



Modeling [FeFe] hydrogenase: Synthesis and protonation of a diiron dithiolate complex containing a phosphine-N-heterocyclic-carbene ligand

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ABSTRACT

The ligand exchange reaction of $I_{Me}-(CH_2)_2-PPh_2$ (I_{Me} = 1-methylimidazol-2-ylidene) and the hexacarbonyl complex $[Fe_2\{\mu-S(CH_2)_3S\}(CO)_6]$ (**1**) resulted in the formation of the chelated complex $[Fe_2\{\mu-S(CH_2)_3S\}(CO)_4(I_{Me}-(CH_2)_2-PPh_2)]$ (**2**). The molecular structure of **2** was confirmed by spectroscopic and X-ray analyses. This complex catalyzes proton reduction. Low temperature NMR studies on the protonation of **2** revealed the formation of a terminal hydride intermediate.

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1. Introduction

[FeFe]-hydrogenases are metalloenzymes which very efficiently catalyze the reversible reduction of protons to dihydrogen ($2H^+ + 2e^- = H_2$) [1]. Crystal structure determinations revealed that the active site, the so-called H-cluster, contains an organometallic subsite, which consists of a dithiolate bridged diiron core bearing CO and CN^- ligands [2]. As a result, studies on diiron dithiolate complexes as models for [FeFe]-hydrogenases have considerably increased with the goal of understanding the mechanistic steps involved in the uptake and evolution of dihydrogen by the enzyme and of replicating hopefully its high activity [3]. Monosubstitution of carbonyl groups at both iron centers in complex $[Fe_2\{\mu-S(CH_2)_3S\}(CO)_6]$ (**1**) for better electron-donating ligands, such as CN^- , RNC, PR_3 and N-heterocyclic carbene (NHC) ligands, induced protonation at the diiron site in a bridging position in presence of strong acids [4]. By using bidentate reagents L_2 (L_2 = diphosphane, bis-NHC, phenanthroline), unsymmetrical systems $[Fe_2\{\mu-S(CH_2)_3S\}(CO)_4(L_2)]$, where one iron is chelated by the ligand, are formed [5,6]. DFT calculations have shown that the presence of electron-donating ligands at one iron centre in complexes $[Fe_2\{\mu-S(CH_2)_3S\}(CO)_4(L_2)]$ might facilitate a transition state with a "rotated" structure similar to the one observed in the enzyme [7]. The existence of this inverted pyramid at one iron centre could fa-

vor the formation of a terminal hydride in the protonation process. Terminal hydrides species may be regarded as key reactive intermediates in the catalytic production of dihydrogen by [FeFe] hydrogenases [8]. Recently, we showed that nonsymmetric dithiolato-diiron complexes undergo protonation at a single metal prior to forming bridging hydride species [6]. In the case of the chelated complex $[Fe_2\{\mu-S(CH_2)_3S\}(CO)_4(dppe)]$ ($dppe$ = bis(diphenylphosphanyl)ethane) [6a] the protonation reaction was very slow at $-90^\circ C$, whereas that of the bis-NHC analogue $[Fe_2\{\mu-S(CH_2)_3S\}(CO)_4(I_{Me}-CH_2-I_{Me})]$ (I_{Me} = 1-methylimidazole-2-ylidene) [6c] gave a very unstable terminal hydride intermediate. These results encouraged us to investigate whether a diiron complex containing a bidentate ligand, with both NHC and phosphine functionalities, promotes the formation of a stable terminal hydride compound in the presence of acids. In this paper, we report the synthesis of the precursor of the carbene-phosphine ligand, as well as its reactivity towards the hexacarbonyl complex $[Fe_2\{\mu-S(CH_2)_3S\}(CO)_6]$ (**1**) and the reactivity of the chelated complex $[Fe_2\{\mu-S(CH_2)_3S\}(CO)_4(I_{Me}-(CH_2)_2-PPh_2)]$ (**2**) towards protons.

