Synthesis and characterization of carboxy-functionalized diiron model complexes of [FeFe]-hydrogenases: Decarboxylation of Ph_2PCH_2COOH promoted by a diiron azadithiolate complex

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ABSTRACT

Two carboxy-functionalized diiron complexes $[\{(\mu\text{-}SCH_2)_2X\}\{Fe(CO)_3\}\{Fe(CO)_2L\}]$ (X = NC_3H_7, L = Ph_2PCH_2CH_2COOH, **4**; X = CH_2, L = Ph_2PCH_2COOH, **5**) were prepared, as biomimetic models of the [FeFe] hydrogenase active site, from the CO-replacement of $[\{(\mu\text{-}SCH_2)_2NC_3H_7\}Fe_2(CO)_6]$ (**1**) and $(\mu\text{-}pdt)Fe_2(CO)_6$ (**2**) by phosphine ligands in CH_3CN at 40 °C, respectively. In contrast, the reaction of **1** with Ph_2PCH_2COOH under the same condition afforded complex $[\{(\mu\text{-}SCH_2)_2NC_3H_7\}\{Fe(CO)_3\}\{Fe(CO)_2(Ph_2PCH_3)\}]$ (**3**) with a decarboxylated phosphine ligand. The molecular structures of complexes **3–5** were determined by X-ray crystallographic analyses, which show that they have similar frameworks with the phosphine ligand on the apical position. The interesting C–H$\cdots$S contacts between the methylene hydrogen atoms of the $PhCH_2COOH$ ligand and the μ-S atoms of the pdt-bridge are found in the crystal of **5**. According to the experimental evidence, a plausible mechanism, via sequential phosphine coordination, N-protonation, and decarboxylation steps, is proposed for the formation of **3** and for explanation of the contrastive reactivities of the adt- (2-aza-1,3-propanedithiolato) and the pdt- (1,3-propanedithiolato) bridged diiron complexes toward decarboxylation of the Ph_2PCH_2COOH ligand.

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1. Introduction

Iron hydrogenases have captured the interest of many biologists and chemists in recent years, due to their high efficiency in H_2 production (6000–60,000 molecules H_2 s^{-1} per site) as compared to other types of hydrogenases in nature [1,2]. The structure of the [FeFe] hydrogenase active site (H-cluster) has been determined by the X-ray crystallographic and IR spectroscopic studies [3,4]. In addition to the unusual diatomic ligands, CO and CN^-, and a sub-cluster $Fe_4S_4(SCys)_4$ in the coordination sphere of the iron atoms, there is a three-atom linker $(–CH_2XCH_2–)$ bridging two S atoms of the Fe_2S_2 subunit. The X of the three-atom linker is not clearly defined, which is proposed to be CH_2, NH (NH_2^+), or O moiety [5–7]. Density functional calculations suggest that the bridging-N atom may act as a proton carrier in the mechanism of enzymatic H_2 evolution [8], but the potential function of the bridging-N atom in the catalytic proton reduction process by the [FeFe] hydrogenases is still a question. Studies on the chemical reactivity of diiron model complexes bridged by the pdt- (1,3-propanedithiolato) as

compared to the adt- (2-aza-1,3-propanedithiolato) ligand may give us some enlightenment for understanding the role of the bridging-N atom of the H-cluster in the mechanism of enzymatic H_2 evolution.

In recent research on the structural and functional biomimics of the H-cluster, we introduced a carboxy-functionalized phosphine ligand to the diiron complex for the purposes of (1) preparing precursors to be connected to photosensitizers [9,10], semiconductors, electrodes [11], or proteins [12] and (2) exploring the reactivity of diiron dithiolate complexes with carboxy-functionalized substrates. In preparation of carboxy-functionalized diiron complexes, we found that the adt-bridged diiron complex $[\{(\mu\text{-}SCH_2)_2NC_3H_7\}Fe_2(CO)_6]$ (**1**) could promote the decarboxylation of Ph_2PCH_2COOH under mild condition, while its pdt-bridged diiron analogue $[(\mu\text{-}pdt)Fe_2(CO)_6]$ (**2**) could not. Undoubtedly, the distinct reactivities of the adt- and the pdt-bridged diiron complexes result from the bridging-N atom, which can act as a built-in basic site in the reaction. Here we contrast the reactions of the adt- and the pdt-bridged diiron complexes with carboxy-functionalized phosphine ligands, the molecular structures of $[\{(\mu\text{-}SCH_2)_2NC_3H_7\}\{Fe(CO)_3\}\{Fe(CO)_2(Ph_2PCH_3)\}]$ (**3**), formed by decarboxylation of the phosphine ligand, and the carboxy-functionalized diiron complexes $[\{(\mu\text{-}SCH_2)_2X\}\{Fe(CO)_3\}\{Fe(CO)_2L\}]$ (X = NC_3H_7, L = Ph_2PCH_2CH_2COOH, **4**; X = CH_2, L = Ph_2PCH_2COOH, **5**). The mechanism of the Ph_2PCH_2COOH decarboxylation promoted by

