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# Synthesis, characterization and electrochemical reductive properties of complexes [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph</sup><sub>2</sub>N<sup>R</sup><sub>2</sub>)( $\mu$ -dithiolato)] related to the H-cluster of [FeFe]-H<sub>2</sub>ases

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Abstract: A series of dithiolato carbonyl diiron complexes with cyclic azadiphosphine, related to the active site of [FeFe]-hydrogenases, has been prepared. Several combinations of diphosphines and dithiolato bridges have been examined in order to obtain information on the influence of electronic and steric effects of the group linked to the nitrogen atom of the phosphine (phenyl or benzyl) and the bridgehead of the dithiolate (CH<sub>2</sub>, CEt<sub>2</sub>, CBn<sub>2</sub>). Products were spectroscopically and structurally characterized. Protonation experiments show that depending on the nature of the amine in the diphosphine, protonation processes are different. With NBn group, the process is arrested at N-protonated species, while with NPh, the proton is transferred to the diiron site giving bridging-hydrido species. The effect of the bridge-head group of the dithiolate is very slight on the electronic properties of compounds. Depending on the steric crowding of the bridge, different isomers related to the dibasal or basal-apical position of the diphosphine, are observed in solution or in solid state. Electrochemical study was performed to examine the activity of these compounds in the presence of acid.

#### Introduction

The important role of the amine function, as a proton relay, in the  $H^+/H_2$  catalytic conversion induced by the active site of the [FeFe]hydrogenases (Scheme 1)<sup>[1]</sup> is now well demonstrated.<sup>[2]</sup> Numerous works on diiron complexes with an aminefunctionalized-dithiolato bridge have been reported during the last decade.<sup>[3]</sup> That is worth noting that only one structural model of the key intermediary featuring a {N-H...H-Fe} interaction was reported and that tetra-substituted azadithiolato diiron complexes are among the most efficient diiron catalysts for proton reduction into dihydrogen.<sup>[4]</sup>



Scheme 1. Schematical view of the H-cluster of [FeFe]hydrogenases.

Another approach has been widely developed for introducing in diiron biomimics a pendant base, as a proton relay, via the use of terminal ligands functionalized with a base.<sup>[5-7]</sup> Especially, the presence of cyclic diphosphines of general formula  $(R'PCH_2NRCH_2)_2$   $(P^{R'}_2N^R_2)$  in the coordination sphere of bioinspired complexes may improve the efficiency of these species as catalysts for the oxidation of H<sub>2</sub> or its production.<sup>[8-10]</sup> A few years ago, the combination of such diphosphines with diiron compounds has been examined in a preliminary account<sup>[9]</sup> by our group in order to study the influence of such ligands on the proton and electron transfers at a diiron site. The diiron complex  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Ph}_2)(\mu-pdt)]$  was obtained from the reaction between  $[Fe_2(CO)_6(\mu-pdt)]$  and  $P^{Ph}_2N^{Ph}_2$ , the reactivity towards proton and the electrochemical behaviour of this species were partly studied.<sup>[9]</sup> Herein, we will present an extension of this work through the preparation of diiron complexes chelated with PPh2NR2 ligand. A series of diiron complexes with different combinations of dithiolato bridges (dithiolato = pdt, pdt<sup>Et</sup>, pdt<sup>Bn2</sup>) and diphosphines  $P^{Ph}_{2}N^{R}_{2}$  (R = Ph, Bn) have been prepared and characterized in order to examine the influence of the dithiolato bridges and the diphosphines on the molecular structure and electrochemical reductive properties of such diiron biomimics.

#### **Results and Discussion**

1 Preparation and characterization of complexes  $[Fe_2(CO)_4(\kappa^2 - P^{Ph_2}N^R_2)(\mu\text{-dithiolato})]$  (*R* = *Ph*, *Bn* and dithiolato = pdt, pdt<sup>Et2</sup>, pdt<sup>Bn2</sup>) (**1-6**)

Cyclic diphosphines  $P^{Ph}{}_2N^{R}{}_2$  (R = Ph, Bn) were obtained by using literature procedures<sup>[11]</sup> and then reacted with hexacarbonyl diiron precursors [Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -dithiolato)], in presence of two equivalents of (CH<sub>3</sub>)<sub>3</sub>NO.2H<sub>2</sub>O (Scheme 2) in a mixture of toluene-acetonitrile (4:1), allowing the substitution of two carbonyl groups by the diphosphine to form dinuclear disubstituted compounds [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph</sup><sub>2</sub>N<sup>R</sup><sub>2</sub>)( $\mu$ -dithiolato)] (Yield = 50 – 55%). All the complexes were characterized by IR, <sup>1</sup>H, <sup>31</sup>P-{<sup>1</sup>H} NMR spectroscopies, X-ray diffraction and elemental analysis. Spectroscopic and structural data of **1**<sup>[9]</sup> and **4**<sup>[10a]</sup> were previously reported. After purification by column chromatography of the crude product, the main fraction, eluted with CH<sub>2</sub>Cl<sub>2</sub>/hexane, gave the chelated diphosphine complexes **1-6**.





The IR spectra of complexes 1-6, in CH<sub>2</sub>Cl<sub>2</sub>, in the carbonyl region show three bands, between 2021 and 1885 cm<sup>-1</sup>, which corresponds to a typical shape for terminal carbonyls in dissymmetrically disubstituted diiron species  $[Fe_2(CO)_4(\kappa^2-L_2)(\mu$ dithiolato)] (Figure S1, table 1).<sup>[12]</sup> The wavenumbers are logically lower than those observed for the carbonyl bands of the starting diiron hexacarbonyl complexes. Their values show that the bridge-head substituents have only a slight influence on the electron density at the diiron centre. <sup>1</sup>H NMR spectra of 1-6 display signals expected for the different groups present in these compounds, which were attributed to  $\mathsf{P}^{\mathsf{Ph}}{}_2\mathsf{NR}_2$  and dithiolato ligands (see experimental part). <sup>31</sup>P-{<sup>1</sup>H} NMR spectra recorded at 25°C in CDCl<sub>3</sub> of  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Ph}_2)(\mu-dithiolato)]$  (1-3), show broadened peaks around 50-55 ppm, indicating that dynamic processes, related to the diphosphine, are operative in solution (Figure S2). The recording of the spectra at low temperature indicates that different isomers associated to the position of the diphosphine and the orientation of the dithiolato bridge exist in solution (Figure S2, table 1). That is well known that two types of fluxional processes exist in complexes  $[Fe_2(CO)_4(\kappa^2-diphosphine)(\mu-dithiolato)].^{[13]}$ One of them corresponds to the tilting of the bridge-head group CR<sub>2</sub> of the dithiolato bridge which can be oriented towards one or the other iron atom. This phenomenon is associated to the non-rigidity of the dithia-metalla-cyclohexane {FeS<sub>2</sub>C<sub>3</sub>}, which can adopt either a chair or a boat conformation. The second dynamic process

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consists of the exchange between the ligands carried on the same iron atom in basal and apical position. Thus, a diphosphine chelated at one iron atom may be symmetrically bound in a dibasal position or asymmetrically coordinated in a basal-apical position (Scheme 3). At low temperature, the broad signal observed at room temperature splits into two sets of resonnances: a singlet that is assigned to one isomer with a diphosphine in dibasal position and a pair of doublets characteristic of a basalapical coordination of the diphosphine. Interestingly, in the case of 3 (Figure S2) the <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum, at -65°C, only shows a single peak which indicates that the basal-apical isomer is not observed in solution suggesting that the steric crowding of the pdt<sup>Bn2</sup> bridge limits the isomerization process in favour of the dibasal form. <sup>31</sup>P-{<sup>1</sup>H} NMR spectra, recorded at different temperatures for 4-6 (Figure S3, table 1), show broadened singlets at 25°C that refine when temperature decreases to -65°C, suggesting the presence of isomers with only dibasal coordination because of the more steric crowding of the diphosphine P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>. Steric hindrance of the dithiolato bridges and that of the CH<sub>2</sub>Ph (Bn) group of the diphosphine limit the dynamic processes in 4-6. Dibasal coordination of the PPh2NBn2 diphosphine is also observed in solid state (see X-ray structures in figure 1).



Scheme 3. Possible isomers for complexes 1-6.

Single crystals of 1-6, suitable for X-ray crystallography, were grown upon slow diffusion of hexane into dichloromethane solution of the diiron complexes at -30°C. The ORTEP views of 1-6 are shown in figure 1 and confirm the overall structure of these complexes; structural data (selected bonds and angles) are given in table 2 (see table S1 for crystallographic data and refinement parameters). The Fe2S2 core in 1-6 adopts the expected butterfly conformation. Fe1-Fe2 distances (2.5537(8) - 2.5927(11) Å) are typically in the range of Fe-Fe lengths found in other diiron complexes in which a single Fe-Fe bond is considered.<sup>[3]</sup> The main difference between the solid state structures of the two series of compounds. 1-3 and 4-6. is that the diphosphine P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub> is coordinated to one iron atom in basal-apical position in 1-3 while P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub> is in a dibasal position in 4-6, which accords with the observations made in solution by NMR spectroscopy. The  $P^{Ph_2}N^{R_2}$  ligand forms with the iron atom (Fe1) two six-members {FePCNCP} rings having both boat and chair conformations. The central carbon atom of the S-to-S linker in 1 and 2 points towards

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the {Fe(CO)( $P^{Ph}_2N^{Ph}_2$ )} unit while in **3** it is oriented towards the {Fe(CO)<sub>3</sub>} moiety. The angle C2-Fe2-Fe1 for **1** and **2** is around 145° while in **3** it is 158° which can be explained by the more important steric effect of the dithiolato bridge-head group CBn<sub>2</sub>. In the case of **4-6**, the S-to-S bridge points towards the {FeCO( $P^{Ph}_2N^{Bn}_2$ )} unit. The {Fe1PCN1CP} and {Fe1PCN2CP}

rings adopt a chair and boat conformation, respectively, in **4** while in **5** and **6**, the {Fe1PCN1CP} ring presents a boat conformation and the {Fe1PCN2CP} ring has a chair conformation.

Table 1. IR (CH<sub>2</sub>Cl<sub>2</sub>, 25°C) and  ${}^{31}P-{}^{1}H$  NMR (CDCl<sub>3</sub>, -65°C for 1-6 and 25°C for 7-10) data of complexes 1-10.