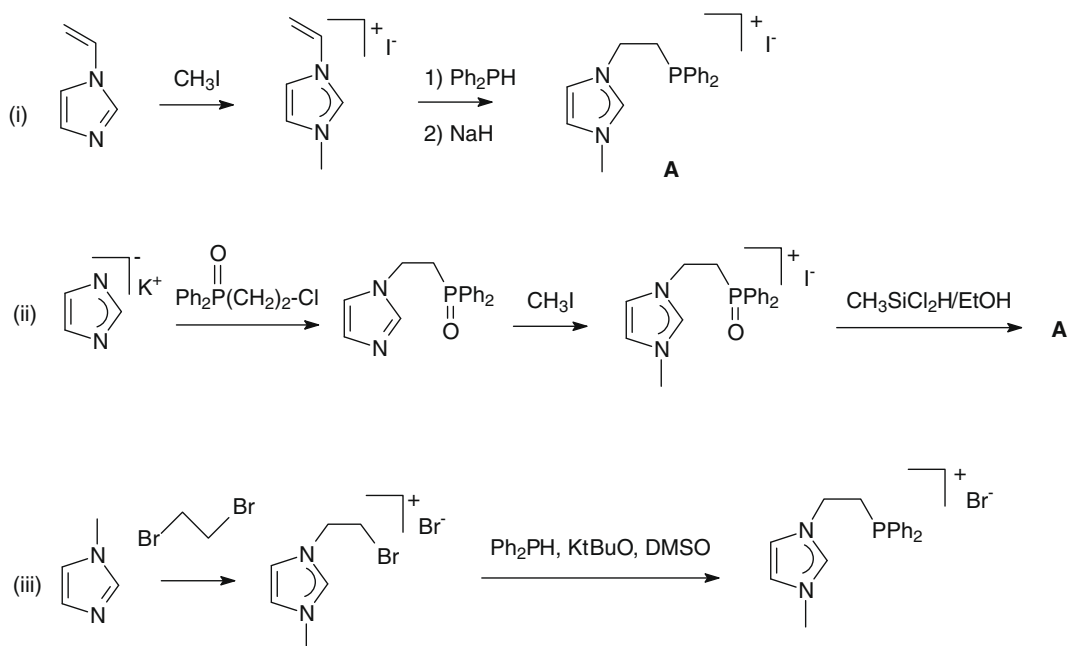
2. Results and discussion

2.1. Synthesis

The phosphine imidazolium salt 3-[2-diphenylphosphinoethyl]-1-methylimidazolium iodide **A** was easily prepared according to the procedure (i) depicted in Scheme 1, i.e. by addition of

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Scheme 1.

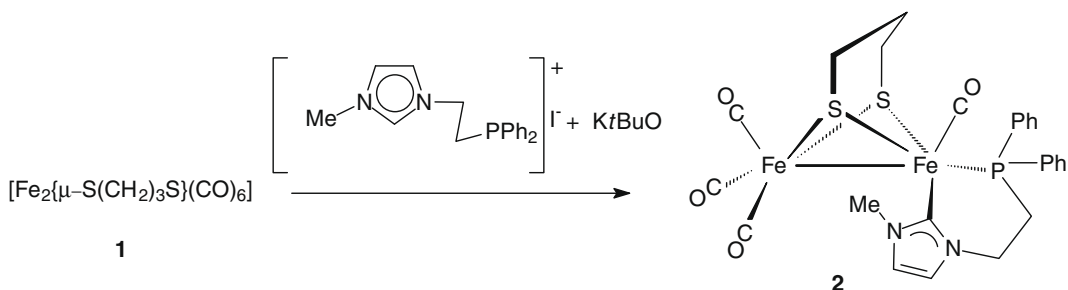
diphenylphosphine to 3-methyl-1-vinylimidazolium iodide in presence of NaH. This synthetic procedure is more convenient than the previous methodology based on the use of phosphine oxide followed by reduction by $\text{CH}_3\text{SiCl}_2\text{H}/\text{EtOH}$ (Scheme 1, procedure (ii)) [9]. A similar strategy was reported for the synthesis of 3-[2-diphenylphosphino-ethyl]-1-mesitylimidazolium salts [10]. Syntheses of phosphine-imidazolium chloride, bromide, and hexafluorophosphate compounds have been also described on reacting 1-methylimidazole with 1,2-dihaloethane to give 3-(2-haloethoxy)-1-methylimidazolium compounds, further addition of potassium diphenylphosphine in dimethylsulfoxide affords the desired phosphine-imidazolium salt (Scheme 1, procedure (iii)) [11]. It should be noted that in this procedure (iii), long reaction periods are required to avoid the formation of bis-imidazolium side-products, whereas according to path (i) the reaction goes to completion in less than 2 h.

The precursor imidazolium salt **A** was treated with the strong base KtBuO to generate the free NHC, $\text{I}_{\text{Me}}-(\text{CH}_2)_2-\text{PPh}_2$, before reaction with the hexacarbonyl complex $[\{\text{Fe}_2\{\mu-\text{S}(\text{CH}_2)_3\text{S}\}(\text{CO})_6\}]$ (**1**). Heating a toluene solution of **1** with an excess of free NHC for 1.5 h at 80°C afforded $[\text{Fe}_2\{\mu-\text{S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{I}_{\text{Me}}-(\text{CH}_2)_2-\text{PPh}_2)]$ (**2**), isolated as a red complex, after column chromatography (Scheme 2).

The desired chelated complex **2** was obtained in 20% yield; it was characterized by IR and NMR spectroscopy, elemental analysis,

mass spectrometry and X-ray crystallography. Three strong $\nu(\text{CO})$ bands at 2006, 1933 and 1882 cm^{-1} are observed in the IR spectrum. The $\nu(\text{CO})$ values of **2** are between those of the chelated bis-NHC complex $[\text{Fe}_2\{\mu-\text{S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{I}_{\text{Me}}-(\text{CH}_2)_2-\text{I}_{\text{Me}})]$ (1994, 1921, 1869 cm^{-1}) [6c] and those of the dppe analogue $[\text{Fe}_2\{\mu-\text{S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{dppe})]$ (2019, 1949, 1904 cm^{-1}) [6a], which is consistent with the stronger electron-donating ability of the NHC ligand relative to that of the phosphine ligand. The large difference between the highest and the lowest $\nu(\text{CO})$ band ($\Delta\nu_{\text{CO}} = 124\text{ cm}^{-1}$) of **2** is consistent with a phosphine-carbene ligand chelating a single iron atom as observed in $[\text{Fe}_2\{\mu-\text{S}(\text{CH}_2)_2\text{S}\}(\text{CO})_4(\text{dppv})]$ ($\text{dppv} = \text{cis Ph}_2\text{PCH}=\text{CHPPh}_2$) [5e], which displays $\nu(\text{CO})$ bands at 2023, 1953, 1915 cm^{-1} ($\Delta\nu_{\text{CO}} = 108\text{ cm}^{-1}$). For comparison the value of $\Delta\nu_{\text{CO}} = 90\text{ cm}^{-1}$ is smaller for the disubstituted derivative $[\text{Fe}(\text{CO})_2(\text{PMe}_3)\{\mu-\text{S}(\text{CH}_2)_3\text{S}\}\text{Fe}(\text{CO})_2(\text{IMes})]$ ($\text{IMes} = 1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{imidazol-2-ylidene}$) [12] than in complex **2**.