the diiron azadithiolate complex is discussed and the different chemical reactivities of the adt- and pdt-bridged diiron complexes have been compared on the basis of the experimental results. Although numerous diiron dithiolate model complexes and their derivatives have been reported in recent years, to the best of our knowledge, there is only one report on the preparation of carboxy-functionalized diiron dithiolate complexes [13].

2. Experimental

2.1. Instruments and materials

All reactions and manipulations were performed using standard schlenk and high-vacuum techniques. Starting compound $Fe(CO)_5$ and other organic reagents were purchased from commercial suppliers and used without further purification. All solvents were dried with standard methods, distilled before use and stored under nitrogen atmosphere. Ligands Ph_2PCH_2COOH and $Ph_2PCH_2CH_2COOH$ were prepared according to the literature procedures [14]. The adt- and the pdt-bridged all-CO diiron complexes **1** and **2** were synthesized following reported protocols [15–17].

Proton and ^{31}P NMR spectra were obtained using a Varian INO-VA 400 MHz spectrometer. Infrared spectra were recorded on a JASCO FT/IR 430 spectrophotometer. High resolution mass spectra (HR-MS) were performed by electrospray ionization (ESI) on an HPLC-Q-TOF MS (Micromass) mass instrument.

2.2. Reaction of $[\{(\mu\text{-}SCH_2)_2NC_3H_7\}Fe_2(CO)_6]$ (**1**) with Ph_2PCH_2COOH

The ligand Ph_2PCH_2COOH (0.12 g, 0.5 mmol) was added to a solution of complex **1** (0.10 g, 0.23 mmol) in CH_3CN (10 mL). The mixture was stirred overnight at 40 °C and the solution turned dark red. The crude product was purified by column chromatography on silica gel using CH_2Cl_2/hexane (1/10, v/v) as eluent. The main red band gave a decarboxylated diiron complex $[\{(\mu\text{-}SCH_2)_2NC_3H_7\}[Fe(CO)_3][Fe(CO)_2(Ph_2PCH_3)]$ (**3**) as a dark red solid (0.06 g, 43%). Recrystallization in CH_2Cl_2/hexane (1/20, v/v) afforded crystals of **3** suitable for X-ray crystallography study. IR (CH_3CN): v_{CO} 2043 (m), 1983 (s), 1929 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): 7.66 and 7.42 (2s, 10H, Ph), 3.01 (s, 4H, SCH_2), 2.16 (br, 2H, NCH_2 of NC_3H_7), 1.11 (br, 2H, CCH_2C of NC_3H_7), 0.86 (s, 3H, PCH_3), 0.68 (br, 3H, CH_3 of NC_3H_7) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 48.11 (s) ppm. HR-MS: m/z calcd. for [M+H]+ 601.9611. Found: 601.9635.

2.3. Reaction of $[\{(\mu\text{-}SCH_2)_2NC_3H_7\}Fe_2(CO)_6]$ (**1**) with $Ph_2PCH_2CH_2COOH$

The reaction was made under the same reaction condition as the aforementioned procedure for preparation of **3** but using **1** (0.10 g, 0.23 mmol) and $Ph_2PCH_2CH_2COOH$ (0.13 g, 0.5 mmol). The crude product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent. The CO-replaced diiron complex $[\{(\mu\text{-}SCH_2)_2NC_3H_7\}\{Fe(CO)_3\}\{Fe(CO)_2(Ph_2PCH_2CH_2COOH)\}]$ (**4**) was obtained from the main red band as a dark red solid (0.1 g, 65%). Recrystallization in CH_2Cl_2/hexane (1/10, v/v) afforded crystals of **4**. IR (CH_3CN): v_{CO} 2045 (m), 1979 (s), 1928 (vs), $v_{C=O}$ 1706 (w) cm^{-1}. ^1H NMR ($CDCl_3$): 7.67 and 7.43 (2s, 10H, Ph), 2.88 (br, 2H, CH_2COOH), 2.76 (br, 4H, SCH_2), 2.60 (br, 2H, PCH_2), 2.16 (br, 2H, NCH_2 of NC_3H_7), 1.15 (br, 2H, CCH_2C of NC_3H_7), 0.68 (br, 3H, CH_3 of NC_3H_7) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 57.02 (s) ppm. HR-MS: m/z calcd. for [M+H]$^+$, 659.9665. Found: 659.9658.