Complex	IR (CH <sub>2</sub> Cl <sub>2</sub> , cm <sup>-1</sup> ), ū(CO)	<sup>31</sup> P-{ <sup>1</sup> H} NMR (CDCl <sub>3</sub> , δ: ppm)
[Fe <sub>2</sub> (CO) <sub>4</sub> (κ <sup>2</sup> -P <sup>Ph</sup> <sub>2</sub> N <sup>Ph</sup> <sub>2</sub> )(μ-pdt)] ( <b>1</b> ) <sup>[9]</sup>	2021 (s), 1945 (s), 1898 (w)	61.0 (d), 52.1 (d), <sup>2</sup> J <sub>pp</sub> = 79.2 Hz 55.1 (s)
$[Fe_2(CO)_4(\kappa^2 - P^{Ph_2}N^{Ph_2})(\mu - pdt^{Et2})] \ (\textbf{2})$	2019 (s), 1943 (s), 1894 (w)	57.3 (d), 50.5 (d), <sup>2</sup> J <sub>pp</sub> = 82.0 Hz 54.2 (s)
$[Fe_{2}(CO)_{4}(\kappa^{2}-P^{Ph}_{2}N^{Ph}_{2})(\mu-pdt^{Bn2})] (3)$	2015 (s), 1946 (s), 1892 (w)	54.0 (s)
[Fe <sub>2</sub> (CO) <sub>4</sub> (κ <sup>2</sup> -P <sup>Ph</sup> <sub>2</sub> N <sup>Bn</sup> <sub>2</sub> )(μ-pdt)] ( <b>4</b> ) <sup>[10a]</sup>	2011 (s), 1939 (s), 1892 (w)	52.4 (s)
$[Fe_{2}(CO)_{4}(\kappa^{2}-P^{Ph}_{2}N^{Bn}_{2})(\mu-pdt^{Et2})] (5)$	2009 (s), 1936 (s), 1888 (w)	52.4 (s)
$[Fe_2(CO)_4(\kappa^2 - P^{Ph_2}N^{Bn_2})(\mu - pdt^{Bn2})] (6)$	2011 (s), 1940 (s), 1885 (w)	52.5 (s)
$[Fe_2(CO)_5(\kappa^1-P^{Ph}_2N^{Ph}_2S)(\mu-pdt)] \ (\textbf{7})^{[9]}$	2042 (s), 1984 (s), 1961 (sh), 1923 (w)	55.7 (br), 32.0 (br)
[{Fe <sub>2</sub> (CO) <sub>5</sub> ( <i>µ</i> -pdt)} <sub>2</sub> ( <i>µ</i> -P <sup>Ph</sup> <sub>2</sub> N <sup>Ph</sup> <sub>2</sub> )] (8)	2040 (s), 1980 (s), 1963 (sh), 1916(w)	60.1 (s)
[{Fe <sub>2</sub> (CO) <sub>5</sub> ( <i>µ</i> -pdt)} <sub>2</sub> ( <i>µ</i> -P <sup>Ph</sup> <sub>2</sub> N <sup>Bn</sup> <sub>2</sub> )] ( <b>9</b> )	2044 (s), 1980 (s), 1960 (sh), 1925 (w)	54.0 (s)
$[\{Fe_2(CO)_5(\mu\text{-}pdt^{Et2})\}_2(\mu\text{-}P^{Ph}_2N^{Bn}_2)] \ (\textbf{10})$	2040 (s), 1979 (s), 1960 (sh), 1919 (w)	53.0 (s)





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Table 2. Selected distances and bond angles of complexes 1-6.

		<b>1</b> <sup>[9]</sup>	2	3	<b>4</b> <sup>[10a]</sup>	5	6
Length (Å)	Fe1-Fe2	2.5655(9)	2.5589(6)	2.5588(19)	2.5927(11)	2.5537(8)	2.5619(9)
	Fe1-P1	2.1862(13)	2.1955(8)	2.172(2)	2.1894(17)	2.1966(13)	2.2033(13)
	Fe1-P2	2.1833(14)	2.1911(9)	2.173(2)	2.1846(17)	2.1911(13)	2.1946(12)
	Fe1-C1	1.759(5)	1.755(3)	1.728(10)	1.747(6)	1.756(5)	1.749(5)
	Fe2-CO <sub>terminal</sub>	1.782(6)-	1.785(4)-	1.737(10)-	1.770(7)-	1.762(5)-	1.786(5)-
		1.786(6)	1.795(3)	1.790(10)	1.791(7)	1.799(5)	1.789(5)
Angles (°)	P1-Fe1-P2	82.41(5)	81.65(3)	82.09(9)	80.83(6)	80.78(5)	80.34(5)
	C2-Fe2-Fe1	145.95(18)	145.55(11)	158.1(3)	142.12(19)	147.49(15)	143.08(16)

Side-products (Scheme 4) were occasionally isolated in very low yields depending on the preparation of 1-6 : P-sulfido complexes such as  $[Fe_2(CO)_5(\kappa^1-P^{Ph}_2N^{Ph}_2S)(\mu-pdt)]$  (7),<sup>[9]</sup> resulting from sulfurization of the diphosphine upon decomposition of diiron complexes; tetrairon compounds  $[{Fe_2(CO)_5(\mu-dithiolato)}_2(\mu-dithiolato)]_2(\mu-dithiolat$ P<sup>Ph</sup><sub>2</sub>N<sup>R</sup><sub>2</sub>)] (R = Ph, dithiolato = pdt<sup>Et2</sup> (8); R = Bn, dithiolato = pdt (9),  $pdt^{Et2}$  (10)), in which the cyclic diphosphine bridges the two diiron systems. The IR spectra in CH<sub>2</sub>Cl<sub>2</sub> of 7-10 display, in the carbonyl region, a typical pattern for monosubstituted complexes  $[Fe_2(CO)_5(\kappa^1-L)(\mu-dithiolato)]$  (Table 1, figure S4,). 7 has been already characterized by an X-ray diffraction analysis which revealed the presence of a P=S bond and a diphosphine that is coordinated in a monodentate fashion.<sup>[9] 31</sup>P-{<sup>1</sup>H} NMR spectra (25°C) of [{Fe<sub>2</sub>(CO)<sub>5</sub>( $\mu$ -dithiolato)}<sub>2</sub>( $\mu$ -P<sup>Ph</sup><sub>2</sub>N<sup>R</sup><sub>2</sub>)] (8-10) show one peak indicating that the two phosphorus atoms are equivalent (Table 1).



**Scheme 4.** Side-products obtained during the preparation of **1-6**: [Fe<sub>2</sub>(CO)<sub>5</sub>( $\kappa^{1}$ -P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>S)( $\mu$ -pdt)] (**7**) and [{Fe<sub>2</sub>(CO)<sub>5</sub>( $\mu$ -dithiolato)}<sub>2</sub>( $\mu$ -P<sup>Ph</sup><sub>2</sub>N<sup>R</sup><sub>2</sub>)] (**8-10**) (R = Ph, Bn, dithiolato = pdt, pdt<sup>El2</sup>).

The molecular structure of **10** was confirmed by a poor X-ray diffraction analysis (Figure S5, table S2). The P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub> ligand is linked between two diiron fragments in dibasal coordination mode which is different from that generally observed in other [{Fe<sub>2</sub>(CO)<sub>5</sub>( $\mu$ -dithiolato)}<sub>2</sub>( $\mu$ -diphosphine)] in which the diphosphine is coordinated in apical-apical position.<sup>[14]</sup>

# 2 Reactivity of complexes [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ - $P^{Ph}_2N^R_2$ )( $\mu$ -dithiolato)] (1-6) towards protons

The reactivity of complexes **1-6** towards acids was explored by *in situ* protonation experiments which were monitored by IR and NMR (<sup>1</sup>H, <sup>31</sup>P-{<sup>1</sup>H}) spectroscopies. Protonation studies were carried out in dichloromethane with [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph</sup><sub>2</sub>N<sup>R</sup><sub>2</sub>)( $\mu$ -dithiolato)] complexes using trifluoromethanesulfonic acid (CF<sub>3</sub>SO<sub>3</sub>H, pKa<sup>MeCN</sup> = 2.6 in acetonitrile)<sup>[15]</sup>.

2.1 Protonation of [Fe<sub>2</sub>(CO)<sub>4</sub>(
$$\kappa^2$$
-P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)( $\mu$ -dithiolato)] (1-3)