The room temperature $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of compound **2** shows two low field doublets at 224.0 ppm ($^2J_{\text{P-CO}} = 14\text{ Hz}$) and 190.6 ppm ($^2J_{\text{P-Carbone}} = 33\text{ Hz}$) due respectively, to the carbonyl and the $\text{C}_{\text{Carbone}}$ of the $\{\text{Fe}(\text{CO})_3(\text{I}_{\text{Me}}-(\text{CH}_2)_2-\text{PPh}_2)\}$ moiety, while a singlet at 214.4 ppm is noted for the carbonyls of the $\{\text{Fe}(\text{CO})_3\}$ moiety. The room-temperature $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of **2** consists of one singlet at 66.3 ppm; upon lowering the temperature to -60°C , three signals are observed at 68.0, 66.1 and 64.2 ppm in a 10:2:1 ratio. These signals are tentatively attributed to a mix-



Scheme 2.

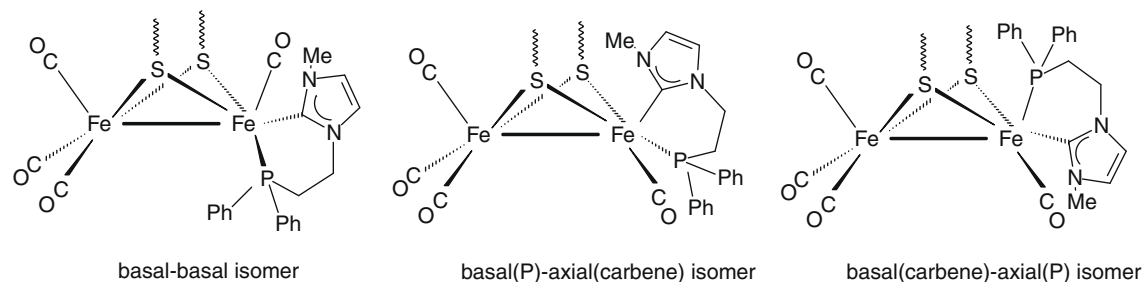


Fig. 1. Structures of various isomers discussed.

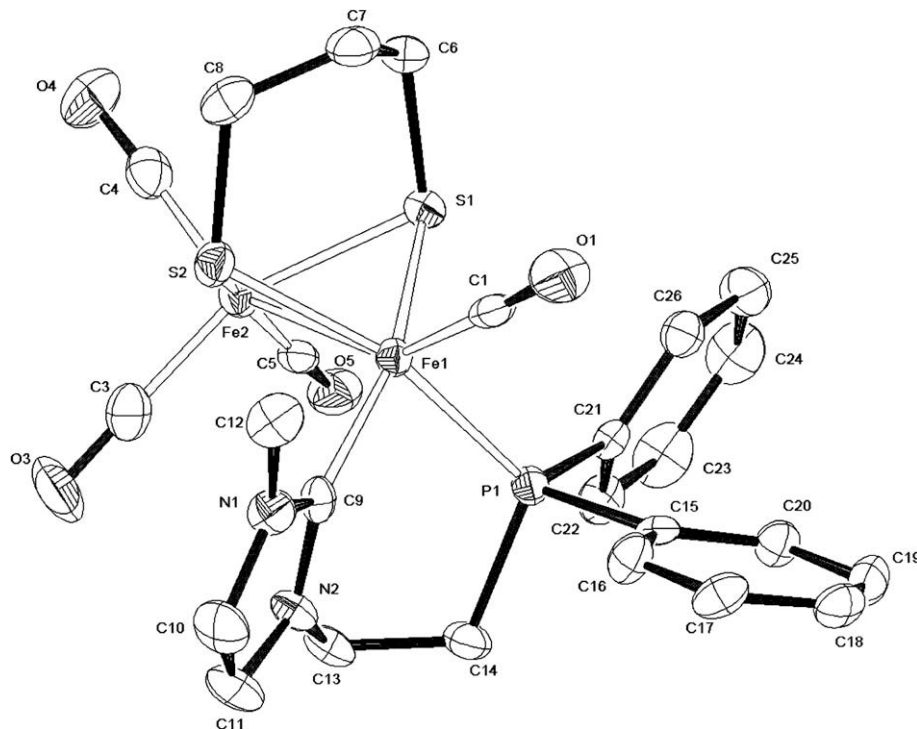


Fig. 2. ORTEP view of **2**. The thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): C1–O1 = 1.164(3), C1–Fe1 = 1.736(3), C3–O3 = 1.158(3), C3–Fe2 = 1.762(3), C4–O4 = 1.146(3), C4–Fe2 = 1.800(3), C5–O5 = 1.149(3), C5–Fe2 = 1.775(3), C9–Fe1 = 1.961(3), P1–Fe1 = 2.2320(8), S1–Fe1 = 2.2471(7), S1–Fe2 = 2.2639(8), S2–Fe1 = 2.2412(8), S2–Fe2 = 2.2622(8), Fe1–Fe2 = 2.5995(5), S2–Fe2–Fe1 = 54.37(2), S1–Fe2–Fe1 = 54.51(2), S2–Fe1–Fe2 = 55.12(2), S1–Fe1–Fe2 = 55.12(2), C9–Fe1–P1 = 87.80(8).

ture of basal–basal, basal(P)–axial(carbene) and basal(carbene)–axial(P) isomers (Fig. 1).