2.4. Reaction of $(\mu\text{-}pdt)Fe_2(CO)_6$ (**2**) with Ph_2PCH_2COOH

The reaction was made under the same reaction condition as aforementioned procedure for preparation of **3** but using complex

Table 1
Crystallographic data and processing parameters for **3**, **4**, and **5**.

Complex	3	4	5
Empirical formula	$C_{23}H_{24}Fe_2NO_5PS_2$	$C_{25}H_{26}Fe_2NO_7PS_2$	$C_{22}H_{19}Fe_2O_7PS_2$
M_w	601.22	673.26	602.16
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.6159(6)	11.9703(18)	7.9235(6)
b (Å)	11.7468(6)	12.7017(18)	11.8191(8)
c (Å)	19.5424(7)	20.777(3)	13.4805(9)
α (°)	90.00	86.267(2)	108.056(12)
β (°)	93.300(3)	74.829(2)	94.312(4)
γ (°)	90.00	89.490(2)	95.374(5)
V (Å^3)	2662.1(2)	3042.3(8)	1228.90(15)
Z	4	4	2
ρ_{calcd} (g cm^{-3})	1.500	1.470	1.627
$F(0\,0\,0)$	1232	1380	612
Crystal size (mm^3)	0.32 × 0.20 × 0.15	0.32 × 0.22 × 0.16	0.30 × 0.20 × 0.12
$\theta_{min/max}$ (°)	1.99/28.39	1.96/22.49	1.54/26.78
Reflections collected/unique	18 863/6607	12 342/7898	17 568/5173
Parameters refined	307	703	307
Goodness-of-fit on F^2	1.038	0.972	1.025
Final R_1 [$I > 2\sigma(I)$]	0.0410	0.0626	0.0405
Final wR_2	0.0609	0.1272	0.0873
Residual electron density (e Å^{-3})	0.369, −0.334	0.791, −0.362	1.039, −0.545

2 (0.097 g, 0.25 mmol) and Ph_2PCH_2COOH (0.12 g, 0.5 mmol). The crude product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent. The CO-replaced diiron complex $[(\mu\text{-}pdt)\{Fe(CO)_3\}\{Fe(CO)_2(Ph_2PCH_2COOH)\}]$ (**5**) was obtained as an orange red solid (0.08 g, 54%). Recrystallization in CH_2Cl_2/hexane (1/1, v/v) afforded crystals of **5**. IR (CH_3CN): v_{CO} 2042 (s), 1980 (s), 1929 (m), $v_{C=O}$ 1701 (w) cm^{-1}. ^1H NMR ($CDCl_3$): 7.70 and 7.43 (2s, 10H, Ph), 3.66 (s, 2H, CH_2COOH), 1.86 (br, 4H, SCH_2), 1.61 (br, 2H, $SCH_2CH_2CH_2S$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 59.28 (s) ppm. HR-MS: m/z calcd. for [M+Cl]$^-$, 636.8697. Found: 636.8679.

2.5. X-ray diffraction studies of complexes **3–5**

Crystallographic data were measured on a Siemens SMART System CCD diffractometer using graphite monochromated Mo Kα radiation with a wavelength (λ) of 0.71073 Å at a temperature of 293 ± 2 K. Data processing was accomplished with the SAINT processing program [18]. Intensity data were corrected for absorption by the SADABS program [19]. The structures were solved by direct methods and refined on F^2 against full-matrix least-squares methods using the SHELXTL97 program [20]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by geometrical calculation, and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data and processing parameters for **3**, **4**, and **5** are shown in Table 1. The quality of the crystal of **4** is not good and the solvent molecules (CH_3OH) in the lattice are disordered, which cause Alerts of level A in the checkcif, but the main structure of **4** can be determined by the collected X-ray analysis data.