IR monitoring of the protonation of  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Ph}_2)(\mu$ pdt)](1), at 25°C in dichloromethane, shows a shift of the  $\bar{u}(CO)$ bands towards higher wavenumbers after the addition of the first equivalent of CF<sub>3</sub>SO<sub>3</sub>H, (Figure 2 and S6). The bands observed at 2094 (s), 2034 (s), 1978 (m) cm<sup>-1</sup> are typical of a bridginghydrido species (Scheme 5 (a), table 3). The IR spectra of 2-3, in the presence of one equivalent of CF<sub>3</sub>SO<sub>3</sub>H, display a similar ū(CO) pattern, indicating the formation of analogous cationic complexes. The preparation of the protonated stable complexes 1µH<sup>+</sup>-3µH<sup>+</sup> was readily performed by addition of one equivalent of CF<sub>3</sub>SO<sub>3</sub>H to 1-3. Unfortunately, no suitable crystal could be obtained for an X-ray structural analysis. The IR spectra in CH<sub>2</sub>Cl<sub>2</sub> of the isolated products show similar patterns than those observed when the protonation of 1-3 was performed in situ, indicating that there is no loss of proton after purification of the solids. The <sup>1</sup>H NMR spectra (Figure S7) of  $1\mu H^+-3\mu H^+$  are characterized by two ill resolved signals in the hydride region, that consists of a triplet and a doublet at ca -13 ppm, due to  ${}^{2}J_{PH}$ coupling constants. This indicates the presence of two isomers in solution, that were assigned in reason of symmetrical coordination or not of the diphosphine, with respect to the hydrido bridge, to dibasal and basal apical isomers, respectively (Table 3). The <sup>31</sup>P-{<sup>1</sup>H} NMR spectra show a singlet at ca 50 ppm for a dibasal isomer and two doublets at ca 60 and 45 ppm (Table 3) for a basal-apical form. The more the dithiolato bridge is sterically crowding, the more the dibasal isomer is favoured (Figure S7e). Addition of further equivalents of CF<sub>3</sub>SO<sub>3</sub>H to  $[Fe_2(CO)_4(\kappa^2 P^{Ph}_{2}N^{Ph}_{2})(\mu-pdt)(\mu-H)](CF_{3}SO_{3})$  (**1\muH**<sup>+</sup>) leads to a shift of the IR bands of ca 10 cm<sup>-1</sup> (Figure 2). This indicates that there is a second protonation at the nitrogen atom giving doubly protonated species (Scheme 5 (b)). Attempts to isolate this species were unsuccessful because of the loss of the proton at the nitrogen atom during the purification by precipitation through addition of pentane. Indeed, bridging-hydrido derivatives  $1\mu H^+-3\mu H^+$  were identified in the precipitate. <sup>1</sup>H NMR and <sup>31</sup>P-{<sup>1</sup>H} NMR variable temperature (VT) experiments, previously reported,<sup>[9]</sup> suggested a mechanism of protonation of 1 shown in scheme 5. Experiments with one equivalent of CF<sub>3</sub>SO<sub>3</sub>H revealed the initial formation at low temperature (-80°C) of a N-protonated species (step c in scheme 5) that isomerizes into a bridging-hydrido compounds (step d) when the temperature increases. In the presence of an excess of acid (3 equiv. of CF<sub>3</sub>SO<sub>3</sub>H) the mixture evolves into the formation of a bridging-hydrido isomer (1µHNH<sup>2+</sup>). Other signals were detected at -80°C suggesting the formation of other transient species that could result from the protonation of a sulfur atom, but no further information could be obtained to identify them. VT NMR protonation experiments with  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Ph}_2)(\mu-pdt^{Et2})]$  (2) did not give further information about this process and led to the formation of the doubly protonated species (2µHNH<sup>2+</sup>),

**Table 3.** IR (CH<sub>2</sub>Cl<sub>2</sub>), <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) and high-field region of <sup>1</sup>H NMR data of complexes [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)( $\mu$ -dithiolato)( $\mu$ -H)](CF<sub>3</sub>SO<sub>3</sub>) (**1** $\mu$ H<sup>+</sup> -**3** $\mu$ H<sup>+</sup>) at 25°C.

Complex	IR (CH <sub>2</sub> Cl <sub>2</sub> , cm <sup>-1</sup> ), ū(CO)	$^{31}P-{^{1}H} NMR (CD_2Cl_2, \delta : ppm)$	<sup>1</sup> H NMR (CD <sub>2</sub> Cl <sub>2</sub> , δ : ppm)
1 <i>µ</i> H⁺	2094 (s), 2034 (s), 1978 (w)	64.1 (d, <sup>2</sup> J <sub>PP</sub> = 96.3 Hz), 47.0 (d, <sup>2</sup> J <sub>PP</sub> = 96.3 Hz) 51.3 (s)	-13.52 (d, <sup>2</sup> J <sub>PH</sub> = 14.5 Hz), -13.56 (t, <sup>2</sup> J <sub>PH</sub> = 14.5 Hz)
2 <i>µ</i> H⁺	2091 (s), 2031 (s), 1976 (w)	66.4 (d, ${}^{2}J_{PP}$ = 104.2 Hz), 45.5 (d, ${}^{2}J_{PP}$ = 104.2 Hz) 50.7 (s)	-13.30 (d, <sup>2</sup> J <sub>PH</sub> = 20.0 Hz), -12.99 (t, <sup>2</sup> J <sub>PH</sub> = 15.0 Hz)
3 <i>µ</i> H⁺	2092 (s), 2037 (s), 1956 (w)	60.4 (d, ${}^{2}J_{PP}$ = 103.2 Hz), 47.0 (d, ${}^{2}J_{PP}$ = 103.2 Hz) 50.0 (s)	-13.34 (d, <sup>2</sup> J <sub>PH</sub> = 15.0 Hz), -12.93 (t, <sup>2</sup> J <sub>PH</sub> = 18.0 Hz)

when temperature increases. The expected pattern for dibasal and basal-apical isomers of a doubly protonated species ( $\mu$ HNH<sup>2+</sup>) was detected in the <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum, consisting in two doublets at 40.9 and at 25.0 ppm with a coupling constant <sup>2</sup>J<sub>PP</sub> of 96.1 Hz, and a singlet at 31.3 ppm, (Figure S8a). A triplet at -15.1 ppm (<sup>2</sup>J<sub>PH</sub> = 23.7 Hz) and a doublet at -13.73 ppm (<sup>2</sup>J<sub>PH</sub> = 20.4 Hz) were detected in the high field region of the <sup>1</sup>H NMR spectrum (Figure S8b).

the carbonyl pattern of the starting compound ( $\bar{u}(CO) = 2011$ , 1939, 1892 cm<sup>-1</sup>) by a set of bands at 2030, 1957, 1904 cm<sup>-1</sup>, which suggests the formation of an ammonium species through protonation at the amine function of the diphosphine (Figures 3, S9 and scheme 6 (a)).<sup>[5a,b]</sup> IR spectra of analogous complexes **5NH<sup>+</sup>-6NH<sup>+</sup>** are very similar to that of **4NH<sup>+</sup>** (Table 4).



**Figure 2.** IR monitoring of the reaction of  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Ph}_2)(\mu-pdt)]$  (1) with acid at 25°C in CH<sub>2</sub>Cl<sub>2</sub> (black curve: 1; red curve: after addition of one equivalent of CF<sub>3</sub>SO<sub>3</sub>H; blue curve: after addition of three equivalents of CF<sub>3</sub>SO<sub>3</sub>H.



Scheme 5. Proposed mechanism for protonation of complexes [Fe\_2(CO)\_4( $\kappa^2-P^{Pn}{}_2N^{Pn}{}_2)(\mu\text{-dithiolato})]$  (1-3)

#### 2.2 Protonation of [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)( $\mu$ -dithiolato)] (4-6)

IR monitoring of the protonation of  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Bn}_2)(\mu-pdt)]$ (4) in solution, in dichloromethane at 25°C, showed after the addition of one equivalent of CF<sub>3</sub>SO<sub>3</sub>H the readily replacement of



**Figure 3.** IR monitoring of the reaction of  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Bn}_2)(\mu-pdt)](4)$  with CF<sub>3</sub>SO<sub>3</sub>H at 25°C in CH<sub>2</sub>Cl<sub>2</sub> (black curve: **4**; red curve: after addition of one equivalent of CF<sub>3</sub>SO<sub>3</sub>H; blue curve : after addition of a second equivalent of CF<sub>3</sub>SO<sub>3</sub>H).

Complex	IR (CH <sub>2</sub> Cl <sub>2</sub> , cm <sup>-1</sup> ), ū(CO)	<sup>31</sup> P-{ <sup>1</sup> H} NMR (CD <sub>2</sub> Cl <sub>2</sub> , δ : ppm)
4NH⁺	2030 (s), 1957 (s), 1904 (w)	36.6 (s)
5NH⁺	2029 (s), 1956 (s), 1902 (w)	35.2 (s)
6NH⁺	2024 (s), 1959 (s), 1897 (w)	35.8 (s)

The ammonium diiron complexes **4NH**<sup>+</sup>-**6NH**<sup>+</sup> were obtained as red crystalline solids in good yield after washing with pentane. <sup>1</sup>H NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> of isolated powders of complexes [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>H)( $\mu$ -dithiolato)]<sup>+</sup> (**4NH**<sup>+</sup>-**5NH**<sup>+</sup>) display low field signals at ca 12 ppm that were tentatively assigned to the proton linked to the nitrogen atom. The <sup>31</sup>P-{<sup>1</sup>H} NMR spectra at 25°C present one peak at ca 35 ppm. Low temperatures <sup>31</sup>P-{<sup>1</sup>H} NMR spectra of a solution of **4NH**<sup>+</sup> were recorded in CD<sub>2</sub>Cl<sub>2</sub>. This experiment (Figure S10) showed that when the temperature decreases, the singlet observed at 35.0 ppm splits into two signals, typical of a mixture of dibasal and basal-apical isomers, one

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consisting in a AB pattern and the other in a singlet. No formation of a bridging-hydrido species  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Bn}_2)(\mu-pdt)(\mu-H)]^+$ was observed during the time of the experiments (Scheme 6 (b)). X-ray crystal structure analyses of **5NH**<sup>+</sup> (Figure S11, table S3) and **6NH**<sup>+</sup> (Figure 4, table S3) indicate that the protonation occurs at the nitrogen atom of the diphosphine. The diphosphine ligand lies in a basal apical position in the case of **5NH**<sup>+</sup> and in a dibasal one for **6NH**<sup>+</sup>. Both FeP2C2N1 and FeP2C2N2 metallacycles are in chair conformation with the two nitrogen atoms facing each other, which is different from the conformation observed in the parent neutral complexes, indicating a structural 'signature' of the presence of a proton (N-H...N) between the two nitrogen atoms. The distance N1-H2 is 1.900 Å (in **6NH**<sup>+</sup>) and shows a hydrogen bond between these two atoms. The Fe-Fe distance in **6NH**<sup>+</sup> (2.5782(19) Å) is close to that determined in neutral complex.



Figure 4. ORTEP view of [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph<sub>2</sub></sup>N<sup>Bn<sub>2</sub></sup>H)( $\mu$ -pdt<sup>Bn2</sup>)](CF<sub>3</sub>SO<sub>3</sub>) (6NH<sup>+</sup>) (molecules of CH<sub>2</sub>Cl<sub>2</sub> are omitted). Selected distances (Å) and bond angles (°) : Fe1-Fe<sub>2</sub>, 2.5782(19) ; N1-H2, 1.900 ; N2-H2, 0.9300 ; Fe1-P1, 2.179(3) ; Fe1-P2, 2.193(3) ; Fe1-C1, 1.763(10) ; Fe2-CO<sub>terminal</sub>, 1.817(13) – 1.776(13) ; P1-Fe1-P2, 81.31(10) ; C1-Fe1-Fe2, 155.4(3) ; C2-Fe2-Fe1, 144.3(4) ; N1-H2-N2, 139.3.

