

Communication

# Aza-Diphosphido-Bridged Di-Iron Complexes Related to the [FeFe]-Hydrogenases

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**Abstract:** The reaction of the dianionic species  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh})_2]^{2-}$  with  $^t\text{BuN}(\text{CH}_2\text{Cl})_2$  gives the di-iron carbonyl aza-diphosphido-bridged complex  $[\text{Fe}_2(\text{CO})_6(\mu\text{-[P(Ph)CH}_2\text{]}_2\text{N}^t\text{Bu})]$  (**1**). Attempts to prepare **1** by click-chemistry by reacting  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh})_2]$  with  $\text{CH}_2\text{O}$  and  $^t\text{BuNH}_2$  afforded a bis-phosphido compound  $[\text{Fe}_2(\text{CO})_6(\mu\text{-P(Ph)CH}_2\text{NH}^t\text{Bu})_2]$  (**2**) which exists as two, syn and anti, isolable isomers depending on the relative orientation of the groups carried by the phosphorus atoms. In the presence of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ , in dichloromethane, **1** leads to the stabilized ammonium species  $[\text{Fe}_2(\text{CO})_6(\mu\text{-[P(Ph)CH}_2\text{]}_2\text{NH}^t\text{Bu})](\text{BF}_4)$  (**3**). The derivatives **1–3** were characterized by IR and  $^1\text{H}$ ,  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR spectroscopies. Their structures in a solid state were determined by X-ray diffraction analyses, which accord with their spectroscopic characteristics.

**Keywords:** dinuclear complexes; iron; metal-sulfur; aza-diphosphido bridge; carbonyl group; hydrogenases; bioinspiration



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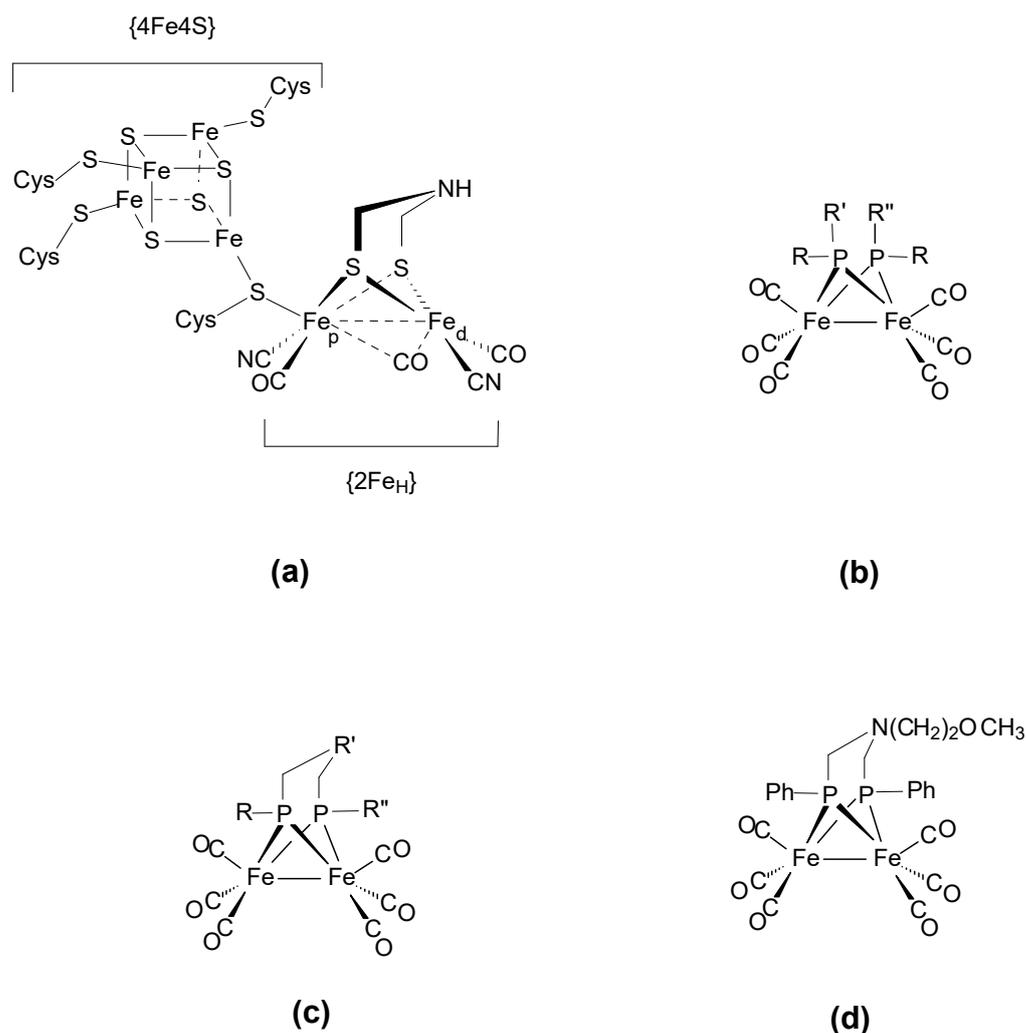
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## 1. Introduction

In recent decades, the chemistry of carbonyl iron complexes has undergone intensive development within the field of biomimicry. Alongside numerous reports on carbonyl dithiolato-bridged di-iron complexes structurally close to the active site of [FeFe]-hydrogenases (H-cluster) (Scheme 1a) [1–5], phosphido-bridged analogues (Scheme 1b,c) were studied in order to compare the electronic and stereochemical effects of the replacement of the  $\mu\text{-S}_2\text{R}$  bridge with the  $\mu\text{-PR}_2$  group on the reactivity and redox properties of such carbonyl di-iron systems [6–19]. The chemistry of bis-phosphido-bridged di-iron complexes of general formula  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PR}_2)_2]$  and linked-diphosphido  $[\text{Fe}_2(\text{CO})_6(\mu\text{-[PR]}_2\text{R}')]_2$  dates back much earlier [20–45]. Electrochemical and theoretical calculations on robust complexes  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PRR}')(\mu\text{-PRR}'')]_2$  were carried out because most of these compounds present a reversible two-electron reduction involving a potential inversion [15,16,44] depending on R, R' and R'' groups which affect Fe-P distances and the geometry of the  $\{\text{Fe}_2\text{P}_2\}$  core. Among these complexes with a  $\{\text{Fe}_2\text{P}_2\}$  core, diphosphido compounds featuring a  $\mu\text{-}\eta^2\text{:}\eta^2\text{-[RP-CH}_2\text{-R'-CH}_2\text{-PR}'']_2$  bridge were more recently the subject of interest (Scheme 1c) [11–17]. To the best of our knowledge, the compound  $[\text{Fe}_2(\text{CO})_6(\mu\text{-[P(Ph)CH}_2\text{]}_2\text{N}(\text{CH}_2)_2\text{OCH}_3)]$  (Scheme 1d) is the sole example of an azadiphosphido-bridged complex [11]. We report herein an extension of our work for preparing such scarce  $\mu\text{-aza-diphosphido}$  complexes. The syntheses, spectroscopic and structural characterizations of the complex  $[\text{Fe}_2(\text{CO})_6(\mu\text{-[P(Ph)CH}_2\text{]}_2\text{N}^t\text{Bu})]$  (**1**), its protonated form (**3**) and a bis-phosphido side-product  $[\text{Fe}_2(\text{CO})_6(\mu\text{-P(Ph)CH}_2\text{NH}^t\text{Bu})_2]$  (**2**) are presented.