3. Results and discussion

3.1. Reactions of **1** and **2** with carboxy-functionalized phosphine ligands and spectroscopic characterization of complexes **3–5**

The initial design was to introduce a carboxy group to the diiron azadithiolate model complex through the convenient reaction of CO-replacement by Ph_2PCH_2COOH, but an unexpected decarboxyl-
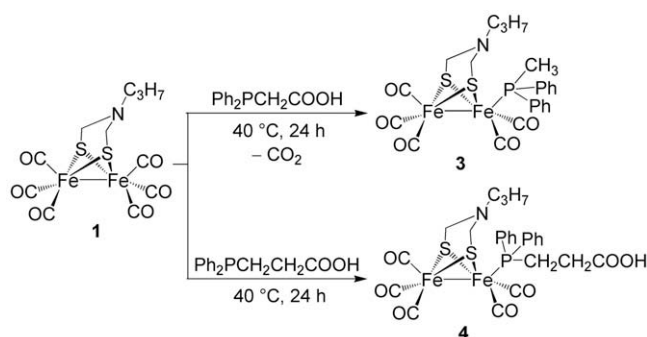
Scheme 1.

ation reaction occurred spontaneously. Treatment of [{(μ-SCH$_2$)$_2$-NC$_3$H$_7$}Fe$_2$(CO)$_6$] (**1**), prepared from [(μ-HS)$_2$Fe$_2$(CO)$_6$] and C$_3$H$_7$N(CH$_2$OH)$_2$ according to the literature procedure [15,16], with 2 equiv. of Ph$_2$PCH$_2$COOH in CH$_3$CN at 40 °C afforded the monosubstituted diiron complex [{(μ-SCH$_2$)$_2$NC$_3$H$_7$}{Fe(CO)$_3$}{Fe(CO)$_2$(Ph$_2$-PCH$_3$)}] (**3**) in a moderate yield (Scheme 1). Although 2 equiv. of Ph$_2$PCH$_2$COOH was added the phosphine disubstituted diiron complex was not detected by ^{31}P NMR spectrometry. It is clear that the ligand Ph$_2$PCH$_3$ in complex **3** was derived from decarboxylation of Ph$_2$PCH$_2$COOH. The designed diiron complex [{(μ-SCH$_2$)$_2$NC$_3$H$_7$}-{Fe(CO)$_3$}{Fe(CO)$_2$(Ph$_2$PCH$_2$COOH)}] was not detected by IR spectrometry and the free ligand Ph$_2$PCH$_3$ was not found in the HPLC/MS spectra of the mother solution. Doorn et al. reported that diphenylphosphinoacetic acid readily forms diphenyl methyl phosphine and carbon dioxide in a toluene solution at 90–100 °C [21]. In our experiment we found that in the absence of complex **1**, Ph$_2$PCH$_2$COOH did not decarboxylate when stirred in CH$_3$CN at 40 °C for 24 h. Experimental results indicate that the decarboxylation of Ph$_2$PCH$_2$COOH is promoted by the diiron azadithiolate complex.

To avoid decarboxylation, the homologous compound Ph$_2$PCH$_2$CH$_2$COOH was used as a carboxy-functionalized phosphine ligand. The reaction of **1** and excess Ph$_2$PCH$_2$CH$_2$COOH in CH$_3$CN at 40 °C gave the expected carboxy-functionalized diiron complex [{(μ-SCH$_2$)$_2$NC$_3$H$_7$}{Fe(CO)$_3$}{Fe(CO)$_2$(Ph$_2$PCH$_2$CH$_2$COOH)}] (**4**) in a good yield (Scheme 1). Again, the phosphine disubstituted diiron complex was not detected by ^{31}P NMR spectrometry.