Further addition of CF<sub>3</sub>SO<sub>3</sub>H, up to two equivalents, results in the complete disappearance of  $\bar{u}(CO)$  bands in **4NH**<sup>+</sup> concomitantly with the appearance of new bands at 2099, 2041, 1984 with a shoulder at 1971 cm<sup>-1</sup> ascribed to a doubly protonated species (Figure 3, Scheme 6 (c)). The straight addition of two equivalents of CF<sub>3</sub>SO<sub>3</sub>H to [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)( $\mu$ -pdt)] (4) results in the same observations, with a shift of ca 80 cm<sup>-1</sup> of the  $\bar{u}(CO)$  bands. <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum in CD<sub>2</sub>Cl<sub>2</sub> at 25°C of the isolated powder of  $[Fe_2(CO)_4(\kappa^2 - P^{Ph}_2 N^{Bn}_2 H)(\mu - pdt)(\mu - H)]^{2+}$  (4µHNH<sup>2+</sup>) presents a singlet at 29.5 ppm and two doublets at 34.9 and 27.6 ppm ( $^{2}J_{PP}$ = 98 Hz) (Figure S12) which indicates the presence in solution of dibasal and basal apical isomers in a 1:3 ratio. The <sup>1</sup>H NMR spectrum of  $4\mu$ HNH<sup>2+</sup> displays a doublet at -14.03 ppm (<sup>2</sup>J<sub>PH</sub> = 15.5 Hz) and ill-resolved signal at -14.80 ppm, assigned to the basal apical and dibasal forms, respectively. <sup>1</sup>H and <sup>31</sup>P-{<sup>1</sup>H} VT-NMR experiments for 4µHNH<sup>2+</sup> and 5µHNH<sup>2+</sup> species, generated in situ at low temperature (3 equiv of CF<sub>3</sub>SO<sub>3</sub>H in 0.5 mL CD<sub>2</sub>Cl<sub>2</sub> in a NMR tube at -80°C), were performed in order to get further information on the process of formation of these doubly protonated species. These experiments showed a dibasal-basal apical isomerization of the doubly protonated species (Figures S13a,b for  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Bn}_2)(\mu-pdt)]$  (4) and S13c,d for  $[Fe_2(CO)_4(\kappa^2-(P^{Ph}_2N^{Bn}_2)(\mu-pdt^{Et2})]$  (5)). The two isomers of **5**µHNH<sup>2+</sup> were detected as a singlet at 29.3 ppm and two doublets at 36.1 and 26.4 ppm ( ${}^{2}J_{PP}$  = 105.5 Hz) in  ${}^{31}P-{}^{1H}$  NMR and two ill-resolved signals at -15.21 ppm and -13.77 ppm in the  ${}^{1}H$  NMR at -80°C. A very poor X-ray analysis of single crystals of **5**µHNH<sup>2+</sup> obtained from NMR experiments solutions (Figure S14, table S4) afforded crystallographic results that are consistent with the molecular structure proposed for **4**µHNH<sup>2+</sup> and **5**µHNH<sup>2+</sup>.



Scheme 6. Proposed mechanism for protonation of complexes [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)(µ-dithiolato)] (4-6)

IR recording (Figure S15) showed that  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Bn}_2H)(\mu$ pdt)](CF<sub>3</sub>SO<sub>3</sub>) (4NH<sup>+</sup>) undergoes a isomerization process into its bridging-hydrido form in the presence of Na(BAr<sup>F</sup><sub>4</sub>). After 15 min, the carbonyl bands of **4NH**<sup>+</sup> were replaced by a new set of strong bands at higher wavenumbers corresponding to those expected for a bridging-hydrido species  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Bn}_2)(\mu-pdt)(\mu-pdt)]$ H)](BAr<sup>F<sub>4</sub></sup>) ( $4\mu$ H<sup>+</sup>). The <sup>1</sup>H NMR spectrum in CD<sub>2</sub>Cl<sub>2</sub> of a powder prepared, following the previous procedure, showed new illresolved signals appearing at -13.59 (major isomer) and -14.44 ppm, which supports the fact that the ammonium derivative has been converted into species possessing a bridging-hydrido ligand that was structurally (Figure 5) and spectroscopically characterized. The <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum of  $[Fe_2(CO)_4(\kappa^2 P^{Ph}_2N^{Bn}_2)(\mu-pdt)(\mu-H)](BAr^F_4)$  (4 $\mu$ H<sup>+</sup>) in CD<sub>2</sub>Cl<sub>2</sub> at 25°C displays the typical pattern and chemical shifts of bridging-hydrido species that have been already characterized: a singlet at 53.1 ppm for a dibasal isomer and two doublets at 59.7 and 46.7 ppm ( $^{2}J_{PP}$  = 100.2 Hz) for the basal-apical form (Figure S16). Such ammonium-hydride tautomerization controlled by the nature of the counter-anion has been already reported.<sup>[16]</sup> Different singlecrystals were obtained from CH2Cl2-hexane mixtures used as solvent for cristallization of 4µH<sup>+</sup> at -30°C. X-ray analysis of these crystals characterized a side species  $\mathbf{4^{\prime\prime}}$  in which the diphosphine lies in a dibasal position, unlike in 4µH<sup>+</sup>. The presence of one counter-anion  $(BAr^{F_4})^{-}$  suggests its monocationic nature (Figure S17 and table S5). Unfortunately, the poor quality of the crystals did not allow to position experimentally the site of protonation. Nevertheless, a structure with a proton at the N atom pointing towards the diiron site was tentatively proposed but could not be ascertained without any ambiguity.

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Figure 5. ORTEP view of  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Bn}_2)(\mu-pdt)(\mu-H)](BAr^F_4)$  (4 $\mu$ H<sup>+</sup>) (The counter-anion BAr<sup>F</sup>\_4 is omitted for clarity). Selected distances (Å) and bond angles (°) : Fe1-Fe2, 2.5549(19) ; Fe1-P1, 2.206(3) ; Fe1-P2, 2.189(3) ; Fe1-C1, 1.750(12) ; Fe2-CO<sub>terminal</sub>, 1.787(12)-1.805(13)v ; Fe1-H, 1.70(10) ; Fe2-H, 1.71(10) ; P1-Fe1-P2, 82.07(10) ; P2-Fe1-Fe2, 156.90(10) ; C4-Fe2-Fe1, 141.0(3).

# 3 Electrochemical behaviour in reduction of complexes **1-6** in the absence and presence of acid

The electrochemical properties of complexes **1-6** have been studied in  $CH_2Cl_2$ -[NBu<sub>4</sub>][PF<sub>6</sub>] 0.2M by cyclic voltammetry (CV) on a vitreous carbon electrode. All the potentials are given versus the couple (Fc<sup>+</sup>/Fc). Except contra-indication, cyclic voltammograms are under an inert atmosphere (argon).

3.1 Electrochemical behaviour in reduction of complexes  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{R}_2)(\mu-dithiolato)]$  (1-6) under inert atmosphere in the absence of protons.

The cyclic voltammograms show that **1** has an irreversible reduction at  $E_p^{\text{red}} = -2.32 \text{ V}^{[9]}$  and a reversible oxidation at  $E_{1/2}^{\text{ox1}}$  = -0.10 V with a ratio ( $i_p^{\text{c. ox1}}/i_p^{\text{a. ox1}}$ ) equal to 1, followed with a second irreversible oxidation at  $E_p^{\text{ox2}} = 0.45 \text{ V}$  (Figure 6). The behaviour of the analogous complexes **2-6** are similar to that of **1** (Figure S18). Their reduction potentials are given in table 5.



Figure 6. Cyclic voltammetry of  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Ph}_2)(\mu$ -pdt)] (1) (0.99 mM) in CH<sub>2</sub>Cl<sub>2</sub>-[NBu<sub>4</sub>][PF<sub>6</sub>] 0.2 M under Ar at 0.2 V s<sup>-1</sup>.

Table 5 Reduction potentials (V) of the propanedithiolato complexes (1-6).

Complex	$E_{p}^{red}$	Complex	$E_{p}^{red}$	-
1	-2.32	4	-2.40	-
2	-2.36	5	-2.34	
3	-2.36	6	-2.40	

Comparison of the current function versus the scan rate of 1 and the complex  $[Fe_2(CO)_4(\kappa^2-I_{Me}-CH_2-I_{Me})(\mu-pdt)]$  (I<sub>Me</sub> = 1methylimidazol-2-ylidene) which has a one-electron oxidation,[17] indicates that the first oxidation of 1 involves one electron (Figure S19). The deviation of the current function for the reduction of 1 suggests an ECE mechanism whose product is detected on the reverse scan by a reversible (not shown) peak at -1.41 V. In fact, an ECCE mechanism must be considered to explain why the reduction peak of 1 remains irreversible when the scan rate increases (Figure S20). Usually, the reversibility is observed as soon as the chemical reaction is defeated as for the complex  $[Fe_2(CO)_4(\kappa^2 - PNP^{Me})(\mu - pdt)]$  (PNP<sup>Me</sup> =  $(Ph_2PCH_2)_2NMe)$ .<sup>[5a]</sup> Finally, this reduction process is different from that of other asymmetrically disubstituted complexes. Indeed, the reduction of the complex  $[Fe_2(CO)_4(\kappa^2-dppe)(\mu-pdt)]$  for example leads to its bridged isomer [Fe2(CO)4(µ-dppe)(µ-pdt)] according to a ETC mechanism (reaction catalyzed by electron transfer).[18] Such a process is also observed with the complex  $[Fe_2(CO)_4(\kappa^2-dmpe)(\mu$ adt<sup>Bn</sup>)].[19]

3.2 Electrochemical behaviour in reduction of complexes  $[Fe_2(CO)_4(\kappa^2 - P^{Ph}_2N^{Ph}_2)(\mu\text{-dithiolato})]$  dithiolato = pdt (1), pdt<sup>Et2</sup> (2), pdt<sup>Bn2</sup> (3)) in the presence of acid.