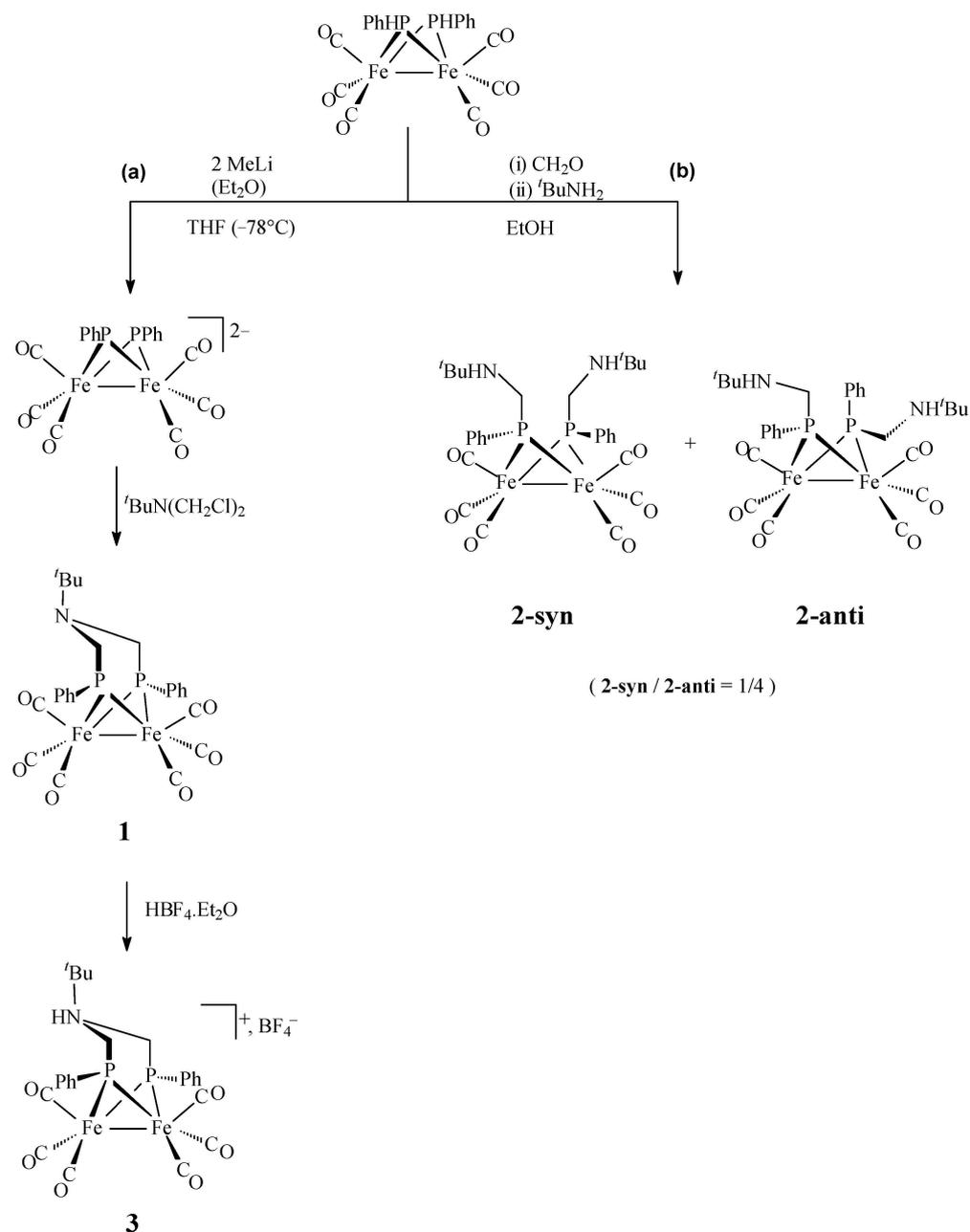


**Scheme 1.** Representations of (a) the H-cluster, (b) carbonyl di-iron bis-phosphido complexes, (c) carbonyl diphosphido complexes and (d) aza-diphosphido complexes.