Crystals suitable for X-ray diffraction studies were grown from dichloromethane/diethylether mixture (60/40) at 4 °C. The molecular structure of the complex **2** (Fig. 2) features the typical butterfly Fe_2S_2 skeleton found in related diiron derivatives [3], and the binding mode of the bidentate phosphine–carbene ligand to a single iron atom in a basal–basal position like other Fe_2S_2 models containing chelating bis-NHC [6c] or carbene–pyridine [13] ligands. The six membered metallacycle (Fe(1)P(1)C(14)C(13)N(2)C(9)) adopts a boat-like conformation. The Fe(1)–S distances (2.2471(7)–2.2412(8) Å) are about 0.02 Å shorter than those to the $\text{Fe}(\text{CO})_3$ unit. The Fe–Fe distance of 2.5995(5) Å is longer than the average Fe–Fe distance (2.54 ± 0.03 Å) [2e] found in Fe_2S_2 models but is close to that observed in other basal–basal diphosphane complexes [3k].

2.2. Protonation studies

The substitution of carbonyl ligands in $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_6]$ by better electron-donating ligands afforded compounds with an

increased electron density at the diiron center and, in the case of monosubstituted compounds at both iron centers, e.g. $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{L})(\text{L}')]]$, the protonation reactions afforded bridging hydride species $[\text{Fe}_2(\mu\text{-H})\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{L})(\text{L}')]^+$ [3]. ^1H NMR spectra of these compounds display typical high field signals in the range (–12 to –20 ppm) due to the bridging hydride. In the family of diiron dithiolate compounds, only one terminal hydride complex, $[\text{Fe}(\text{H})(\text{PMe}_3)_2(\mu\text{-CO})\{\mu\text{-S}(\text{CH}_2)_2\text{S}\}\text{Fe}(\text{CO})(\text{PMe}_3)_2](\text{PF}_6)$, has been structurally characterized: it exhibits a ^1H NMR signal at –4.6 ppm, that was assigned to the terminal hydrido ligand [14]. Terminal hydrides were previously found in diphosphido-bridged diiron compounds [15].

The protonation of **2** with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in CH_2Cl_2 at room temperature afforded the bridging hydride $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\mu\text{-H})(\text{CO})_4(\text{Ime}-(\text{CH}_2)_2\text{-PPh}_2)](\text{BF}_4)$ (**3**) (Fig. 5) which was isolated as a brown powder after addition of diethylether. The presence of a high field signal that appears as a doublet at –15.9 ppm (d , $^2J_{\text{PH}} = 21$ Hz) in the ^1H NMR spectrum confirms the existence of the bridging hydride. The $^2J_{\text{PH}}$ coupling constant of 21 Hz accords with a basal position of the phosphine ligand in **3** [16]. Its IR spectrum displays $\nu(\text{CO})$ at 2092, 2039, 1972 cm^{-1} which are as expected shifted to

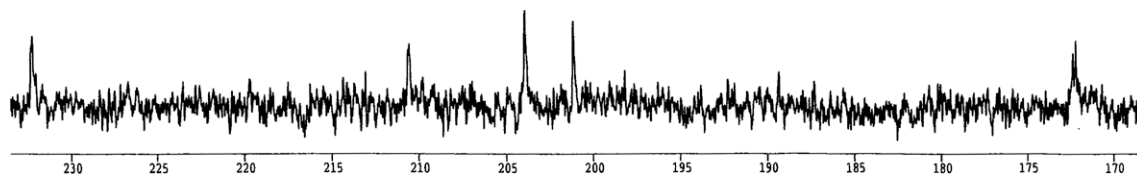


Fig. 3. $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of the terminal hydride **4** in the low field region recorded at $-90\text{ }^\circ\text{C}$ in CD_2Cl_2 .

higher wavenumbers (by about 90 cm^{-1}) as compared to the neutral complex **2** ($\nu(\text{CO})$: 2006, 1933 and 1882 cm^{-1}) [17]. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum shows a singlet at 53.7 ppm. ^{31}P and ^1H NMR spectra revealed also the existence of non-identified products, and therefore, no analytical data are available for this product.

Monitoring of the protonation reaction of a CD_2Cl_2 solution of **2** with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ by ^1H and ^{31}P NMR spectroscopy at $-90\text{ }^\circ\text{C}$ revealed the clean formation of a new hydride intermediate as indicated by the appearance of a singlet at -5.2 ppm in the ^1H NMR spectrum and of a singlet at 32.4 ppm in the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum. The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum (Fig. 3) showed three low field signals at 232.3, 203.9 and 201.1 ppm due to carbonyl ligands. A $^1\text{H}\text{-}^{13}\text{C}$ HMBC 2D NMR experiment indicated correlations between the hydride signal at -5.2 ppm and these three carbonyl signals (Fig. 4).

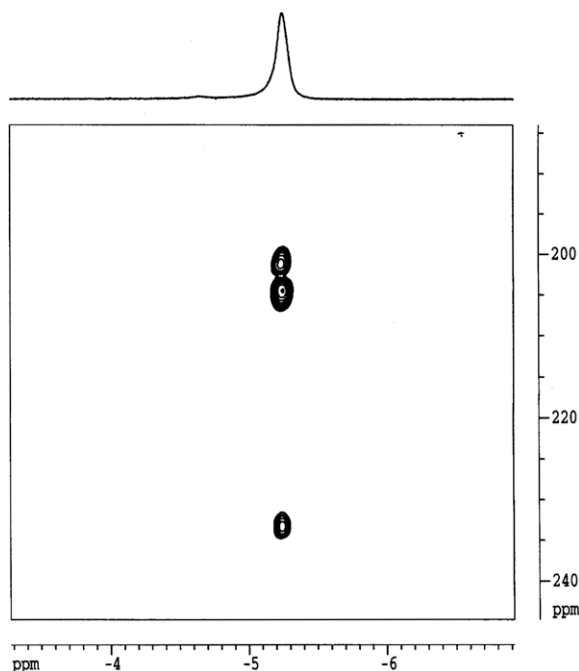


Fig. 4. Partial contour plot of the $^1\text{H}\text{-}^{13}\text{C}$ HMBC 2D NMR experiment in the hydride region, recorded at $-90\text{ }^\circ\text{C}$ in CD_2Cl_2 , for the terminal hydride **4**.