To understand more about the decarboxylation reaction, the similar reaction of [(μ-pdt)Fe$_2$(CO)$_6$] (**2**) and Ph$_2$PCH$_2$COOH was explored. The usual monosubstituted diiron complex [(μ-pdt){Fe-(CO)$_3$}{Fe(CO)$_2$(Ph$_2$PCH$_2$COOH)}] (**5**) was obtained from the reaction of (μ-pdt)Fe$_2$(CO)$_6$ with Ph$_2$PCH$_2$COOH in CH$_3$CN at 40 °C for 24 h in 54% yield (Scheme 2). The decarboxylated compound Ph$_2$PCH$_3$, either as free compound or as a ligand coordinating to one of the iron atoms of the diiron complex, was not detected by HPLC-MS and IR spectra. The different reactivities of pdt- and adt-bridged all-CO diiron complexes are clearly caused by the bridging-N atom, which can act as a built-in basic site in the reaction. We will discuss in the latter section the role of the bridging-N atom in the decarboxylation of Ph$_2$PCH$_2$COOH promoted by the diiron azadithiolate complex.
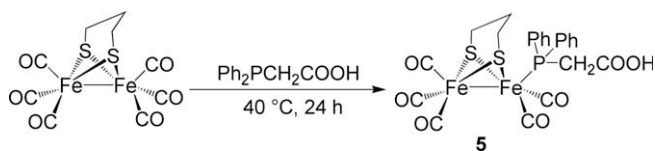
Complexes **3–5** were characterized by IR, ^{1}H and ^{31}P NMR spectroscopy and HR-MS spectrometry. The mass spectra display primary peaks of mono-charged species [M+H]$^+$ at m/z 601.9635 (calcd. 601.9611) for **3**, 659.9658 (calcd. 659.9665) for **4** and 636.8697 (calcd. 636.8679) for **5**. Complexes **3**, **4**, and **5** each show three νCO bands in the region of 1920–2050 cm^{-1} (in CH$_3$CN) with quite similar frequencies. Compared with all-CO complex **1**, the average values (ν$_{COav}$) of the three strong ν$_{CO}$ bands of **3** and **4** shift by 58 and 51 cm^{-1} to low frequency, respectively. A 39 cm^{-1} red-shift of the ν$_{COav}$ frequency complex **5** as compared to that of its parent all-CO complex **2**. In addition to the ν$_{CO}$ bands, complexes **4** and **5** also display the bands at 1706 and 1701 cm^{-1}, respectively, attributed to the vibration of the carbonyl group of the carboxy-functionalized phosphine ligands. Single crystal X-ray diffraction studies were made to determine the molecular structures of complexes **3–5**.

3.2. Molecular structures of complexes 3–5

The molecular structures of **3–5** are depicted in Fig. 1 and selected bond lengths and angles are listed in Table 2. The frameworks of **3**, **4**, and **5** are similar, with the phosphine ligand on an apical position. In the central [2Fe2S] unit of **3–5**, two Fe atoms and two S atoms form a butterfly conformation as in previously reported models [13,22–24]. The Fe–Fe single bonds are 2.5205(6), 2.512(2), and 2.5126(6) Å for **3**, **4**, and **5**, respectively. As shown in Fig. 1, complex 4 exists as two conformational isomers with the rotation of the phosphine ligand around the Fe–P bond. One isomer is in the conformation with the carboxy group pointing forward (Fig. 1b) and the carboxy group of the other conformation isomer points backward (Fig. 1b′). The two conformation isomers pair up in a crystal cell. The crystal structure and the carbonyl absorption of **4** indicate that the framework of the diiron azadithiolate complex is quite stable toward the common carboxy group, which cannot protonate the bridging tertiary amine of the diiron model complex.

The packing diagram (Fig. S1 in ESI) of molecules in the crystal of complex **4** shows that three kinds of intermolecular hydrogen bonds are present in the crystal state of **4**. The O–H···O distances between two Ph$_2$CH$_2$CH$_2$COOH ligands are in the range of 2.64–2.69 Å, the O$_{CO}$···H–C$_{Ph}$ distance between the oxygen atom of a CO ligand and one of the ortho-hydrogen atoms of the phenyl group is 3.218 Å, and the O$_{OH}$···H–C$_{Ph}$ distance between the OH group of the Ph$_2$PCH$_2$CH$_2$COOH ligand and the para-hydrogen of the phenyl group is 3.496 Å. The packing diagram of molecules in the crystal of complex **5** is given in Fig. 2. The extended networks are constructed by two kinds of intermolecular H-bonds. As expected, there are the H-bonds (O–H···O 2.66 Å) among the carboxy groups of the phosphine ligands as that existing in the crystal of **4**. It is interesting to find that the hydrogen atoms on the methylene group of the PhCH$_2$COOH ligand form hydrogen bonds with the μ-S atoms of the pdt-bridge in the crystal of **5**. The distance of C···S is 3.71 Å with the C–H···S angle of 144.2°, which is in the range (3.55–4.01 Å) of the C–H···S intermolecular hydrogen bonds [25]. It gives another support for the protophilicity of the μ-S atoms in the [2Fe2S] model complexes of the [FeFe] hydrogenase active site [26].