## 2. Results and Discussion

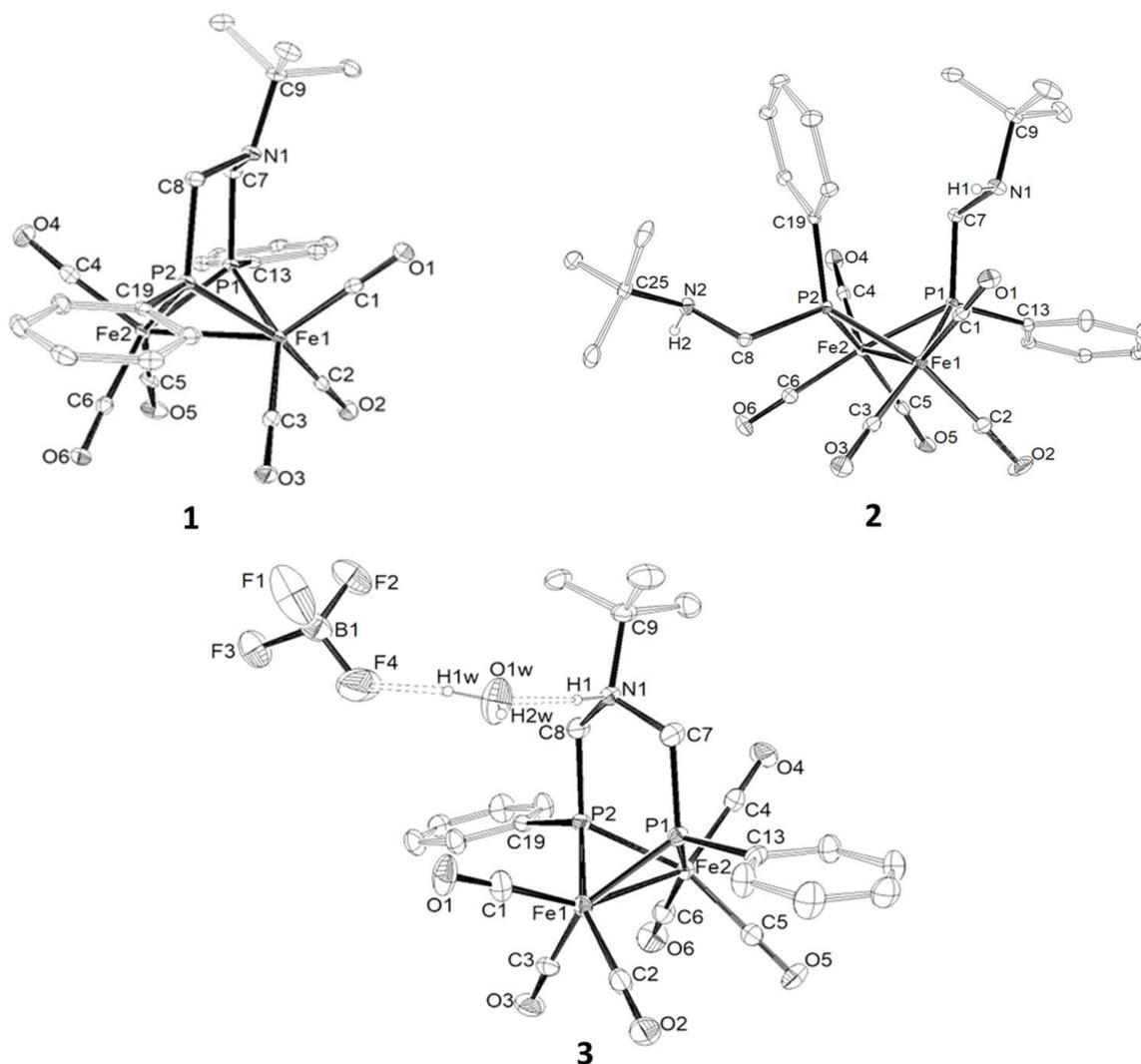
The complex  $[\text{Fe}_2(\text{CO})_6(\mu\text{-}\{\text{P}(\text{Ph})\text{CH}_2\}_2\text{N}^t\text{Bu})]$  (**1**) was obtained from the reaction of  $^t\text{BuN}(\text{CH}_2\text{Cl})_2$  with the dianion  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh})_2]^{2-}$  (Scheme 2, path (a)). This latter dianion was prepared by the reaction of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh})_2]$  with two equivalents of methyllithium [21,31,41]. In the presence of 1 equivalent of  $\text{HBF}_4$ ,  $\text{Et}_2\text{O}$ , the protonation of **1** occurred at the nitrogen atom of the azadiphosphido bridge, which produced the cationic complex  $[\text{Fe}_2(\text{CO})_6(\mu\text{-}\{\text{P}(\text{Ph})\text{CH}_2\}_2\text{NH}^t\text{Bu})](\text{BF}_4)$  (**3**). Attempts to prepare **1** through a one-pot reaction following a click process were also performed (Scheme 2, path (b)). The two isomers **2-anti** and **2-syn** were isolated by reacting a solution of the complex  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh})_2]$  in ethanol with an aqueous solution of  $\text{CH}_2\text{O}$ , followed by the addition of  $^t\text{BuNH}_2$ . Compounds **1–3** were characterized by spectroscopic analyses (IR, NMR), and their structures were confirmed by X-ray analyses of single crystals (see Appendix A and Tables S1–S3). The strong bands observed at 2053, 2013, 1984 and  $1970\text{ cm}^{-1}$  in the carbonyl region of the infrared spectrum of a  $\text{CH}_2\text{Cl}_2$  solution of **1** are typical of hexacarbonyl diiron ( $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ ) complexes with a diphosphido bridge [11]. The protonation at the amine function in **1**, giving the ammonium species **3**, is revealed by a shift of ca  $12\text{ cm}^{-1}$  (average) of the  $\nu(\text{CO})$  bands at higher wavenumbers compared to those of **1**, which is typical of a protonation in the second sphere of coordination of the di-iron centre. It is worth noting that few examples of isolated N-protonated forms of thiolato analogues have been reported [2,5]. The IR spectra of **2-syn/anti** are similar to

that of **1**. The  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$  exhibits the expected set of resonances for the aza-diphosphido bridge  $\{\text{P}(\text{Ph})\text{CH}_2\}_2\text{N}^t\text{Bu}$  according to a symmetrical molecule. Similar signals were observed in the  $^1\text{H}$  NMR spectrum of **3** in  $\text{CD}_3\text{CN}$ , but shifted at higher chemical shifts due to its cationic nature. The proton of the ammonium group could not be observed. The  $^1\text{H}$  NMR spectra of **2-syn/anti** in  $\text{CDCl}_3$  differ from those of **1** and **3** in the  $^t\text{Bu}/\text{CH}_2/\text{C}_6\text{H}_5$  ratio, which shows that there are two  $^t\text{Bu}$  groups instead of one. In the case of the syn isomer, a singlet is observed for the  $^t\text{Bu}$  groups, while the  $^1\text{H}$  NMR spectrum of the anti isomer displays two inequivalent singlets. Symmetrical species **1**, **2-syn**, **3** present in their  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra a singlet above 110 ppm. Interestingly, in the case of the **2-anti** species, an AB pattern with a coupling constant of 130 Hz was detected at 147.7 ppm. These chemical shifts are in the range of those observed when phosphido groups bridge two metal centres connected by a metal–metal interaction [46].