All the complexes  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Ph}_2)(\mu$ -dithiolato)] (**1-3**) have the same behaviour in the presence of methanesulfonic acid (CH<sub>3</sub>SO<sub>3</sub>H, pKa<sup>MeCN</sup> = 10.0 in acetonitrile).<sup>[15]</sup> Upon addition of 1 equivalent of CH<sub>3</sub>SO<sub>3</sub>H, a new reduction peak appears at ca -1.3 V followed by another one at ca -1.6 V (Table 6, Figures 7a and S21-S22) while the intensity of the oxidation peak of the neutral starting material decreases indicating the protonation of the complex in solution (Figures 7b and S21-S22).



Figure 7. CV of  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Ph}_2)(\mu-pdt^{E12})]$  (2) upon successive additions of CH<sub>3</sub>SO<sub>3</sub>H in CH<sub>2</sub>Cl<sub>2</sub>-[NBu<sub>4</sub>][PF<sub>6</sub>] 0.2 M under Ar at 0.2 V s<sup>-1</sup>. (a) reduction; (b) oxidation.

Table 6. Potential values (V) of reduction peaks of complexes [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)( $\mu$ -dithiolato)] (1-3) at 0.2 V s<sup>-1</sup>.

Complex	without acid	1 equiv. CH₃SO₃ŀ	1	
	$E_{p}^{c, red}$	Ep	$E_p - E_p^{c, red}$	
1	-2.32	-1.34 (-1.60)	0.98	
2	-2.36	-1.26 (-1.62)	1.10	
3	-2.36	-1.23 (-1.63)	1.13	

Since the protonation is not complete, the reaction is proposed to be not quantitative, which means that the pKa of the protonated complex is less than that of  $CH_3SO_3H$  (the acid used). The sigmoidal shape that the oxidation curve takes after the addition of a second equivalent is characteristic of a CE mechanism. The oxidation of the neutral complex at a less positive potential than the protonated complex shifts the protonation equilibrium to the left.

2 + HA 
$$\leftrightarrows$$
 2H<sup>+</sup> + A<sup>-</sup>  
with log K =  $pKa_{(2\mu)}^{+}(2) - pKa_{(HA)A}$ 

w

The new reduction peak at ca -1.3 V is assigned to the bridginghydrido derivative by comparison with the reduction potential of an authentic sample (see table 7 and figure S23). The difference between the potential of the reductive peak of the neutral complex and the protonated derivative one ( $E_p$ - $E_p^{c, red}$ ) is ca 1.1 V. This result is consistent with those concerning protonation process reported in the literature  $^{\rm [20]}$  Oxidation of the bridging-hydrido species is around 0.8 V.

Table 7. Potential values (V) of reduction and oxidation peaks of the bridging-<br/>hydrido complexes [Fe2(CO)4( $\kappa^2$ -PPh2NPh2)( $\mu$ -pdtEl2)( $\mu$ -H)](CF3SO3) (1 $\mu$ H+-3 $\mu$ H+)<br/>at 0.2 V s<sup>-1</sup>.

	$E_{p}^{red1}$	$E_{p}^{red2}$	Ep red3	E <sub>p</sub> ox1	
1 <i>µ</i> H⁺	-1.36	-1.64	-2.13	0.84	-
2µH⁺	-1.28	-1.62	-2.22	0.83	
3µH⁺	-1.23	-1.59	-2.21	0.80	_

Further additions of CH<sub>3</sub>SO<sub>3</sub>H (Figure S24) resulted in an increase of the reduction current at the potential of the reduction of the bridging-hydrido complex. The variations in the ratio icat/io (icat being the current of the catalytic peak and io the oxidation current measured before the addition of acid) as a function of the amount of added acid show that after an initial linear increase, characteristic of a catalytic proton reduction process, a plateau is reached. The fact that the current becomes independent of the acid concentration means that the overall kinetics of the catalytic cycle is no longer controlled by a protonation reaction, but by a reaction in which the acid (the protons) does not participate. It can be reasonably assumed that for significant acid concentrations, the formation and/or release of the H<sub>2</sub> ligand becomes kinetically limited (Scheme 7).<sup>[21]</sup> The kinetics constants determined according to the DuBois' method<sup>[22]</sup> are 19 s<sup>-1</sup> for 1, 4.8 s<sup>-1</sup> for 2 and 10 s<sup>-1</sup> for 3. This suggests that the catalytic proton reduction is not very efficient.



Scheme 7. Mechanism proposed for the H<sub>2</sub> evolution.

When one equivalent of the stronger trifluoromethane sulfonic acid was added, the protonation of **1** was complete and led to  $1\mu$ H<sup>+</sup> (Figure S25).<sup>[9]</sup> The disappearance of the oxidation peak of **2** and **3** in the presence of one equivalent of CF<sub>3</sub>SO<sub>3</sub>H indicates also the formation of  $2\mu$ H<sup>+</sup> and  $3\mu$ H<sup>+</sup>. In presence of an excess of acid, a shoulder peak appears at -1.12 V suggesting that a diprotonation may occur (Figures S25-S26).

3.3 Electrochemical behaviour in reduction of complexes  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Bn}_2)(\mu\text{-dithiolato})]$  dithiolato = pdt (4), pdt<sup>Et2</sup> (5), pdt<sup>En2</sup> (6)) in the presence of acid.

The behaviour of complexes  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^{Bn}_2)(\mu-dithiolato)]$ (**4-6**) in the presence of CH<sub>3</sub>SO<sub>3</sub>H is different from that of complexes with  $(P^{Ph}_2N^{Ph}_2)$  ligand. Upon addition of 2 equivalents of CH<sub>3</sub>SO<sub>3</sub>H, the oxidation of **5** is replaced by another one at a potential more positive (at 0.08 V for **5**) indicating that the complex formed in solution is not the bridging-hydrido derivative that oxidizes at around 0.8 V, but another protonated complex. Concomitantly, a reduction peak around -1.4 V also appears followed by another one (Figure 8, table 8 and figures S27-29). Upon addition of 3-4 equivalents of acid, a peak at a potential less negative than -1.4 V (Table 8) appears while the oxidative curve changes indicating the formation of a second protonated derivative.



Figure 8. CV of 5 upon successive additions of CH\_3SO\_3H in CH\_2Cl\_2-[NBu4][PF\_6] 0.2 M under Ar at 0.2 V s^-1.

**Table 8.** Potential values of reduction peaks of complexes  $[Fe_2(CO)_4(\kappa^2 - P^{Pn}_2N^{Bn}_2)(\mu\text{-dithiolato})](4-6)$  in the absence and presence of CH<sub>3</sub>SO<sub>3</sub>H.

Complex	Without acid <i>E</i> p <sup>c, red</sup>	1 equiv. CH <sub>3</sub> SO <sub>3</sub> H E <sub>p</sub> <sup>red1</sup> ( E <sub>p</sub> <sup>red1</sup> - E <sub>p</sub> <sup>c, red</sup> )	4 equiv. CH <sub>3</sub> SO <sub>3</sub> H <i>E</i> p <sup>red1'</sup> ( <i>E</i> p <sup>red1'</sup> - <i>E</i> p <sup>c, red</sup> ) <sup>[a]</sup>
4	-2.40	-1.43 (0.97)	-1.18 (1.22)
5	-2.34	-1.43 (0.91)	-1.13 (1.21)
6	-2.40	-1.42 (0.98)	-1.04 (1.36)

[a] : the peak 1 decreases as the peak 1' appears and grows upon 3-4 equiv. of acid

The difference ( $E_p^{\text{red1}}-E_p^{\text{c.red}}$ ) between the potential of the reductive peak of the neutral complexes and the ammonium derivatives (**NH**<sup>+</sup>) is ca 1V and suggests that the peak at ca -1.1 V corresponds to the doubly protonated form ( $\mu$ HNH<sup>2+</sup>).<sup>[20]</sup> The comparison of these CV with those of authentic samples of ammonium complexes (**NH**<sup>+</sup>) allows to assign the peak at around -1.4 V to complexes **4-6NH**<sup>+</sup> that generates a doubly protonated complex in the presence of acid (Table 9 and figures S30-31).

Complex	Without					1 equiv.
	CF₃SO₃H					CF <sub>3</sub> SO <sub>3</sub> H
	$E_{p}^{red1}$	$E_{p}^{red2}$	$E_{p}^{red3}$	Ep <sup>red4</sup>	$E_{p}^{ox1}$	$E_{p}^{red}$
4NH⁺	-1.44		-1.94	-2.40	0.14	-1.15
5NH⁺	-1.46	-1.70	-1.92	-2.37	0.05	-1.07
6NH⁺	-1.43		-1.98	-2.34	0.02	-1.04

When the concentration of acid increases (Figure S32), the reduction peak current of this species becomes equal to  $i_o$  ( $i_o$  = the oxidation peak current of the neutral starting material i.e.  $i_p^{a,ox1}$ ) indicating that the doubly protonated derivative does not catalytically reduce the protons. On the other hand, a catalytic current is observed at the reduction potential situated at ca -2.0 V. The same behaviour is observed for **6**. For **4**, the intensity of its reduction peak current is twice  $i_o$  suggesting an ECE mechanism but not a catalytic process. It is necessary to reach ca -2.0 V to obtain catalytic currents. With stronger acid, such as CF<sub>3</sub>SO<sub>3</sub>H, diprotonated species were obtained as soon as the second equivalent of CF<sub>3</sub>SO<sub>3</sub>H was added (Figure S33).