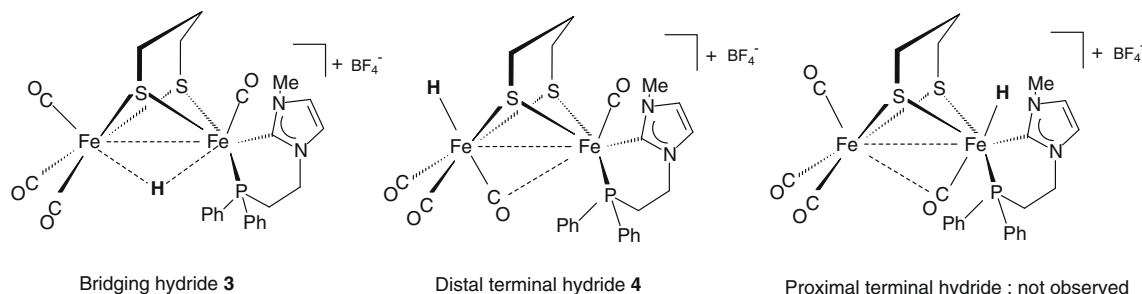


Fig. 5. Structures of various hydride species discussed.

The $\text{C}_{\text{carbene}}$ atom was observed as a doublet ($^2J_{\text{PC}} = 22\text{ Hz}$) at 172.4 ppm in the ^{13}C NMR spectrum. A doublet ($^2J_{\text{PC}} = 12\text{ Hz}$) at 210.6 ppm was attributed to the fourth carbonyl ligand. These data provide strong support for the presence of a distal terminal hydride $[\text{Fe}(\text{H})(\text{CO})_3\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}\text{Fe}(\text{CO})(\text{I}_{\text{Me}}\text{-}(\text{CH}_2)_2\text{-PPh}_2)](\text{BF}_4)$ (**4**) (Fig. 5).

Protonation at the distal iron center was also observed in tetracarbonyl complexes $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{L}_2)]$ for $\text{L}_2 =$ phenanthroline [6d], bis(dimethylphosphanylethane) (dmpe) [6e] and dppe [6a] below $-50\text{ }^\circ\text{C}$. An increase of the temperature to $-40\text{ }^\circ\text{C}$ led to the appearance of the doublet at -15.9 ppm in the ^1H NMR spectrum, which corresponds to the bridging hydride **3**. The transformation of **4** into **3** was completed above $-20\text{ }^\circ\text{C}$. Compound **4** did not evolve dihydrogen in the presence of an excess of HBF_4 . When the protonation reaction was performed at $-50\text{ }^\circ\text{C}$, only signals due to hydride compounds **3** and **4** were observed, no other terminal hydride complex was detected. For example, there was no evidence of the formation of proximal hydride compounds (Fig. 5), that were reported to be obtained as minor species in the protonation of the chelated complexes $[\{\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{L}_2)\}]$ ($\text{L}_2 =$ dppe [6a] or bis(diphenylphosphanylpropane) (dppp) [18]). When the chelating bidentate ligand (L_2) adopts a basal–basal conformation as the major isomer, protonation is favored at the $\text{Fe}(\text{CO})_3$ moiety [3k]. Protonation at the $\text{Fe}(\text{CO})(\text{L}_2)$ moiety was observed only in the case of the complexes $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{L}_2)]$, where the basal–apical isomer is predominant [3k]. Accordingly, we propose that the major isomer observed in the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum ($-60\text{ }^\circ\text{C}$) of **2** at 68.0 ppm may be the basal–basal isomer **2**. It should be noted that the terminal hydride compound **4** is more stable towards isomerization into the bridging form than its dppe analogue. It has been reported recently that the protonation of a symmetrical tetrasubstituted complex $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_2(\text{L}_2)_2]$ ($\text{L}_2 =$ dppv, *cis* $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$) afforded a terminal hydride which is more stable than compound **4** [19]. This difference of stability could be explained by stronger basicity of the metal site in the tetrasubstituted complex with respect to that in **2**. Recent results [3k] suggest that the reactivity of unsymmetrical complexes $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{L}_2)]$ depends on its ability to generate a transition state having a rotated structure bearing a vacant site at one iron center. For these systems, the inversion of the $\text{Fe}(\text{CO})_3$ moiety may be easier than that of the $\text{Fe}(\text{CO})(\text{L}_2)$ one; this explains that the initial site of protonation is the $\text{Fe}(\text{CO})_3$ moiety.