**Scheme 2.** Synthetic pathways for complexes **1**–**3**: (a) Sequential steps pathway and (b) one-pot pathway.

Single crystals suitable for X-ray diffraction studies were obtained, at  $-15\text{ }^{\circ}\text{C}$ , from  $\text{CH}_2\text{Cl}_2$ :  $\text{Et}_2\text{O}$  or  $\text{EtOH}$ :  $\text{Et}_2\text{O}$  solutions for compounds **1**, **3** and **2**, respectively (Figure 1 and Table 1). The overall geometry of the three complexes **1**–**3** is similar to those of analogous compounds with a butterfly  $\{\text{Fe}_2\text{P}_2\}$  core, two eclipsed square-pyramidal  $\{\text{Fe}(\text{CO})_3\}$  moieties bridged by two phosphido groups and an Fe–Fe interaction [11]. The distances of the Fe–Fe bond in **1** and **3**, 2.6361(5) Å and 2.6242(8) Å, respectively, are close to that observed in  $[\text{Fe}_2(\text{CO})_6(\mu\text{-}\{\text{P}(\text{Ph})\text{CH}_2\}_2\text{N}(\text{CH}_2)_2\text{OMe})]$  (2.631(1) Å), while such a distance is much longer in **2** (2.6693(5) Å) (Table 1). The intramolecular P1...P2 contact is significantly shorter in complexes **1** and **3** (2.6880(9) Å and 2.6816(14) Å, respectively) relative to that determined in **2-anti** (2.8899 Å) due to the steric constraint imposed by the aza-diphosphido bridge. The  $\text{Fe}_2\text{—P}_2\text{—C}_8\text{—N}_1\text{—C}_7\text{—P}_1$  metalloheterocycle in **1** and **3** adopts a chair conformation with the  $^t\text{Bu}$  substituent in an equatorial position. The geometry around N1 in **1** is a nearly trigonal pyramid (see  $\text{C}_8\text{—N}_1\text{—C}_7$ ,  $\text{C}_8\text{—N}_1\text{—C}_9$ ,  $\text{C}_7\text{—N}_1\text{—C}_9$  angles in Table 1). Indirect hints of the N-protonation in **3** are revealed by the opening of the  $\text{Fe}(1)\text{—Fe}(2)\text{—C}(1)$  angle of  $7^{\circ}$  to minimize H/CO steric clash ( $\text{Fe}1\text{—Fe}2\text{—C}1 = 152.48(16)^{\circ}$  in **3** and  $144.79(9)^{\circ}$  in **1**) and by a slight lengthening of N–C bonds in **3** compared with those in **1** (Table 1). In addition, the N–H proton is involved in a stabilizing hydrogen bond interaction to a hydrous  $\text{H}_2\text{O} \cdots \text{F}\text{—BF}_3^-$  anion [ $d(\text{N}1\text{—H}1 \cdots \text{O}1\text{W}) = 2.7056(1)$  Å,  $(\text{N}1\text{—H}1\text{—O}1\text{W}) = 172.418(4)^{\circ}$ ,  $d(\text{F}4 \cdots \text{O}1\text{W}) = 2.7081(1)$  Å,  $(\text{F}4\text{—H}1\text{W—O}1\text{W}) = 160.799(4)^{\circ}$ ].



**Figure 1.** Molecular structure of compounds **1**–**3** with thermal ellipsoids at 20% probability.

**Table 1.** Selected bond lengths (Å) and angles (°) of 1–3.

	1	2	3
Fe(1)—Fe(2)	2.6361(5)	2.6693(5)	2.6242(8)
P(1)—Fe(1)	2.2129(7)	2.2198(7)	2.1957(11)
P(2)—Fe(1)	2.2108(7)	2.2151(7)	2.2005(11)
P(1)—Fe(2)	2.1939(7)	2.2240(7)	2.1938(11)
P(2)—Fe(2)	2.1979(7)	2.2313(7)	2.1836(11)
P(1)—P(2)	2.6880(9)	2.8899	2.6816(14)
C(7)—P(1)	1.848(2)	1.846(3)	1.857(4)
C(13)—P(1)	1.825(2)	1.834(2)	1.816(4)
C(8)—P(2)	1.863(3)	1.859(2)	1.839(4)
C(19)—P(2)	1.820(2)	1.827(2)	1.809(4)
N(1)—C(7)	1.453(3)	1.457(3)	1.482(5)
N(1)—C(8)	1.455(3)		1.486(5)
N(1)—C(9)	1.504(3)	1.489(3)	1.559(5)
N(2)—C(8)		1.442(3)	
Fe(1)—Fe(2)—C(1)	144.79(9)	142.18(8)	152.48(16)
Fe(1)—P(1)—Fe(2)	73.48(2)	73.84(2)	73.43(4)
Fe(1)—P(2)—Fe(2)	73.44(2)	73.79(2)	73.53(4)
P(1)—Fe(1)—P(2)	74.84(3)	81.33 (3)	75.18(4)
P(1)—Fe(2)—P(2)	75.48(3)	80.88(3)	75.56(4)
C(13)—P(1)—Fe(1)	127.38(8)	117.89(9)	125.89(14)
C(13)—P(1)—Fe(2)	121.82(9)	122.98(8)	120.25(13)
C(19)—P(2)—Fe(1)	125.90(8)	122.61(8)	123.34(12)
C(19)—P(2)—Fe(2)	118.26(8)	126.87(8)	123.92(13)
C(7)—P(1)—Fe(1)	115.55(8)	123.29(8)	123.93(14)
C(7)—P(1)—Fe(2)	119.27(8)	117.32(8)	115.56(14)
C(8)—P(2)—Fe(1)	115.94(8)	116.36(8)	123.21(14)
C(8)—P(2)—Fe(2)	121.33(9)	119.35(9)	116.33(14)
C(7)—N(1)—C(8)	111.1(2)		119.1(3)
C(7)—N(1)—C(9)	112.77(19)	115.8(2)	112.8(3)
C(8)—N(1)—C(9)	116.69(19)		113.3(3)
C(8)—N(2)—C(25)		117.2 (2)	
N(1)—C(7)—P(1)	113.03(17)	111.34(17)	119.1(3)
N(1)—C(8)—P(2)	111.44(16)		120.1(3)
N(2)—C(8)—P(2)		111.84(17)	
C(19)—P(2)—P(1)	170.23(8)		174.05(12)
C(13)—P(1)—P(2)	174.1(9)		171.98(13)
C(13)—P(1)—C(7)	99.89(11)	101.65(11)	98.18(17)
C(19)—P(2)—C(8)	101.92(11)	98.62(11)	97.87(17)
H(1W)—O(1W)—H(2W)			110(4)

### 3. Materials and 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. A literature method was used for the preparation of the starting compound  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh})_2]$  [47] and  $t\text{BuN}(\text{CH}_2\text{Cl})_2$  [48]. All other reagents were commercially available and used as purchased. NMR spectra ( $^1\text{H}$ ,  $^{31}\text{P}\{-^1\text{H}\}$ ) were recorded at room temperature with Bruker AMX 400 or AC 300 spectrometers (Bruker, Billerica, MA, USA) of the “Service général des plateformes, Université de Bretagne Occidentale, Brest” and were referenced to  $\text{SiMe}_4$  ( $^1\text{H}$ ) and  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). The infrared spectra were recorded with Bruker Vertex 70 and FT IR Perkin Elmer spectrum 2 spectrometer (PerkinElmer Inc., Waltham, MA, USA). Crystal data of compounds 1–3 were collected with an Oxford Diffraction X—Calibur –2 CCD diffractometer (Agilent Technologies Inc., Santa Clara, CA, USA), equipped with a jet cooler device and graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved and refined using standard procedures [49]. Deposition numbers CCDC 2330851, 2330852 and 2330853 contain the supplementary crystallographic data for 1, 2 and 3. These

data can also be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (accessed on 4 February 2024).