#### Conclusion

The results described in this study show that the combination of electronic/steric behaviours of the dithiolato bridge and those of the azadiphosphine P<sup>Ph</sup><sub>2</sub>N<sup>R</sup><sub>2</sub> is essential in this series of carbonyl dithiolato diiron compounds  $[Fe_2(CO)_4(\kappa^2 - P^{Ph}_2N^R_2)(\mu - dithiolato)]$ to induce the right conformation for the capture of proton and then for its transfer to the diiron site. The position of the diphosphine relatively to the diiron site is controlled through steric clash that can occur between the bridge-head group and the diphosphine, but it depends also of the protic state of the complex. An increase of the pKa of the amine combined with the choice of the counteranion allows to obtain arrested N-protonation species and to differently orientate the course of the process. In the case of complexes with NBn group and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> as counter-anion, Nprotonated species are isolated while with NPh group and the same counter-anion, the transfer to the diiron site giving a bridging-hydride is quick. That is worth noting that this  $NH \rightarrow Fe_2(\mu H)$  prototropic process is strongly dependent on the nature of the counter-anion. In the case of NBn/  $CF_3SO_3^-$ , it is reactivated by introducing Na(BArF<sub>4</sub>) salt in the medium. In terms of activity towards reduction of proton, the catalytic activity of this series of chelated dinuclear PPh<sub>2</sub>NR<sub>2</sub> complexes is moderate in the experimental conditions of the study. This efficiency is close to that observed for diiron analogues with other aminefunctionalized diphosphine.<sup>[5]</sup> Among all the protic forms observed with this dinuclear 'platform', bridging-hydrido species appear as key species for having an electrocatalytic activity. No activity of doubly protonated species (µHNH)<sup>2+</sup> is detected presumably in reason of the unfavoured position of Fe-H hydride and NH proton, despite the fact that the potential of reduction would be more suitable. Finally, a very fine tuning of these dinuclear catalysts is still required for having an efficient activity, which has to be supported by a deep understanding of the processes involving proton and electron transfers. Moreover, the control of the overall medium and its building, as a matrix for homogeneous catalytic process, is required for controlling the activity of molecular systems.

#### **Experimental Section**

General methods. All the experiments were carried out under an inert atmosphere, using Schlenk techniques for the syntheses. Solvents were deoxygenated and dried according to standard procedures. 2,2dialkylpropane-1,3-dithiol,[23]1,3,5,7-tetraphenyl-1,5,3,7-

diazadiphosphocane,[11], 1,5-dibenzyl-3,7-diphenyl-1,5,3,7diazadiphosphocane,<sup>[11]</sup>, complexes [Fe<sub>2</sub>(CO)<sub>6</sub>(µ-pdt<sup>R2</sup>)]<sup>[24]</sup> were prepared according to the reported procedure. The NMR spectra (<sup>1</sup>H, <sup>31</sup>P) were recorded at room temperature in deuterated solvents on a Bruker AMX 400 or AC300 spectrometer of the 'Service général des plateformes, Université de Bretagne Occidentale, Brest'. VT-NMR experiments were performed with a Bruker DRX500 spectrometer. NMR spectra (<sup>1</sup>H, <sup>31</sup>P) were referenced to SiMe<sub>4</sub> (<sup>1</sup>H), H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). The infrared spectra were recorded on a Bruker Vertex 70 and Perkin-Elmer spectrometers. Chemical analyses were made by the "Service de Microanalyse I.C.S.N.", Gif sur Yvette (France)

Electrochemical measurements were conducted using a PG-STAT 128 N Autolab or a µ-autolab (type III) electrochemical analyser driven by the GPES software. All the electrochemical studies were carried out in a conventional three-electrode cell under an inert atmosphere (argon). The preparation and the purification of the supporting electrolyte [NBu<sub>4</sub>][PF<sub>6</sub>] were as described previously.<sup>[25]</sup> The working electrode was a vitreous carbon disk of 0.3 cm in diameter, polished with alumina prior to use. A platinum wire was used as counter electrode. The reference electrode was an Ag|Ag<sup>+</sup> electrode, however, all the potentials (text, tables, and figures) are quoted against the (Fc<sup>+</sup>/Fc) couple; ferrocene was added as an internal standard at the end of the experiments.

Crystal data for all the compounds were collected on a Oxford Diffraction X-Calibur-2 CCD diffractometer, equipped with a jet cooler device and graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Structures were solved and refined by standard procedures.<sup>[26]</sup>

Deposition number CCDC 2031566, 2031567, 2031568, 2031569, 2031570, 2031571, 2032278, 2031573, 2031572, 2031574 contain the supplementary crystallographic data for 2, 3, 5, 6, 10, 5NH<sup>+</sup>, 6NH<sup>+</sup>, 5µHNH2+, 4µH+, 4'H+, respectively,

Preparation of [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ - $P^{Ph}_2N^{Ph}_2$ )( $\mu$ -dithiolato)] (dithiolato = pdt, pdt<sup>Et2</sup>, pdt<sup>Bn2</sup>) 1-3

In a typical procedure, to a solution of  $[Fe_2(CO)_6(\mu-dithiolato)]$  (0.40 g) (dithiolato = pdt (1.03 mmol), pdt<sup>Et2</sup> (0.90 mmol), pdt<sup>Bn2</sup> (0.70 mmol) solubilized in 75 mL of toluene, 2 equivalents of Me<sub>3</sub>NO.2H<sub>2</sub>O (0.23 g, 2.06 mmol (pdt) ; 0.20 g, 1.80 mmol (pdt<sup>Et2</sup>) ; 0.15 g, 1.40 mmol (pdt<sup>Bn2</sup>)) solubilized in acetonitrile (30 mL) were added. After stirring for a few minutes, one equivalent of PPh2NPh2 (0.47 g, 1.03 mmol (pdt); 0.41 g, 0.90 mmol (pdtEt2); 0.32 g, 0.70 mmol (pdtBn2)) solubilized in 30 mL of toluene was added to the reaction mixture that was then warmed under reflux for 3 hours. After evaporation under vacuum to dryness, the residue was purified by chromatography on a silica gel column. Complexes 1-3 were separated from very minor side-products by elution with hexane / dichloromethane (70/30, 50/50) mixtures. 1-3 were obtained as red-brown powders from the collected red band after removal of solvent. Single crystals of 1-3 were obtained from hexane-dichloromethane solutions at -30°C.

Data for  $[Fe_2(CO)_4(\kappa^2 - P^{Ph_2}N^{Ph_2})(\mu - pdt)]$  (1) m = 0.46 g, Yield = 57 % IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>),  $\vec{v}$ (CO) = 2021 (s), 1945 (s), 1898 (w). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25°C, ppm) : δ = 54.7 (br). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, -65°C, ppm) : δ = 61.0 (d, <sup>2</sup>J<sub>PP</sub> = 79.2 Hz), 55.1 (s), 52.1 (d, <sup>2</sup>J<sub>PP</sub> = 79.2 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C, ppm) :  $\delta$  = 7.79 – 6.89 (m, 20H, Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.08 (m, br, 2H, PCH<sub>2</sub>N), 3.89 (s, 4H, PCH<sub>2</sub>N), 1.69-1.61 (m, 6H, S(CH<sub>2</sub>)<sub>3</sub>S). Data for  $[Fe_2(CO)_4(\kappa^2 - P^{Ph_2}N^{Ph_2})(\mu - pdt^{Et_2})]$  (2)

m = 0.42 g, Yield = 56 %. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>),  $\bar{\nu}$ (CO) = 2019 (s), 1943 (s), 1894 (w). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25°C, ppm) :  $\delta$  = 53.4 (br)

<sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, -65°C, ppm) :  $\delta$  = 57.3 (d, <sup>2</sup>J<sub>pp</sub> = 82 Hz), 54.2 (s), 50.5 (d,  ${}^{2}J_{pp}$  = 82 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C, ppm) :  $\delta$  = 7.78 – 6.91 (m, 20H), 4.31 – 3.84 (4 x

m, br, 8H, PCH<sub>2</sub>N), 1.90 - 1.74 (m, br, 4H, SCH<sub>2</sub>C), 1.01 (m, br, 4H, CH<sub>2</sub>CH<sub>3</sub>), 0.48 (m, br, 6H, CH<sub>3</sub>).

Anal. Calcd (%) for C<sub>81</sub>H<sub>90</sub>Cl<sub>6</sub>Fe<sub>4</sub>N<sub>4</sub>O<sub>8</sub>P<sub>4</sub>S<sub>4</sub> ([2]<sub>2</sub>.3CH<sub>2</sub>Cl<sub>2</sub>): (%) Theoretical: C = 50.47, H = 4.65, N = 2.89 % (%) Experimental: C = 50.89, H = 4.79, N = 2.83 %.

Data for  $[Fe_2(CO)_4(\kappa^2 - P^{Ph_2}N^{Ph_2})(\mu - pdt^{Bn_2})]$  (3)

m = 0.38 g, Yield = 56 %. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>),  $\bar{\nu}$ (CO) = 2015 (s), 1946 (s), 1892 (w).  $^{31}P-{^{1}H} NMR (CDCl_3, 25^{\circ}C, ppm) : \delta = 52.9 (s)$ <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, -65°C, ppm) :  $\delta$  = 54.0 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C, ppm) :  $\delta$  = 7.73 – 6.69 (m, 30H, Ph), 4.40 – 3.76 (3 x m, 8H, PCH<sub>2</sub>N), 2.94 (s, br, 2H, CCH<sub>2</sub>Ph), 2.36 (s, 2H, CCH<sub>2</sub>Ph), 2.02 (d, br, 2H, SCH<sub>2</sub>C), 1.95 (d, 2H,  ${}^{2}J_{HH}$  = 10 Hz, SCH<sub>2</sub>C). Anal. Calcd (%) for C<sub>49</sub>H<sub>46</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>S<sub>2</sub>: (%) Theoretical: C = 61.01, H = 4.81, N = 2.90 % (%) Experimental: C = 60.52, H = 4.87, N = 2.79 %.

Data for [{Fe<sub>2</sub>(CO)<sub>5</sub>(μ-pdt<sup>Et2</sup>)}<sub>2</sub>(μ-P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)] (**8**) IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>),  $\overline{0}$ (CO) = 2040 (m), 1980 (s), 1963 (sh), 1916 (w). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25°C, ppm) :  $\overline{\delta}$  = 60.1 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C, ppm) :  $\overline{\delta}$  = 7.18 – 6.82 (m, 20H, Ph), 4.58 – 4.40 (m, 8H, PCH<sub>2</sub>N), 1.77 (m, 8H, SCH<sub>2</sub>C), 1.13 (2 x q, 8H, CH<sub>2</sub>CH<sub>3</sub>), 0.59 (2

x t. 6H.CH<sub>3</sub>).