3.3. Discussion on the mechanism of decarboxylation of Ph$_2$CH$_2$COOH promoted by the diiron azadithiolate complex

In order to provide insight into the contrast of reactivity between the adt- and the pdt-bridged diiron complexes, control reactions were designed as follows: in the presence of an equivalent of NEt$_3$, the carboxy-functionalized phosphine Ph$_2$PCH$_2$COOH generated a white precipitate in CH$_3$CN at 40 °C without formation of
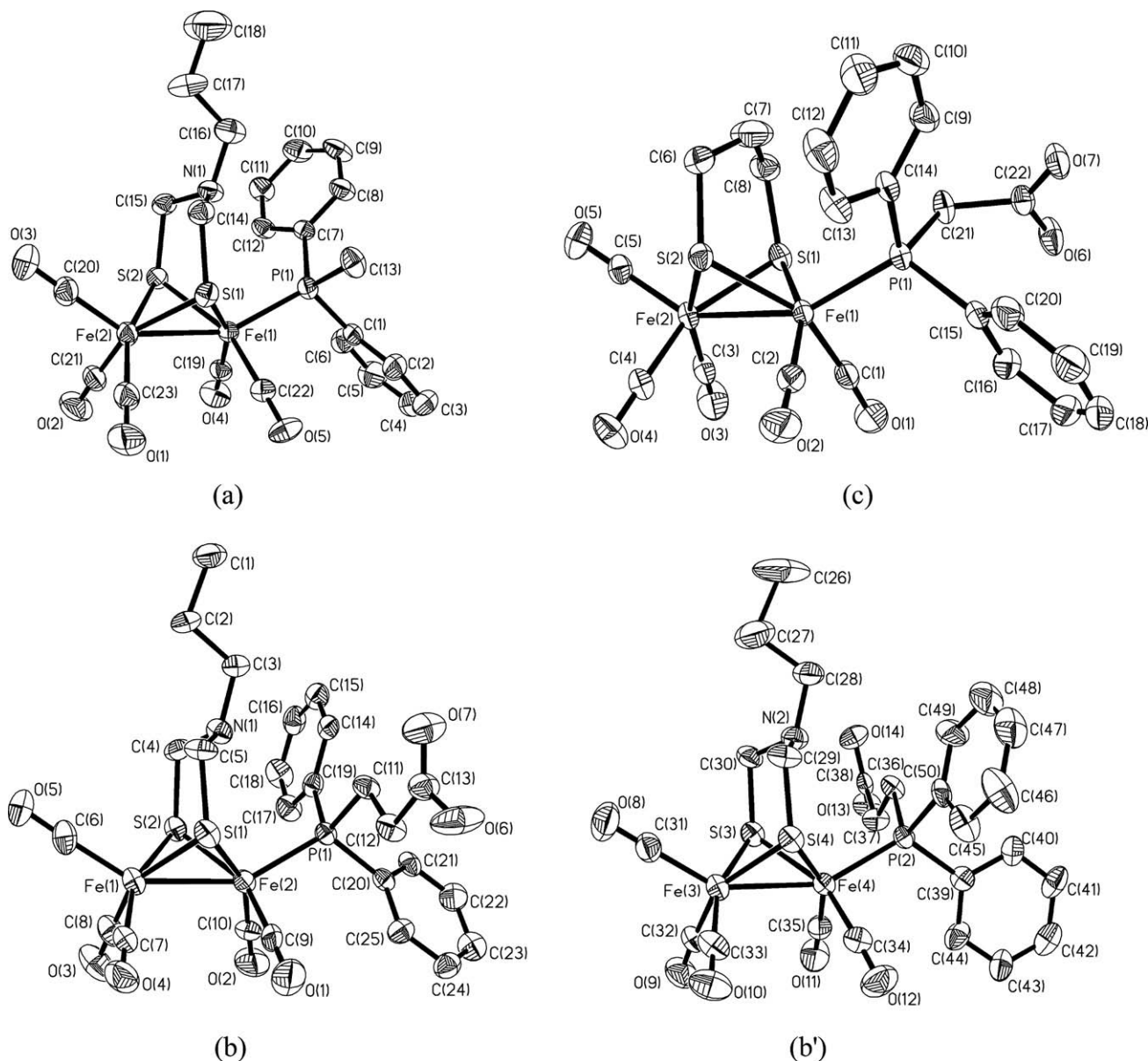

Scheme 2.

Fig. 1. Molecular structures of complexes **3** (a), **4** (b) and (b′), and **5** (c) with 30% thermal ellipsoids.

Table 2
Selected bond lengths (Å) and angles (deg) for **3**, **4**, and **5**.