#### 4. Conclusions

These results show the feasibility of extending the preparation of aza-diphosphido complexes  $[\text{Fe}_2(\text{CO})_6(\mu\text{-P}(\text{Ph})\text{CH}_2)_2\text{NR}]$  with a steric crowding amine function ( $\text{R} = \text{tBu}$ ) through a synthetic pathway involving the handy precursor  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh})_2]$ . The protonation of **1** is directed to the amine site, cleanly affording its stable N-protonated form. X-ray study of the ammonium complex **3** reveals an interesting structural feature with stabilizing hydrogen interactions  $[\text{F}_3\text{BF} \cdots \text{H}_2\text{O} \cdots \text{HN}]$  involving a water molecule between the counter-anion  $\text{BF}_4^-$  and the ammonium function. The one-pot reaction of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh})_2]$  in the presence of  $\text{CH}_2\text{O}$  and  $\text{tBuNH}_2$  turned out differently and afforded the separable anti and syn isomers of the bis-phosphido compound  $[\text{Fe}_2(\text{CO})_6(\mu\text{-P}(\text{Ph})\text{CH}_2\text{NH}^t\text{Bu})_2]$  (**2**) with 'PCH<sub>2</sub>NH<sup>t</sup>Bu' linkages. The intermediate formation of the hydroxo species  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}(\text{CH}_2\text{OH}))_2]$  is involved in this reaction. Its preparation with the aim of investigating its reactivity towards amine should help to understand and improve this click process.

**Supplementary Materials:** Table S1: Crystal data and structure refinement for complex **1**; Table S2: Crystal data and structure refinement for complex **2**; Table S3: Crystal data and structure refinement for complex **3**; Figure S1: IR spectrum in  $\text{CH}_2\text{Cl}_2$  of **1**; Figure S2:  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of **1**; Figure S3:  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ) of **1**; Figure S4: IR spectrum in  $\text{CH}_2\text{Cl}_2$  of **2-anti**; Figure S5:  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of **2-anti**; Figure S6:  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ) of **2-anti**; Figure S7: IR spectrum in  $\text{CH}_2\text{Cl}_2$  of **2-syn**; Figure S8:  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of **2-syn**; Figure S9:  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ) of **2-syn**; Figure S10: IR spectrum in  $\text{CH}_2\text{Cl}_2$  of **3**; Figure S11:  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ) of **3**; Figure S12:  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of **3**.

**Author Contributions:** P.S. and P.D. supervised the syntheses and X-ray, spectroscopic characterizations of the compounds **1–3**. C.E., F.Y.P., P.D. and P.S. contributed to the writing of the manuscript. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** Data are contained within the article and Supplementary Materials.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

#### Appendix A

*Preparation of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-P}(\text{Ph})\text{CH}_2)_2\text{N}^t\text{Bu}]$  (**1**).* A THF solution (50 mL) of  $\text{Li}_2[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh})_2]$ , generated in situ (30 min stirring), at  $-78^\circ\text{C}$ , from  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh})_2]$  (0.4 g, 0.80 mmol) with 2 equiv (1.6 mmol) of MeLi (1.1 mL, 1.5 M in  $\text{Et}_2\text{O}$ ) was treated with a THF solution of  $\text{tBuN}(\text{CH}_2\text{Cl})_2$  (0.15 g, 0.88 mmol). After 30 min, the orange-brown solution was allowed to warm to room temperature and stirred for 1 h. The solvent was then removed, and the crude product was extracted with dichloromethane ( $2 \times 25$  mL). The extracts were evaporated to dryness, and the residue was chromatographed on a silica gel column. Elution with hexane-dichloromethane (1:1) afforded a bright yellow solution of **1**, which was evaporated under vacuum. Yellow crystals grew from  $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$  (3:1) mixtures, yield 0.196 g (41%). Elemental analysis (%) calculated for  $\text{C}_{24}\text{H}_{23}\text{Fe}_2\text{NO}_6\text{P}_2$ : C 48.44, H 3.89, N 2.35; found; C 46.46, H 4.18, N 1.42. Elemental analysis (%) calculated for  $\frac{1}{2}\text{CH}_2\text{Cl}_2 \cdot \text{C}_{24.5}\text{H}_{24}\text{ClFe}_2\text{NO}_6\text{P}_2$ : C 46.15, H 3.79, N 2.19.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 7.72\text{--}7.47$  (m, 10H,  $\text{C}_6\text{H}_5$ ), 2.92 (s, 4H, P-CH<sub>2</sub>-N), 0.97 (s, 9H, N-C( $\text{CH}_3$ )<sub>3</sub>);  $^{31}\text{P}\{-^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 141.79$  (s); IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO}) = 2053(\text{s}), 2013(\text{vs}), 1984(\text{s}), 1970(\text{s}) \text{ cm}^{-1}$ .

*Reaction of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh})_2]$  with  $\text{CH}_2\text{O}$  and  $\text{tBuNH}_2$ .* A solution of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh})_2]$  (0.2 g, 0.40 mmol) in 30 mL of ethanol was treated with 0.1 mL (1.23 mmol)

of an aqueous solution of CH<sub>2</sub>O (37%). After stirring for 30 min at room temperature, 0.5 mL of *t*BuNH<sub>2</sub> (4.8 mmol) was added to the resulting orange-red solution. After the reaction mixture turned brown, the solvent was evaporated to dryness and the crude product was extracted with 3 × 15 mL of Et<sub>2</sub>O. After filtration and evaporation of Et<sub>2</sub>O, the resulting residue was chromatographed on a silica gel column with mixture of hexane-CH<sub>2</sub>Cl<sub>2</sub>. Elution with dichloromethane afforded a yellow fraction of *anti*-[Fe<sub>2</sub>(CO)<sub>6</sub>(μ-P(Ph)CH<sub>2</sub>N<sup>*t*</sup>Bu)<sub>2</sub>] (**2-anti**) as the major product of the reaction. A second yellow fraction of the minor isomer *syn*-[Fe<sub>2</sub>(CO)<sub>6</sub>(μ-P(Ph)CH<sub>2</sub>NH<sup>*t*</sup>Bu)<sub>2</sub>] (**2-syn**) was collected with a mixture of solvents CH<sub>2</sub>Cl<sub>2</sub>-THF (9:1).

Yields: **2-anti**: 136 mg (51%); **2-syn**: 34 mg (13%). Single crystals of **2-anti** grew from EtOH-Et<sub>2</sub>O (1:1) mixtures.