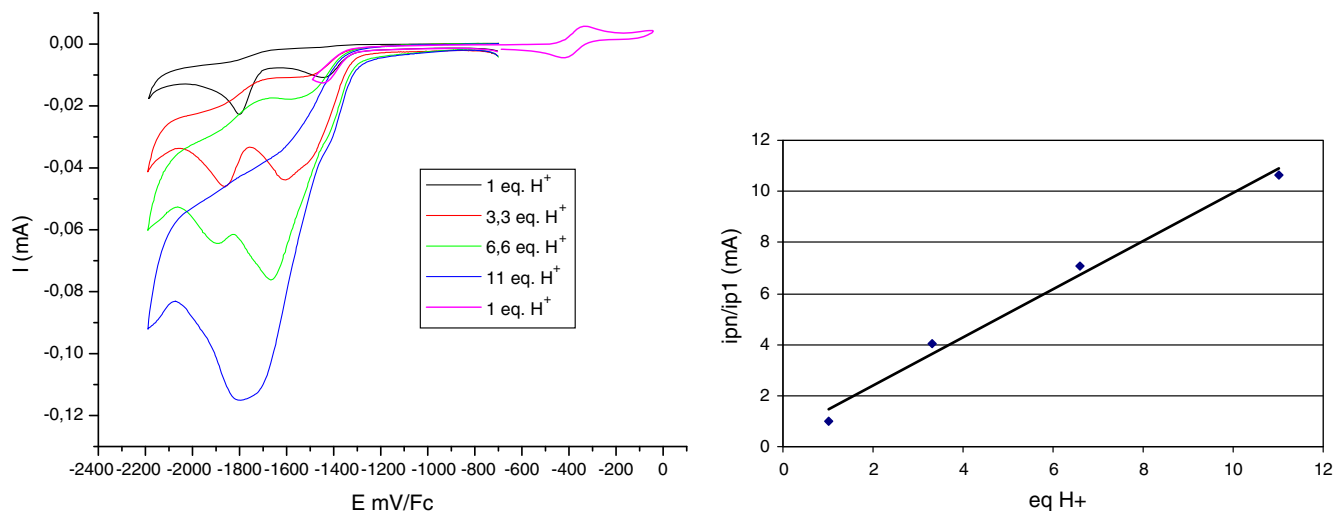


Fig. 6. Dependence of current heights of electrocatalytic waves for **2** in the presence of 1–11 equiv. of HBF₄ · Et₂O in N₂ purged CH₂Cl₂ solution + Bu₄NPF₆ electrolyte and plot of the catalytic peak current (*Ip*/*Ip1*, where *Ip1* is the intensity of the current after addition of one equivalent of HBF₄ · Et₂O) as a function of the acid concentration.

2.3. Electrochemical study

Compound **2** displays a partially reversible reduction at $E_{1/2}^{\text{red}} = -2.25$ V versus Fc^{+/0} in CH₃CN and a reversible oxidation at $E_{1/2}^{\text{ox}} = -0.40$ V. These potentials are in good agreement with the donor ability of the phosphine-N-heterocyclic-carbene ligand respective to dppe and I_{Me}-CH₂-I_{Me} observed in the complexes [Fe₂{μ-S(CH₂)₃S}(CO)₄(I_{Me}-CH₂-I_{Me})] ($E_p^{\text{red}} = -2.42$ V; $E_{1/2}^{\text{ox}} = -0.41$ V) [6c] and [Fe₂{μ-S(CH₂)₃S}(CO)₄(dppe)] ($E_p^{\text{red}} = -2.07$ V; $E_{1/2}^{\text{ox}} = -0.20$ V) [6b]. The reversible oxidation of **2** at $E_{1/2}^{\text{ox}} = -0.40$ V suggests that **2** could be oxidized by ferricinium salts as observed in [Fe(CO)₂(PMe₃)₂{μ-S(CH₂)₃S}Fe(CO)₂(IMes)] [12a], [Fe(CO)₂(PMe₃)₂{μ-S(CH₂CMe₂CH₂)S}Fe(CO)₂(PMe₃)] [20] and [Fe(CO)₂(PMe₃)₂{μ-S(CH₂)₂S}Fe(CO)₂(dppv)] [21]. In the presence of acid HBF₄ · Et₂O, the cyclic voltammogram of **2** exhibits a new reduction wave at about -1.45 V, most certainly corresponding to the reduction of a bridging hydride. This reduction increases in intensity upon increasing the acid concentration, consistent with catalytic proton reduction (Fig. 6). Closer inspection of the CV reveals however that the catalytic wave is composed of several peaks depending on the acid concentration, which suggests that several mechanisms might be involved [22].

3. Conclusion

We have synthesised a nonsymmetric complex [Fe₂{μ-S(CH₂)₃S}(CO)₄(I_{Me}-(CH₂)₂-PPh₂)] (**2**) with a chelating phosphine-N-heterocyclic-carbene ligand on a single iron atom. The study of this compound in acidic media supports that the kinetic protonation site is the Fe(CO)₃ unit and confirms that a terminal hydride is accessible as an intermediate upon protonation of diiron dithiolate complexes. Such a terminally bound hydride species is supposed to be involved in the protonation process of [FeFe] hydrogenases. Complex **2** catalyzes proton reduction at -1.45 V versus Fc^{+/0}. The nonsymmetric complex **2** is an interesting platform for further substitution of carbonyl ligands to obtain trisubstituted or tetrasubstituted diiron species.

4. Experimental

4.1. General procedures

Reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were distilled prior to use

and then they were deoxygenated and dried using conventional methods. Deuterated dichloromethane was stored under argon over molecular sieves before use. NMR spectra were recorded on a Bruker AMX 400 or a Bruker DRX 500 spectrometers with chemical shifts reported in δ values relative to residual protonated solvents for ¹H NMR spectra, and to the solvent CD₂Cl₂ and CD₃OD for ¹³C NMR spectra. Infrared spectra were recorded with a FT-IR NEXUS NICOLET spectrometer. Chemical analyses were carried out by the "Service de microanalyse I.C.S.N." Gif-sur-Yvette (France), or the "Centre de microanalyse du CNRS", Vernaison (France). Cyclic voltammetry experiments were carried out as described elsewhere [23]. The starting complex [Fe₂{μ-S(CH₂)₃S}(CO)₆] (**1**) was prepared according to literature methods [24]. The imidazolium salt, 3-methyl-1-vinylimidazolium iodide, was prepared according to a modified procedure previously reported [25].