Preparation of  $[Fe_2(CO)_4(\kappa^2 - P^{Ph_2}N^{Bn_2})(\mu - dithiolato)]$  (dithiolato = pdt, pdt<sup>Et2</sup>, pdt<sup>Bn2</sup>) 4-6

To a solution of 0.40 g [Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -dithiolato)] (dithiolato = pdt (1.03 mmol), pdt<sup>Et2</sup> (0.90 mmol), pdt<sup>Bn2</sup> (0.70 mmol)) solubilized in 80 mL of acetonitrile, 2 equivalents of Me<sub>3</sub>NO.2H<sub>2</sub>O (0.23 g, 2.06 mmol (pdt); 0.20 g, 1.80 mmol  $(pdt^{El2})$ ; 0.15 g, 1.40 mmol  $(pdt^{Bn2})$  were added. After stirring for a few minutes, one equivalent of  $P^{Ph}_2N^{Bn}_2$  (0.50 g, 1.03 mmol (pdt); 0.43 g, 0.90 mmol ( $pdt^{El2}$ ); 0.34 g, 0.70 mmol ( $pdt^{En2}$ )), solubilized in 40 mL of toluene, was added to the reaction mixture. The mixture was warmed under refluxing for 3 hours. After evaporation under vacuum to dryness, the residue was purified by chromatography on a silica gel column. 4-6 were separated from very minor side-products by elution with hexane / dichloromethane (70/30, 50/50) mixtures. (Yield = 55-57 %). Single crystals of 4-6 were obtained from hexane-dichloromethane 1-1 solutions at -30°C.

Data for  $[Fe_2(CO)_4(\kappa^2 - P^{Ph}_2N^{Bn}_2)(\mu - pdt)]$  (4) m = 0.46 g, Yield = 55 %. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>), ū(CO) = 2011 (s), 1939 (s), 1892 (w). arc (ch2ol<sub>2</sub>, ch<sup>-</sup>), 6(CO) = 2011 (s), 1853 (s), 1852 (w). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25°C, ppm) : δ = 52.1 (s). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, -65°C, ppm) : δ = 52.4 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C, ppm) : δ = 7.48 – 7.10 (m, 20H, Ph), 4.00 (s, 2H, NCH<sub>2</sub>Ph), 3.75 (s, 2H, NCH<sub>2</sub>Ph), 3.24 – 3.02 (3 x m, 8H, PCH<sub>2</sub>N), 2.05 – 5.521.54 (3 x m, 6H, S(CH<sub>2</sub>)<sub>3</sub>S). Anal. Calcd (%) for  $C_{37}H_{38}Fe_2N_2O_4P_2S_2$  with 1 CH<sub>2</sub>Cl<sub>2</sub> : (%) Theoretical: C = 50.84 ; H = 4.46 ; N = 3.12 %. (%) Experimental: C = 50.82 ; H = 4.61 ; N = 3.08 %. Data for  $[Fe_2(CO)_4(\kappa^2 - P^{Ph_2}N^{Bn_2})(\mu - pdt^{Et2})]$  (5) m = 0.43 g, Yield = 55 %. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>), ū(CO) = 2009 (s), 1936 (s), 1888 (w). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25°C, ppm) :  $\delta$  = 51.6 (br). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, -65°C, ppm) :  $\delta$  = 52.4 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C, ppm) :  $\delta$  = 7.54 – 6.94 (m, 20H, Ph), 4.07 (s, 2H, NCH<sub>2</sub>Ph), 3.62 (s, 2H, NCH<sub>2</sub>Ph), 3.33 – 2.90 (x m, 8H, PCH<sub>2</sub>N), 1.96 – 1.77 (2 x m, 4H, SCH<sub>2</sub>C), 1.12 (q, <sup>3</sup>J<sub>HH</sub> = 5 Hz, 4H, 2CH<sub>2</sub>CH<sub>3</sub>), 0.58 (t, <sup>3</sup>J<sub>HH</sub> = 5 Hz, 6H, 2CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd (%) for  $C_{41}H_{46}Fe_2N_2O_4P_2S_2$  : (%) Theoretical: C = 56.70, H = 5.34, N = 3.23 %. (%) Experimental: C = 56.41, H = 5.48, N = 3.03 %. Data for  $[Fe_2(CO)_4(\kappa^2 - P^{Ph}_2N^{Bn}_2)(\mu - pdt^{Bn}_2)]$  (6) m = 0.35 g, Yield = 50 %. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>),  $\bar{u}$ (CO) = 2011 (s), 1940 (s), 1885 (w).  $^{31}P-{^{1}H}$  NMR (CDCl<sub>3</sub>, 25°C, ppm) :  $\delta = 51.9$  (s).  $^{31}P-{^{1}H}$  NMR (CDCl<sub>3</sub>, -65°C, ppm) :  $\delta = 52.5$  (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C, ppm) :  $\delta$  = 7.43 – 6.76 (m, 30H, Ph), 4.08 (s, 2H, NCH<sub>2</sub>Ph), 3.57 (s, 2H, NCH<sub>2</sub>Ph), 3.30 (m, 4H, PCH<sub>2</sub>N), 3.14 (m, 2H, CCH<sub>2</sub>Ph), 3.01 (m, 2H, PCH<sub>2</sub>N), 2.87 (m, 2H, PCH<sub>2</sub>N), 2.32 (s, 2H,

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CCH<sub>2</sub>Ph), 2.03 (d, 2H, SCH<sub>2</sub>C, <sup>2</sup>J<sub>HH</sub> = 10 Hz), 1.90 (d, 2H, SCH<sub>2</sub>C, <sup>2</sup>J<sub>HH</sub> = 10 Hz). Anal. Calcd (%) for C<sub>52</sub>H<sub>52</sub>Cl<sub>2</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>S<sub>2</sub> (6.CH<sub>2</sub>Cl<sub>2</sub>) (%) Theoretical: C = 57.96, H = 4.86, N = 2.60 %

(%) Experimental: C = 57.92, H = 4.99, N = 2.49 %

Data for [{ $Fe_2(CO)_5(\mu-pdt)$ }\_2( $\mu-P^{Ph_2}N^{Bn_2}$ )] (9)

IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>), Ū(CO) = 2044(m), 1980 (s), 1960 (sh), 1925 (w).

<sup>31</sup>P-(<sup>1</sup>H) NMR (CDCl<sub>3</sub>, 25°C, ppm) : δ = 54.0 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C, ppm) : δ = 7.66 – 7.27 (m, br, 20H, Ph), 4.09-3.69

(m, br, 12H, P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>), 1.79-1.26 (m, br 12H, pdt)

Data for [{ $Fe_2(CO)_5(\mu-pdt^{Et2})$ }\_2( $\mu-P^{Ph_2}N^{Bn_2}$ ] (10) IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>),  $\bar{u}(CO)$  = 2040 (m), 1979 (s), 1960 (sh), 1919 (w).

 $^{31}P-{^{1}H}$  NMR (CDCl<sub>3</sub>, 25°C, ppm) :  $\delta = 7.32 - 7.14$  (m, br, 20H, Ph), 4.04 (2 x

s, br, 4H, NCH<sub>2</sub>Ph), 3.77 (m, br, 8H, PCH<sub>2</sub>N), 1.83 (m, br, 8H, SCH<sub>2</sub>C), 1.21-1.18 (m, br, 8H, CH2CH3), 0.62 (t, br, 3H, CH3), 0.51 (t, br, 3H, CH3).

Protonation of  $[Fe_2(CO)_4(\kappa^2 - P^{Ph}_2N^{Ph}_2)(\mu - dithiolato)]$  (dithiolato = pdt, pd<sup>Et2</sup>, pdt<sup>Bn2</sup>) 1-3

0.1 g of complex [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)( $\mu$ -dithiolato)] ((0.12 mmol (pdt) ; 0.11 mmol (pdt<sup>Et2</sup>); 0.10 mmol (pdt<sup>Bn2</sup>)) was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. Then, one equivalent of CF<sub>3</sub>SO<sub>3</sub>H (11.2  $\mu$ L, 0.12 mmol (pdt); 10.4  $\mu$ L, 0.11 mmol (pdt<sup>Et2</sup>); 9.1  $\mu$ L, 0.10 mmol (pdt<sup>Bn2</sup>)) was added to the solution. IR monitoring indicated that after 10 min, complexes **1-3** are protonated. During this time, the color of the solution changed from dark red to red. The concentration of the volume of CH<sub>2</sub>Cl<sub>2</sub> by evaporation under vacuum and the addition of cold pentane led to the precipitation of protonated complexes  $1\mu H^+ \cdot 3\mu H^+$  that were obtained in ca 80% yields.

Data for  $[Fe_2(CO)_4(\kappa^2 - P^{Ph}_2N^{Ph}_2)(\mu - pdt)(\mu - H)](CF_3SO_3)$  (1µH<sup>+</sup>)

m = 0.09 g, Yield = 80 %. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>),  $\bar{\nu}$ (CO) = 2094 (s), 2034 (s), 1978 (w).

<sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm) :  $\delta$  = 64.1 (d, <sup>2</sup>J<sub>pp</sub> = 96.3 Hz), 51.3 (s), 47.0  $(d, {}^{2}J_{DD} = 96.3 \text{ Hz}).$ 

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) : δ = 7.94 – 7.09 (m, 20H, ph), 4.55 – 4.00 (m, 8H, PCH<sub>2</sub>N), 2.86-1.77 (m, 6H, S(CH<sub>2</sub>)<sub>3</sub>S), -13.52 (d,  ${}^{2}J_{HP}$  = 14.5 Hz), -13.56  $(t, {}^{2}J_{HP} = 20.0 \text{ Hz}).$ 

Data for [Fe<sub>2</sub>(CO)<sub>4</sub>(κ<sup>2</sup>-P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)(μ-pdt<sup>Et2</sup>)(μ-H)](CF<sub>3</sub>SO<sub>3</sub>) (**2μH**<sup>+</sup>) m = 0.09 g, Yield = 81 %

IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>), ū(CO) = 2091 (s), 2031 (s), 1976 (w)

<sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm) :  $\delta = 66.4$  (d, <sup>2</sup> $J_{pp} = 104.2$  Hz), 50.7 (s), 45.5  $(d, {}^{2}J_{pp} = 104.2 \text{ Hz}).$ 

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm) : δ = 7.99 – 7.08 (m, 20H), 4.43 – 4.07 (m, 8H, PCH<sub>2</sub>N), 2.46-1.77 (m, 4H, SCH<sub>2</sub>C), 1.32-0.49 (m, 10H, CH<sub>2</sub>CH<sub>3</sub>), -12.99 (t, br), -13.30 (d, br).