**2-anti**: Elemental analysis (%) calculated for C<sub>28</sub>H<sub>34</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>: C 50.33, H 5.13, N 4.19; found; C 50.22, H 5.13, N 4.03. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C): δ = 7.71–7.35 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 3.38 (s, 4H, P-CH<sub>2</sub>-N), 0.82 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.36 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), NH not assigned; <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C): δ = 147.7 (AB, J<sub>PP</sub> = 130.0 Hz); IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) = 2051(s), 2012(vs), 1981(s), 1964(s) cm<sup>-1</sup>.

**2-syn**: Elemental analysis (%) calculated for C<sub>28</sub>H<sub>34</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>: C 50.33, H 5.13, N 4.19; found; C 49.61, H 5.11, N 3.89. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C): δ = 7.10–6.77 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 3.33 (s, 4H, P-CH<sub>2</sub>-N), 0.78 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), NH not assigned; <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C): δ = 136.8 (s); IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) = 2050(s), 2011(vs), 1979(s), 1964(s) cm<sup>-1</sup>.

*Protonation of 1*. A solution of **1** (0.1 g, 0.17 mmol) in dichloromethane (10 mL) was treated with 1 equiv (23 μL) of HBF<sub>4</sub>. Et<sub>2</sub>O (1.19 g/mL). The mixture was stirred for 1 h. The volume was then reduced under vacuum, and diethyl ether was added to precipitate a yellow powder of **3**. Yield 0.11 g (95%). Single crystals grew from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O (3:1) mixtures. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C): δ = 7.79–7.57 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 3.50 (br, 4H, P-CH<sub>2</sub>-N), 1.41 (s, 3H, C(CH<sub>3</sub>)<sub>3</sub>), NH not assigned; <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C): δ = 113.8 (s); IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) = 2070(s), 2032(vs), 2004(s), 1963(s) cm<sup>-1</sup>.

## References

- Hogarth, G. An unexpected leading role for [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-pdt)] in our understanding of [FeFe]-H<sub>2</sub>ases and the search for clean hydrogen production. *Coord. Chem. Rev.* **2023**, *490*, 215174. [[CrossRef](#)]
- Kleinhaus, J.T.; Wittkamp, F.; Yadav, S.; Siegmund, D.; Apfel, U.-P. [FeFe]-Hydrogenases: Maturation and reactivity of enzymatic systems and overview of biomimetic models. *Chem. Soc. Rev.* **2021**, *50*, 1668–1784. [[CrossRef](#)] [[PubMed](#)]
- Li, Y.; Rauchfuss, T.B. Synthesis of di-iron(I) dithiolato carbonyl complexes. *Chem. Rev.* **2016**, *116*, 7043–7077. [[CrossRef](#)] [[PubMed](#)]
- Apfel, U.-P.; Pétilion, F.Y.; Schollhammer, P.; Talarmin, J.; Weigand, W. Chapter 4 [FeFe] Hydrogenase Models an Overview. In *Bioinspired Catalysis*; Weigand, W., Schollhammer, P., Eds.; Wiley-VCH: Weinheim, Germany, 2015; pp. 79–103; ISBN 978-3-527-33308-0.
- Elleouet, C.; Pétilion, F.Y.; Schollhammer, P. Chapter 17 [FeFe]-Hydrogenases Models. In *Advances in Bioorganometallic Chemistry*; Hirao, T., Moriuchi, T., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; pp. 347–364. [[CrossRef](#)]
- Agarwal, T.; Kaur-Ghumaan, S. HER catalyzed by iron complexes without a Fe<sub>2</sub>S<sub>2</sub> core: A review. *Coord. Chem. Rev.* **2019**, *397*, 188–219. [[CrossRef](#)]
- Cheah, M.H.; Borg, S.J.; Bondin, M.I.; Best, S.P. Electrocatalytic proton reduction by phosphido-bridged diiron carbonyl compounds: Distant relations to the H-cluster? *Inorg. Chem.* **2004**, *43*, 5635–5644. [[CrossRef](#)] [[PubMed](#)]
- Cheah, M.H.; Best, S.P. XAFS and DFT characterisation of protonated reduced Fe-hydrogenase analogues and their implications for electrocatalytic proton reduction. *Eur. J. Inorg. Chem.* **2011**, *2011*, 1128–1137. [[CrossRef](#)]
- Gimbert-Suriñach, C.; Bhadbhade, M.; Colbran, S.B. Bridgehead hydrogen atoms are important: Unusual electrochemistry and proton reduction at iron dimers with ferrocenyl-substituted phosphido bridges. *Organometallics* **2012**, *31*, 3480–3491. [[CrossRef](#)]
- Rahaman, A.; Gimbert-Suriñach, C.; Ficks, A.; Ball, G.E.; Bhadbhade, M.; Haukka, M.; Higham, L.; Nordlander, E.; Colbran, S.B. Bridgehead isomer effects in bis(phosphido)-bridged diiron hexacarbonyl proton reduction electrocatalysts. *Dalton Trans.* **2017**, *46*, 3207–3222. [[CrossRef](#)]
- Das, P.; Capon, J.-F.; Gloaguen, F.; Pétilion, F.Y.; Schollhammer, P.; Talarmin, J.; Muir, K.W. Di-iron aza diphosphido complexes: Mimics for the active site of Fe-only hydrogenase, and effects of changing the coordinating atoms of the bridging ligand in [Fe<sub>2</sub>{μ-(E)CH<sub>2</sub>NR}(CO)<sub>6</sub>]. *Inorg. Chem.* **2004**, *43*, 8203–8205. [[CrossRef](#)]
- Cheah, M.H.; Borg, S.J.; Best, S.P. Steps along the path to dihydrogen activation at [FeFe] hydrogenase structural models: Dependence of the core geometry on electrocatalytic proton reduction. *Inorg. Chem.* **2007**, *46*, 1741–1750. [[CrossRef](#)]
- Zaffaroni, R.; Rauchfuss, T.B.; Fuller, A.; De Gioia, L.; Zampella, G. Contrasting protonation behavior of diphosphido vs dithiolato diiron(I) carbonyl complexes. *Organometallics* **2013**, *32*, 232–238. [[CrossRef](#)]