4.2. Preparation of 3-methyl-1-vinylimidazolium iodide

A 100 mL round bottomed flask was charged with vinylimidazole (1.50 g, 15.9 mmol) in 2 mL of iodomethane. The resulting mixture was stirred for 2 h at 70 °C. The volatile compounds were removed in vacuo and the brown residue was washed with dichloromethane until it was no longer sticky. The product 3-methyl-1-vinylimidazolium iodide (3.15 g, 83%) was obtained as an orange powder.

¹H NMR (CD₃OD): δ 9.25 (s, 1H, H_{IMe}), 7.98 (s, 1H, N-CH=CH-N), 7.68 (s, 1H, N-CH=CH-N), 7.25 (dd, *J*_{HH} = 15.6 Hz, *J*_{HH} = 8.6 Hz, 1H, N-CH=CH₂), 5.90 (dd, *J*_{HH} = 15.6 Hz, *J*_{HH} = 2.7 Hz, 1H, N-CH=CH₂), 5.43 (dd, *J*_{HH} = 8.6 Hz, *J*_{HH} = 2.7 Hz, 1H, N-CH=CH₂), 3.98 (s, 3H, N-CH₃). ¹³C-{¹H} NMR (CD₃OD): δ 138.0 (NCHN), 132.4 (N-CH=CH₂), 111.1 (N-CH=CH₂), 127.3 (N-CH=CH-N), 122.0 (N-CH=CH-N), 39.3 (N-CH₃).

4.3. Preparation of 3-[2-diphenylphosphino)-ethyl]-1-methylimidazolium iodide [PPh₂-(CH₂)₂-(H_{IMe})](I) (**A**)

A 250 mL round bottomed flask was charged with 3-methyl-1-vinylimidazolium iodide (1.40 g, 6.00 mmol) under nitrogen. An excess of diphenylphosphine used as solvent (3 mL) and NaH (0.24 g, 6.00 mmol) were then added under intense stirring. The mixture was stirred for 3 h at 80 °C and left to precipitate at room temperature. The solution was removed through a cannula under nitrogen. The crude product was dissolved in dichloromethane

(3 mL) and addition of ether afforded a yellow precipitate. This procedure was repeated once again, in similar conditions, giving 1.95 g of **A** (76% yield) as a yellow powder.

^1H NMR (CD_3OD): δ 8.60 (s, 1H, HIMe), 7.34–7.45 (m, 10H, C_6H_5), 7.58 (s, 1H, N-CH=CH-N), 7.39 (s, 1H, N-CH=CH-N), 4.39 (dt, $J_{\text{HH}} = 7$ Hz, $J_{\text{PH}} = 10.3$ Hz, 2H, N-CH_2), 3.80 (s, 3H, N-CH_3) 2.75 (t, $J_{\text{HH,PH}} = 7$ Hz, 2H, $\text{Ph}_2\text{P-CH}_2$). ^{31}P NMR (CD_3OD): δ -17.0 (s, PPh_2) ppm. ^{13}C - $\{^1\text{H}\}$ NMR (CD_3OD): δ 131–139 (m, PPh_2), 137.1 (NCHN), 125.3 (N-CH=CH-N), 126.4 (N-CH=CH-N), 50.0 (N-CH₂), 37.0 (N-CH₃), 31.1 (d, $J_{\text{CP}} = 15$ Hz, $\text{CH}_2\text{-P}$) ppm. ESIMS (m/z), Calc. for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{P}$ (M^+): 295.1364; found: 295.1366.

4.4. Preparation of $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{Ime}^-(\text{CH}_2)_2\text{-PPh}_2)]$ (**2**)

Potassium tert-butoxide (0.715 g, 6.37 mmol) and THF (100 mL) were added to **A** (2.30 g, 5.40 mmol). After 3 h of vigorous stirring at room temperature, the reaction mixture was filtered and the yellow solution collected was concentrated to 5 mL in a round bottom flask. 50 mL of toluene was then transferred to this solution. The complex $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_6]$ (**1**) (0.615 g, 1.59 mmol) was dissolved in 60 mL of toluene and added dropwise to a yellow solution of the free NHC. The mixture was heated at 80 °C for 1.5 h, and then evaporated to dryness under vacuum. The resulting red solid was dissolved in a minimal amount of CH_2Cl_2 and applied to a silica gel column. Elution with a dichloromethane-hexane (40/60) mixture afforded a red solution which was evaporated under vacuum. The residue was washed with hexane (3 × 10 mL). The red powder obtained was dissolved in a dichloromethane/hexane (10/90) mixture; slow evaporation of the solvents to about 10 mL gave a red powder of compound **2** (100 mg, yield 20%) after filtration of the solvents. No other product was neither isolated nor characterised.