Data for  $[Fe_2(CO)_4(\kappa^2 - P^{Ph_2}N^{Ph_2})(\mu - pdt^{Bn_2})(\mu - H)](CF_3SO_3)(3\mu H^+)$ m = 0.09 g, Yield = 78 %.

IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>), ū(CO) = 2092 (s), 2037 (s), 1956 (w)

 $^{31}P-{^{1}H} NMR (CD_2Cl_2, ppm) : \delta = 60.4 (d, ^2J_{pp} = 103.2 Hz), 50.0 (s), 47.5$ (d, <sup>2</sup>J<sub>pp</sub> = 103.2 Hz).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm) :  $\delta$  = 7.61 – 6.80 (30H, m, Ph), 4.44 – 4.12 (m, 8H, PCH2N), 3.23 (m, 2H, CCH2Ph), 2.54 (s, 2H, CCH2Ph), 2.43 (m, 4H, SCH<sub>2</sub>C), -12.93 (t, br), -13.34 (d, br).

Protonation of  $[Fe_2(CO)_4(\kappa^2 - P^{Ph}_2N^{Bn}_2)(\mu - dithiolato)]$  (dithiolato = pdt, pd<sup>Et2</sup>, pdt<sup>Bn2</sup>) 4-6

To a solution of 0.1 g of complex [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)( $\mu$ -dithiolato)] (0.12 mmol (pdt) ; 0.11 (pdt<sup>El2</sup>) ; 0.10 mmol (pdt<sup>Bn2</sup>)) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added one equivalent of CF<sub>3</sub>SO<sub>3</sub>H (10.8  $\mu$ L, 0.12 mmol (pdt) ; 10.1  $\mu$ L, 0.11 mmol (pdt<sup>E12</sup>); 8.8  $\mu$ L, 0.10 mmol (pdt<sup>Bn2</sup>)). The color of the solution instantly turned from dark red to red. After 15 min stirring, the volume of the solution was reduced to 2 mL under vacuum and the complex was precipitated by addition of pentane. Compounds **4NH<sup>+</sup>-6NH<sup>+</sup>** obtained as red powders in 78-80 % yields. were

Data for  $[Fe_2(CO)_4(\kappa^2-(P^{Ph}_2N^{Bn}_2H))(\mu-pdt)](CF_3SO_3)(4NH^+)$ m = 0.09 g, Yield = 79 %.

IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>), ū(CO) = 2030 (s), 1957 (s), 1904 (w).

<sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C, ppm) :  $\delta$  = 36.6 (s).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C, ppm) :  $\delta$  = 12.06 (s, br, 1H, NH), 7.50 (m, br, 20H, Ph), 4.65 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.31 (m, br, 2H, PCH<sub>2</sub>N), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.42 (s, 2H, NCH<sub>2</sub>Ph), 4.41 (s, 2H, NCH<sub>2</sub> NCH<sub>2</sub>Ph), 4.09 (m, br, 2H, PCH<sub>2</sub>N), 3.55 - 3.43 (m, br, 4H, PCH<sub>2</sub>N), 1.77 – 1.62 (m, br, 6H, S(CH<sub>2</sub>)<sub>3</sub>S).

Data for  $[Fe_2(CO)_4(\kappa^2 - (P^{Ph_2}N^{Bn_2}H))(\mu - pdt^{Et2})](CF_3SO_3)(5NH^+)$ m = 0.09 g, Yield = 78 %. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>),  $\bar{\nu}$ (CO) = 2029 (s), 1956 (s), 1902 (w). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C, ppm) : δ = 35.2 (s). <sup>1</sup>H ŇMŘ (CD<sub>2</sub>Cl<sub>2</sub>, 25°C, ppm) : δ = 12.21 (s, br, 1H, NH), 7.58 – 7.41 (m, 20H, Ph), 4.62 (s, br, 2H, PCH<sub>2</sub>N), 4.41 (s, 2H, NCH<sub>2</sub>Ph), 4.30 (s, 2H, NCH<sub>2</sub>Ph), 4.03 (m, br, 2H, PCH<sub>2</sub>N), 3.55 – 3.48 (2 x m, br, 4H, PCH<sub>2</sub>N), 1.80 - 1.72 (2 x m, br, 4H, SCH<sub>2</sub>C), 1.05 (m, br, 4H, CH<sub>2</sub>CH<sub>3</sub>), 0.51 (m, br, 6H. CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd (%) for  $C_{42}H_{47}F_3Fe_2N_2O_7P_2S_3$ 

(%) Theoretical: C = 49.49, H = 4.61, N = 2.75 %. (%) Experimental: C =48.21, H = 4.53, N = 2.48 %.

Data for  $[Fe_2(CO)_4(\kappa^2-(P^{Ph}_2N^{Bn}_2H))(\mu-pdt^{Bn2})](CF_3SO_3)$  (6NH<sup>+</sup>) m = 0.09 g, Yield = 80 %. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>),  $\bar{\nu}$ (CO) = 2024 (s), 1959 (s), 1897 (w). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C, ppm) :  $\delta$  = 35.8 (s). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C, ppm) :  $\delta$  = 7.70 – 7.16 (m, 30H, Ph), 4.95 – 3.94 (m, 12H, P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>), 3.01 – 2.33 (m, 4H, SCH<sub>2</sub>C + CCH<sub>2</sub>Ph).

 $[Fe_2(CO)_4(\kappa^2-(P^{Ph}_2N^{Bn}_2H))(\mu-pdt)(\mu-H)](CF_3SO_3)_2$ Preparation of (4µHNH<sup>2+</sup>)

0.1 g of [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)( $\mu$ -pdt)] (0.12 mmol) was dissolved in 10 mL of dichloromethane. Then, 2 equivalents of CF<sub>3</sub>SO<sub>3</sub>H (21.6 µL, 0.24 mmol) were added and the solution was stirred for 30 min at room temperature. After this time the reaction was stopped and the solution was concentrated under vacuum. 4µHNH<sup>2+</sup> was isolated after addition of pentane.

Data for  $[Fe_2(\mu-H)(CO)_4(\kappa^2-(P^{Ph_2}N^{Bn_2}H))(\mu-pdt)](CF_3SO_3)_2(4\mu HNH^{2+})$ 

m = 0.1 g, Yield = 76 %. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>),  $\bar{u}$ (CO) = 2099 (vs), 2041 (vs), 1984 (s), 1971 (sh). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C ppm) : δ = 34.8 (d, <sup>2</sup>*J*<sub>PP</sub> = 97.8 Hz), 29.5 (s), 27.5 (d, <sup>2</sup>*J*<sub>PP</sub> = 97.8 Hz).

 $^1\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°Ć, ppm) :  $\delta$  = 11.4 (s, br, 1H, NH), 8.05 – 7.22 (m, 20H, Ph), 4.95 – 3.07 (m, 12H,  $\text{P}^{\text{Ph}_2N^{\text{Bn}}_2)$ , 2.47-1.67 (m, 6H, S(CH<sub>2</sub>)<sub>3</sub>S), - 14.03 (d, 1H,  $^2J_{\text{PH}}$ = 15.5 Hz), -14.80 (t, br, 1H).

#### Preparation of $[Fe_2(CO)_4(\kappa^2 - P^{Ph}_2N^{Bn}_2)(\mu - pdt)(\mu - H)](BAr^{F_4})$ (4µH<sup>+</sup>)

0.1 g of complex [Fe<sub>2</sub>(CO)<sub>4</sub>( $\kappa^2$ -P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)( $\mu$ -pdt)] (0.12 mmol) was dissolved in CH2Cl2. Afterwards one equivalent of CF3SO3H (10.8 µL, 0.12 mmol) was added to the solution. As expected, the IR monitoring showed that after stirring 10 min the complex **4NH**<sup>+</sup> is formed. One equivalent of Na(BAr<sup>F</sup><sub>4</sub>) (0.1 g, 0.12 mmol) was then added to this red solution. After stirring again 10 min, a IR spectrum was recorded and revealed that  $4\mu$ -H<sup>+</sup> is formed. The volume of the solution was reduced under vacuum to 2-3 mL. Then 4µ-H<sup>+</sup>. was precipitated as a red powder by addition of cold pentane.

Data for  $[Fe_2(CO)_4(\kappa^2 - P^{Ph_2}N^{Bn_2})(\mu - pdt)(\mu - H)](BAr^{F_4})$  (**4µH**<sup>+</sup>) m = 0.13 g, Yield = 65 %.

IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>), ū(CO) = 2093 (s), 2034 (s), 1969 (w), 1936 (w). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C, ppm) :  $\delta$  = 59.7 (d, <sup>2</sup>J<sub>PP</sub> = 99.2 Hz), 53.1 (s), 46.7 (d, <sup>2</sup>J<sub>PP</sub> = 99.2 Hz).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C, ppm) high field : -13.59 (d, br, J = 15,5 Hz), -14.44 (m. br).

NMR study of the protonation of  $[Fe_2(CO)_4(\kappa^2-P^{Ph}_2N^R_2)(\mu-dithiolato)]$ (dithiolato = pdt, pdt<sup>Et2</sup> and R = Ph, Bn) (1-2, 4-5)

0.01 g of the diiron complex (0.01 mmol) was solubilized into the NMR tube in CD<sub>2</sub>Cl<sub>2</sub>. The temperature was then decreased to -80°C in a liquid nitrogen-ethanol bath. Afterwards an excess of cooled acid (4.4 µL, 0.03 mmol) was added with a syringe.

#### Acknowledgements

CNRS (Centre National de la Recherche Scientifique) and the Université de Bretagne Occidentale (Brest) are acknowledged for financial support. A.H. was funded by the Region Bretagne. NMR recordings were performed at the 'Service général des plateformes, Brest' (SGPLAT). We are grateful to Dr F. Michaud for the crystallographic measurements of complexes and to the SGPLAT for VT-NMR recordings on Bruker DRX 500 spectrometer.

**Keywords:** diiron complex; aminophosphine ; thiolate ligand ; proton reduction ; bioinspired model of hydrogenases

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## Entry for the Table of Contents



The study of a series of dithiolato carbonyl diiron complexes featuring a cyclic azadiphosphine chelated at one iron centre shows the dependence of the protonation processes on the amine functions and the influence of the bridge-head group of the dithiolate on the coordination mode of the diphosphine.