14. Arrigoni, F.; Rizza, F.; Vertemara, J.; Breglia, R.; Greco, C.; Bertini, L.; Zampella, G.; De Gioia, L. Rational design of  $\text{Fe}_2(\mu\text{-PR}_2)_2(\text{L})_6$  coordination compounds featuring tailored potential inversion. *ChemPhysChem* **2020**, *21*, 2279–2292. [[CrossRef](#)] [[PubMed](#)]
15. Selan, O.T.E.; Cheah, M.H.; Abrahams, B.F.; Gable, R.W.; Best, S.P. Impact of the 2Fe2P core geometry on the reduction chemistry of phosphido-bridged diiron hexacarbonyl compounds. *Austr. J. Chem.* **2022**, *75*, 649–659. [[CrossRef](#)]
16. Shimamura, T.; Maeno, Y.; Kubo, K.; Kume, S.; Greco, C.; Mizuta, T. Protonation and electrochemical properties of a bisphosphido diiron hexacarbonyl complex bearing amino groups on the phosphido bridge. *Dalton Trans.* **2019**, *48*, 16595–16603. [[CrossRef](#)] [[PubMed](#)]
17. Teramoto, Y.; Kubo, K.; Kume, S.; Mizuta, T. Formation of a hexacarbonyl diiron complex having a naphthalene-1,8-bis(phenylphosphido) bridge and the Electrochemical Behavior of Its Derivatives. *Organometallics* **2013**, *32*, 7011–7024. [[CrossRef](#)]
18. Shi, Y.S.; Yang, W.; Shi, Y.; Cheng, D.-C. Syntheses, crystal structures, and electrochemical studies of  $\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-L})$  (L = OH, OPPh<sub>2</sub>, PPh<sub>2</sub>). *J. Coord. Chem.* **2014**, *67*, 2330–2343. [[CrossRef](#)]
19. Mai, Y.; Balzen, A.K.; Torres, R.K.; Callahan, M.P.; Colson, A.C. A modular strategy for expanding electron-sink capacity in noncanonical cluster assemblies. *Inorg. Chem.* **2021**, *60*, 17733–17743. [[CrossRef](#)]
20. Hayter, R.G. Phosphorus- and arsenic—Bridged complexes of metal carbonyls. VI. Reactions of tetrasubstituted biphosphines and a biarsine with monomeric metal carbonyls. *Inorg. Chem.* **1964**, *3*, 711–717. [[CrossRef](#)]
21. Treichel, P.M.; Douglas, W.M.; Dean, W.K. Deprotonation and subsequent alkylation of phosphine-metal carbonyl complexes. *Inorg. Chem.* **1972**, *7*, 1615–1618. [[CrossRef](#)]
22. Clegg, W. Crystal structure of bis( $\mu$ -bis(trifluoromethyl)phosphido)-hexacarbonyldiiron,  $\text{Fe}_2(\text{CO})_6[\mu\text{-P}(\text{CF}_3)_2]_2$ . *Inorg. Chem.* **1976**, *15*, 1609–1613. [[CrossRef](#)]
23. Ginsburg, R.E.; Rothrock, R.K.; Finke, R.G.; Coliman, J.P.; Dahl, L.F. The (metal-metal)-nonbonding  $[\text{Fe}_2(\text{CO})_6(\mu_2\text{-PPh}_2)_2]^{2-}$  dianion. Synthesis, structural analysis of its unusual dimeric geometry, and stereochemical-bonding implications. *J. Am. Chem. Soc.* **1979**, *101*, 6550–6552. [[CrossRef](#)]
24. Collman, J.P.; Rothrock, R.K.; Finke, R.G.; Moore, E.J.; Rose-Munch, F. Role of the metal-metal bond in transition-metal clusters. Phosphido-bridged diiron carbonyl complexes. *Inorg. Chem.* **1982**, *21*, 146–156. [[CrossRef](#)]
25. Yu, Y.-F.; Gallucci, J.; Wojcicki, A. Novel mode of reduction of phosphido-bridged, metal-metal-bonded binuclear complexes. Synthesis and reactivity of an unsymmetrical anion from  $\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)_2$ . *J. Am. Chem. Soc.* **1983**, *105*, 4826–4828. [[CrossRef](#)]
26. Walther, B.; Hartung, H.; Reinhold, J.; Jones, P.G.; Mealli, C.; Böttcher, H.-C.; Baumelster, U.; Krug, A.; Möckel, A. Structure and bonding of the coordinatively unsaturated complexes  $[\text{Fe}_2(\text{CO})_5(\mu\text{-PR}_2)(\mu\text{-PR}'_2)](\text{Fe}=\text{Fe})$  (R = R' = Bu<sup>t</sup>; R = Ph, R' = Bu<sup>t</sup>). Reaction of  $\text{Na}[\text{Fe}_2(\mu\text{-CO})(\text{CO})_6(\mu\text{-PR}_2)]$  with R'<sub>2</sub>PCl (R, R' = Ph, Cy, Me, Bu<sup>t</sup>). *Organometallics* **1992**, *11*, 1542–1549. [[CrossRef](#)]
27. Walther, B.; Hartung, H.; Bambirra, S.; Krug, A.; Böttcher, H.-C. Coordinatively unsaturated complexes  $[\text{Fe}_2(\text{CO})_5(\mu\text{-P}(\text{Bu}^t)_2)(\mu\text{-PR}_2)](\text{Fe}=\text{Fe})$  (R = Cy, Ph): Addition of PBu<sup>n</sup><sub>3</sub>, Ph<sub>2</sub>PH, and dppm (dppm = bis(diphenylphosphino)methane). The unprecedented complex  $[\text{Fe}_2(\text{CO})_3(\mu\text{-P}(\text{Bu}^t)_2)(\mu\text{-PCy}_2)(\mu\text{-dppm})](\text{Fe}=\text{Fe})$ . *Organometallics* **1994**, *13*, 172–179. [[CrossRef](#)]
28. Van der Linden, J.G.M.; Heck, J.; Walther, B.; Böttcher, H.-C. Electrochemical investigation of the electron-poor/precise (n = 5/6) complexes  $[\text{Fe}_2(\text{CO})_n(\mu\text{-PR}_2)(\mu\text{-PR}'_2)]$  (n = 5, R = R' = Bu<sup>t</sup>; n = 6, R = R' = Ph; R = Bu<sup>t</sup>, R' = Ph; R = Bu<sup>t</sup>, R' = Cy). EPR study of the radical anion  $[\text{Fe}_2(\mu\text{-P}(\text{Bu}^t)_2)_2(\text{CO})_5]^-$ . *Inorg. Chim. Acta* **1994**, *217*, 29–32. [[CrossRef](#)]
29. Flood, T.C.; DiSanti, F.J.; Campbell, K.D. Stereochemical Lability of  $(\text{CO})_3\text{Fe}(\mu\text{-ER}_2)_2\text{Fe}(\text{CO})_2\text{PR}_3$ . Evidence for two distinct CO averaging processes without bridge opening. *Inorg. Chem.* **1978**, *17*, 1643–1646. [[CrossRef](#)]
30. McKennis, J.S.; Kyba, E.P. Linked bis( $\mu$ -phosphido) and related ligands for metallic clusters. 1. Application to the hexacarbonyldiiron moiety. *Organometallics* **1983**, *2*, 1249–1251. [[CrossRef](#)]
31. Seyferth, D.; Wood, T.G.; Fackler, J.P., Jr.; Mazany, A.M. Intramolecular nucleophilic attack at iron in an anionic phosphido-bridged  $\text{Fe}_2(\text{CO})_6$  complex. *Organometallics* **1984**, *3*, 1121–1123. [[CrossRef](#)]
32. Rheingold, A.L. A linked diphosphido iron carbonyl complex,  $\mu\text{-P,P'}$ -diphenyltrimethylenebis(phosphido)- $\mu\text{-P}:\mu\text{-P}'$ -bis(tricarbonyliron)(Fe–Fe),  $[\text{Fe}_2(\text{C}_{15}\text{H}_{16}\text{P}_2)(\text{CO})_6]$ . *Acta Crystallogr.* **1985**, *C41*, 1043–1045. [[CrossRef](#)]
33. King, R.B.; Wu, F.-J.; Sadani, N.D.; Holt, E.M. (Carbonylbis((dialkylamino)phosphido))hexacarbonyldiiron complexes: Migration of a carbonyl group from iron to phosphorus. *Inorg. Chem.* **1985**, *24*, 4449–4450. [[CrossRef](#)]
34. King, R.B.; Wu, F.-J.; Holt, E.M. Novel ((diisopropylamino)triphosphine)hexacarbonyldiiron complexes. *Inorg. Chem.* **1986**, *25*, 1733–1734. [[CrossRef](#)]
35. Kyba, E.P.; Davis, R.E.; Clubb, C.N.; Liu, S.-T.; Aldaz Palacio, H.O.; McKennis, J.S. Linked bis( $\mu$ -phosphido) and related ligands for metallic clusters. 5. Evidence for a highly selective backside attack by strong nucleophiles on a  $\mu$ -phosphido center. *Organometallics* **1986**, *5*, 869–877. [[CrossRef](#)]
36. Kyba, E.P.; Kerby, M.C.; Rines, S.P. A Convenient synthesis of symmetrical and unsymmetrical 1,2-bis(phosphino)benzenes as ligands for transition metals. *Organometallics* **1986**, *5*, 1189–1194. [[CrossRef](#)]
37. De, R.L.; Wolters, D.; Vahrenkamp, H. Darstellung und reaktionen des tetraeder-moleküls  $\text{Fe}_2(\text{CO})_6(\text{P-tert-C}_4\text{H}_9)_2$  / Preparation and reactions of the tetrahedrane molecule  $\text{Fe}_2(\text{CO})_6(\text{P-tert-C}_4\text{H}_9)_2$ . *Z. Naturforsch. B* **1986**, *41*, 283–291. [[CrossRef](#)]
38. Seyferth, D.; Wood, T.G. Michael-type addition reactions of bis( $\mu$ -phenylphosphido)bis(tricarbonyliron) with olefinic  $\alpha,\beta$ -unsaturated carbonyl compounds. Construction of chelating bis(phosphido) ligands. *Organometallics* **1987**, *6*, 2563–2567. [[CrossRef](#)]
39. King, R.B.; Wu, F.-J.; Holt, E.M. Dialkylamino phosphorus metal carbonyls. 4. Novel phosphorus-bridging carbonyl derivatives and triphosphine derivatives from reactions of tetracarbonylferrate(-II) with (dialkylamino)dichlorophosphines. *J. Am. Chem. Soc.* **1987**, *109*, 7764–7775. [[CrossRef](#)]