IR (CH_2Cl_2): ν_{CO} 2006(vs), 1933(vs), 1882(s) cm^{-1} . ^1H NMR (CD_2Cl_2): δ 7.50–7.21 (m, 10H, 2 C_6H_5), 6.98 (d, 1H, $J_{\text{HH}} = 7$ Hz, N-CH=CH-N), 6.94 (d, 1H, $J_{\text{HH}} = 7$ Hz, N-CH=CH-N), 4.70 (m, 1H, N-CHH), 4.39 (m, 1H, N-CHH), 4.16 (s, 3H, N-CH_3) 2.81 (m, 1H, P-CHH), 2.41 (m, 1H, PCHH), 2.03–1.08 (m, 6H, $\text{S-(CH}_2)_3\text{-S}$). ^{13}C - $\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 224.2 (d, $J_{\text{PC}} = 14$ Hz, $\text{FeL}_2(\text{CO})$), 214.4 (broad, $\text{Fe}(\text{CO})_3$), 190.6 (d, $J_{\text{PC}} = 33$ Hz, $\text{C}_{\text{carbene}}$), 142.3, 142.5, 133.0, 132.1, 129.5, 129.1, 128.5 and 128.3 (C_6H_5), 123.7 and 122.6 (N-CH=CH-N), 48.3 (N-CH₂), 39.1 (N-CH₃), 30.1, 25.8 and 25.3 ($\text{S-(CH}_2)_3\text{-S}$), 26.7 (d, $J_{\text{PC}} = 21$ Hz, PCH_2). ^{31}P NMR (CD_2Cl_2 , 25 °C): δ 66.3 (s). ^{31}P NMR (CD_2Cl_2 , -60 °C): δ 68.0 (s) 66.1 (s), 64.2 (s). LSIMS (m/z), Calc. for $\text{C}_{25}\text{H}_{25}\text{Fe}_2\text{N}_2\text{O}_4\text{S}_2\text{P}$ (M^+): 623.9692; found: 623.9725. Anal. Calc. for $\text{C}_{25}\text{H}_{25}\text{Fe}_2\text{N}_2\text{O}_4\text{S}_2\text{P}$: C, 48.10; H, 4.04; N, 4.49; P, 4.96. Found: C, 47.75; H, 4.04; N, 4.23; P, 4.89%.

4.5. Protonation of **2** in situ

A slight excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ was added to a CD_2Cl_2 solution of **2** (7.0 mg, 1.1×10^{-5} mol) in a NMR tube at -95 °C and the spectrum was recorded at -90 °C.

Compound 3: ^1H NMR (CD_2Cl_2 , -60 °C): δ 7.90–6.70 (m, 12H, 2 C_6H_5 and N-CH=CH-N), 4.60 (m, 2H, N-CH_2), 3.98 (s, 3H, N-CH_3), (PCH_2) and ($\text{S-(CH}_2)_3\text{-S}$) signals were hidden by ($\text{HBF}_4 \cdot \text{Et}_2\text{O}$) resonances, -15.92 (d, $J_{\text{PH}} = 21$ Hz, 1H, $\text{Fe}(\mu\text{-H})\text{Fe}$). ^{31}P NMR (CD_2Cl_2): δ 53.7 (s).

Compound 4: ^1H NMR (CD_2Cl_2 , -90 °C): δ 7.86–6.90 (m, 10H, C_6H_5), 6.92 (s, 1H, N-CH=CH-N), 6.85 (s, 1H, N-CH=CH-N), 4.93 (m, 1H, N-CHH), 4.65 (m, 1H, N-CHH), 3.89 (s, 3H, N-CH_3), (PCH_2) and ($\text{S-(CH}_2)_3\text{-S}$) signals were hidden by ($\text{HBF}_4 \cdot \text{Et}_2\text{O}$) resonances, -5.17 (s, 1H, $\text{HFe}(\text{CO})_3$). ^{31}P NMR (CD_2Cl_2): δ 32.4 (s). ^{13}C - $\{^1\text{H}\}$ NMR (CD_2Cl_2 , recorded for 3 days at -90 °C): δ 232.3 (CO), 210.6 (d, $J_{\text{PC}} = 12$ Hz, $\text{FeL}_2(\text{CO})$), 203.9 and 201.1 (CO), 172.4 (d, $J_{\text{PC}} = 22$ Hz, $\text{C}_{\text{carbene}}$) ppm. Data given in the low field region only.

Table 1

Crystal data for **2**.

Asymmetric unit	$\text{C}_{25}\text{H}_{25}\text{Fe}_2\text{N}_2\text{O}_4\text{PS}_2$
Formula weight	624.26
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>a</i> (Å)	12.2377(5)
<i>b</i> (Å)	14.5514(4)
<i>c</i> (Å)	14.9746(4)
β (°)	99.965(3)
<i>V</i> (Å ³)	2626.38(15)
<i>Z</i>	4
ρ_{calc} (g cm^{-3})	1.579
Crystal size (mm)	$0.15 \times 0.12 \times 0.04$
Absorption coefficient (mm^{-1})	1.359
<i>F</i> (000)	1280
θ Range for data collection (°)	2.74–26.37
Limiting indices	$-14 \leq h \leq 14$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$
Reflections collected/unique	17749/4991 [$R_{\text{int}} = 0.0473$]
Completeness to $\theta = 26.37^\circ$ (%)	92.9
Absorption correction	Empirical (SCALE3 ABSPACK)
Maximum and minimum transmission	0.9476 and 0.8537
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4991/0/326
Goodness-of-fit on F^2	0.919
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0296$, $wR_2 = 0.0554$
<i>R</i> indices (all data)	$R_1 = 0.0618$, $wR_2 = 0.0624$
Largest difference in peak and hole (e Å^{-3})	0.395 and -0.295

4.6. X-ray crystallography

Crystal data for compound **2** were collected with an Oxford Diffraction X-Calibur-2 CCD diffractometer equipped with a jet cooler device and graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å), and are detailed in Table 1. The structure was solved and refined by standard procedures [26].

5 Supplementary material

CCDC 706317 contains the supplementary crystallographic data for compound **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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