as **3d** under excess TFA and electrochemical condition.

On the basis of these CV findings discussed above for 2a-2d and some similar cases reported previously for diphosphine-chelate diiron dithiolate complexes [49–51], the electrocatalytic processes of proton reduction to H₂ by **2a-2d** are proposed at their new reduction potentials of $E_{\rm nc} = ca. -1.70$ or -1.65 V, wherein that of **2d** as a representative of 2a-2d is presented in Scheme 4. Firstly, mononuclear neutral complex 2d (labeled [Ni^{II}]⁰) is completely protonated with excess TFA to form a dinuclear Ni(II)-Ni(II) species [3d]²⁺ (labeled [Ni^{II}-N^{II}]²⁺). Then, the resultant dication [3d] $^{2+}$ is reduced at -1.65 V (but as for 2a-2c, $E_{pc} =$ ca. -1.70 V) to produce its reduced species $[3d]^+$ (labeled $[Ni^{II}-N^{I}]^+$), which is protonated by TFA to generate the hydride species $[3d(\mu H)]^{2+}$ (labeled $[Ni^{III}(\mu H)N^{II}]^{2+}$). Afterwards, the resulting species $[3d(\mu H)]^{2+}$ would be further protonated by TFA to afford the hydrogen-binding species $[3d(H_2)]^{3+}$ (labeled $[Ni^{III}(H_2)N^{II}]^{3+}$), which finally accepts an electron to form H_2 and return [3d]²⁺ and completes a catalytic cycle. It is therefore worth pointing out that these dinclear Ni(II)-Ni(II) species



Fig. 7. CVs of 1.0 mM **2a** (A), **2b** (B), **2c** (C), and **2d** (D) in 0.1 M *n*-Bu₄NPF₆/MeCN solution upon additions of 0–10 mM TFA at a scan rate of 0.1 V s⁻¹. *Insert:* Plots of the catalytic peak current (i_{cat}) against the added acid concentrations ([TFA]). All potentials are *versus* the ferrocene/ferrocenium (Fc^{0/+}) couple.



Fig. 8. Comparisons for CVs (A-D) of complexes 2a-2d with 10 mM TFA (1.0 mM, dash line) versus the respective main protonated products 3a, 4b, 4c, and 3d prepared above (1.0 mM, solid line).



Scheme 4. Proposed electrocatalytic processes of proton reduction to H₂ by complex 2d as a representive of mononuclear Ni(II) complexes 2a-2d under excess TFA.

3a-3d, which are formed *in situ* from the complete protonations of **2a-2d** with excess TFA under CV condition, are all found to be electrocatalytically active for proton reduction to H_2 .

4. Conclusions

In summary, we synthesized and characterized three new mononuclear Ni(II) dithiolate complexes **2a-2c** with PCNCP ligands and a known reference analogue **2d** with dppp, which are structurally related to the Fe_d core of [FeFe]-H₂ases and the Ni core of [NiFe]-H₂ases. Notably, the comparative studies on the chemical protonations and electrochemical properties of **2a-2d** suggest that (i) a new series of dinuclear Ni(II)-Ni(II) dication complexes **3a-3d** were unexpectedly formed from the facile protonations of precursors **2a-2d** with excees TFA; and (ii) they as electroactive species are responsible for the catalytic proton reduction to H₂ under electrochemical condition and excess strong acid (TFA). Further X-ray crystallographic analysis of **3d** shows that its Ni—Ni distance is closer to those found in [NiFe]-H₂ases but is much larger than those observed in [FeFe]-H₂ases. Thus, this new type of dinuclear Ni₂S₂ complexes like **3a-3d** could be considered as active

site models of [NiFe]-H2ases.

Declaration of Competing Interest

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.

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Appendix A. Supplementary data

CCDC numbers 2053145 (1b), 2053146 (2a), 2053147 (2b), 1962470 (2c), 2053148 (2d), and 2053149 (3d) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or e-mail: dep osit@ccdc.cam.ac.uk. Preparation and characterization of new PCNCP ligands (Ph₂PCH₂)₂NR (General synthetic procedure and Figs. S1-S4), spectroscopic characterization for protonated products of **2a**–2d (Figs. S1–S10), additional electrochemical studies of **2a**–2d (Figs. S14–S34) are found online in the Supporting Information section associated with the article. Supplementary data to this article can be found online at https://doi.org/10.1016/j.jinorgbio.20 21.111449.

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