40. King, R.B.; Wu, F.-J.; Holt, E.M. Dialkylamino phosphorus metal carbonyls. 5. Chemical reactivity of the phosphorus-bridging carbonyl group in carbonylbis[(diisopropylamino)phosphido]hexacarbonyldi-iron. *J. Am. Chem. Soc.* **1988**, *110*, 2775–2782. [[CrossRef](#)]
41. Seyferth, D.; Wood, T.G.; Henderson, R.S. Reactions of lithium bis( $\mu$ -phenylphosphido)-bis(tricarbonyliron),  $(\mu\text{-PhPLi})_2\text{Fe}_2(\text{CO})_6$ , with organic halides. A novel anionic rearrangement of a chelating diphosphido ligand. *J. Organomet. Chem.* **1987**, *336*, 163–182. [[CrossRef](#)]
42. Seyferth, D.; Wood, T.G. Michael-type addition reactions of bis(phenylphosphido)bis(tricarbonyliron) with acetylenic  $\alpha,\beta$ -unsaturated carbonyl compounds: Multiple reaction pathways. *Organometallics* **1988**, *7*, 714–718. [[CrossRef](#)]
43. Kumar, V.; Newton, M.G.; King, R.B. Insertion of a carbenoid unit into an  $\text{Fe}_2\text{P}_2$  cluster. *J. Organomet. Chem.* **1994**, *472*, C13–C14. [[CrossRef](#)]
44. Baik, M.-H.; Ziegler, T.; Schauer, C.K. Density functional theory study of redox pairs. 1. Dinuclear iron complexes that undergo multielectron redox reactions accompanied by a reversible structural change. *J. Am. Chem. Soc.* **2000**, *122*, 9143–9154. [[CrossRef](#)]
45. Burdett, J.K. A molecular-orbital study of some di-phosphido-bis(tricarbonyliron) complexes. The importance of metal-bridging ligand interactions in determining molecular geometry. *J. Chem. Soc. Dalton Trans.* **1977**, *5*, 423–428. [[CrossRef](#)]
46. Garrou, P.E.  $\Delta_R$ -ring contributions to phosphorus- $^{31}\text{NMR}$  parameters of transition-metal-phosphorus chelate complexes. *Chem. Rev.* **1981**, *81*, 229–266. [[CrossRef](#)]
47. Bartsch, R.; Hietkamp, S.; Morton, S.; Stelzer, O. Reaktionen koordinierter Liganden: X. Reaktivität zweikerniger eisencarbonylkomplexe mit sekundären phosphidobrüken  $\mu\text{-rph}$ . *J. Organomet. Chem.* **1981**, *222*, 263–273. [[CrossRef](#)]
48. Lawrence, J.D.; Li, H.; Rauchfuss, T.B. Beyond Fe-only hydrogenases: N-functionalized 2-aza-1,3-dithiolates  $\text{Fe}_2[(\text{SCH}_2)_2\text{NR}](\text{CO})_x$  ( $x = 5, 6$ ). *Chem. Commun.* **2001**, *16*, 1482–1483. [[CrossRef](#)]
49. Farrugia, L.J. WinGX suite for small molecule single-crystal crystallography. *J. Appl. Crystallogr.* **1999**, *32*, 837–838. [[CrossRef](#)]

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