	3	**4**	**4′**	**5**
Fe–Fe	2.5205(6)	2.5136(17)	2.5153(17)	2.5126(6)
Fe–P	2.2271(9)	2.231(2)	2.233(3)	2.2260(9)
Fe–S[a]	2.2586(9)	2.263(3)	2.260(5)	2.2568(9)
Fe–C$_{CO}$[b]	1.7757(6)	1.768(7)	1.772(1)	1.776(2)
Fe–S–Fe (deg)[c]	67.83(3)	67.48(3)	67.62(3)	67.65(3)
S–Fe–S (deg)[d]	56.02(7)	84.31(9)	83.93(4)	84.76(8)

[a] Average over four Fe–S bonds.
[b] Average over five Fe–C$_{CO}$ bonds.
[c] Average over two Fe–S–Fe angles.
[d] Average over two S–Fe–S angles.

the decarboxylated compound Ph$_2$PCH$_3$. As aforementioned, the reaction of the pdt-bridged diiron complex **2** with Ph$_2$PCH$_2$COOH in CH$_3$CN at 40 °C gave an expected CO-replaced diiron complex **5**, and the decarboxylation of the Ph$_2$PCH$_2$COOH ligand did not occur. The results of these two control reactions indicate that both

the coordination of Ph$_2$PCH$_2$COOH and the presence of a basic species are sine qua nons for promoting decarboxylation of Ph$_2$PCH$_2$COOH under mild condition. Furthermore, neither the reaction of the pdt-bridged diiron complex **2** with Ph$_2$PCH$_2$COOH and NEt$_3$, nor the reaction of isolated complex **5** with NEt$_3$ could afford a Ph$_2$PCH$_3$ coordinate diiron complex like **3** in CH$_3$CN at 40 °C. The results indicate that the crucial role of the bridging-N atom as a built-in basic site cannot be replaced by the external base NEt$_3$.

The thermal decarboxylation of Ph$_2$PCH$_2$COOH that occurs in apolar solvents at 90–100 °C is proposed to involve a phosphonium carboxylate zwitterion [21]. Apparently, this is not the case for the decarboxylation of Ph$_2$PCH$_2$COOH in CH$_3$CN at 40 °C in the presence of diiron azadithiolate complex **1**. According to the experimental results of the control reactions, a plausible mechanism (Scheme 3), via sequential phosphine coordination, N-protonation, and decarboxylation steps, is proposed for the formation of **3** and for explanation of the contrastive reactivities of the adt- (2-aza-1,3-propanedithiolato) and the pdt-(1,3-propanedithiolato)
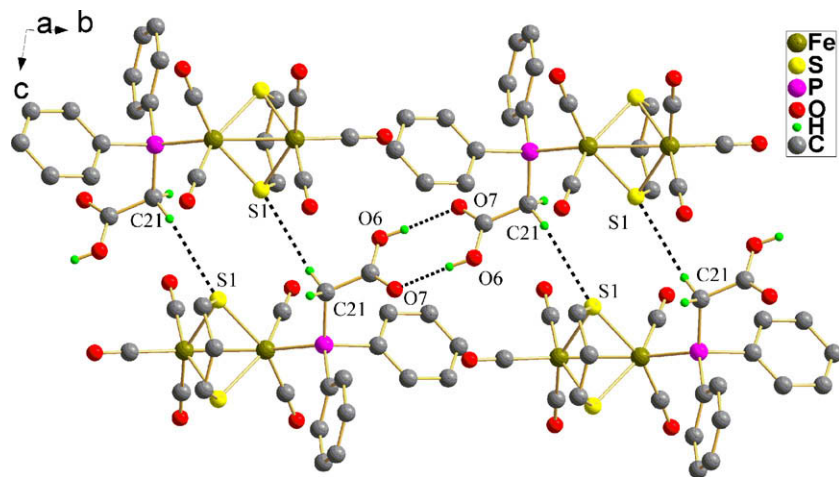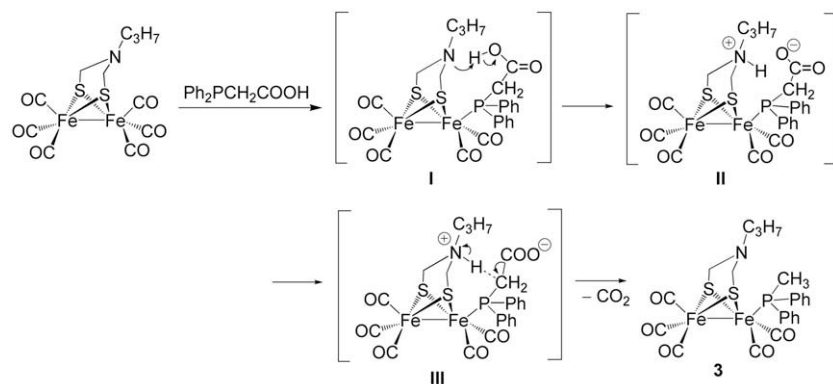
Fig. 2. Stereoplot of molecules in the crystal of complex **5**. The dotted lines represent the intermolecular H-bond interactions.

Scheme 3.

bridged diiron complexes toward decarboxylation of the Ph₂PCH₂COOH ligand. Similar N-coordination followed by intramolecular protonation processes have accounted for the catalytic decarboxylation of cyanoacetic acid by tungsten complexes [27]. The coordination of Ph₂PCH₂COOH to the iron atom makes the phosphorus more electron deficient relative to that in the free phosphine ligand, thereby leading to an increase of the acidity of the carboxy group. The HPLC/MS spectrum of the mother solution, obtained from the reaction of **1** with Ph₂PCH₂COOH in CH₃CN at −30 °C for 12 h, shows two small peaks with [M+H]⁺ at m/z 645.9 for the intermediate **I** and 601.9 for the decarboxylated diiron complex **3**, respectively, in addition to the large peaks for the unreacted complex **1** and the ligand Ph₂PCH₂COOH (Fig. S2 in ESI). The other experimental result supporting the initial coordination of the phosphine ligand is that no new peak appears in the cyclic voltammogram of **1** upon addition of 2 equiv. of Ph₂PCH₂COOH in CH₃CN, indicating that the bridging-N atom of **1** cannot be protonated by Ph₂PCH₂COOH. Followed by the coordination of Ph₂PCH₂COOH, the next step involves intramolecular proton transfer between the carboxy group and the bridging-N atom. Decarboxylation of the ammonium carboxylate zwitterion (**II**) occurs with the incipient carbanion being stabilized by intramolecular N−H⋯CH₂ hydrogen bonds (intermediate **III**) followed by proton transfer between the ammonium-N and the carbanion to give complex **3**, like described for the mechanism of W(0)-catalyzed decarboxylation of NCCH₂COOH [27]. In the mechanism the

bridging-N atom acts as an intramolecular proton carrier, which seems an indispensable factor for the [2Fe₂S] complex-promoted decarboxylation of Ph₂PCH₂COOH.

4. Conclusions

Two carboxy-functionalized diiron model complexes (**4** and **5**) of the [FeFe] hydrogenase active site were prepared and well characterized, which can be used as ready building blocks for construction of catalyst-photosensitizer, -semiconductor and -electrode assemblies. The X-ray crystallographic study shows the interesting C−H⋯S intermolecular hydrogen bonds between the methylene hydrogen atoms of the PhCH₂COOH ligand and the μ-S atoms of the pdt-bridge in the crystal of **5**. It implies that the bridging-S atoms are also possible protophilic sites of the H-cluster. The adt- and the pdt-bridged diiron complexes displayed contrastive reactivities for decarboxylation of Ph₂PCH₂COOH. The adt-bridged diiron complex [{(μ-SCH₂)₂NC₃H₇}Fe₂(CO)₆] (**1**) can promote the decarboxylation of the Ph₂PCH₂COOH ligand in CH₃CN at 40 °C, giving Ph₂PCH₃-coordinate diiron complex **3**. In contrast, the reaction of the pdt-bridged diiron analogue [(μ-pdt)Fe₂(CO)₆] (**2**) with Ph₂PCH₂COOH under the same reaction condition afforded the usual CO-replaced complex [(μ-pdt){Fe(CO)₃}{Fe(CO)₂(Ph₂PCH₂-COOH)}] (**5**) without formation of the detectable amount of the decarboxylated phosphine ligand. The experimental results suggest that the bridging-N atom of complex **1** may act as an intramo-

lecular proton carrier in the reaction, reminiscent of the proposed proton transfer function of the bridging-N atom in the H-cluster in enzymatic proton reduction to molecular hydrogen [8,28].

Acknowledgements

Appendix A. Supplementary material

CCDC 699699, 699698 and 699700 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center 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.jorganchem.2009.03.039.

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