# Diiron species containing a cyclic $P^{Ph}{}_2N^{Ph}{}_2$ diphosphine related to the [FeFe]$H_2$ases active site†‡

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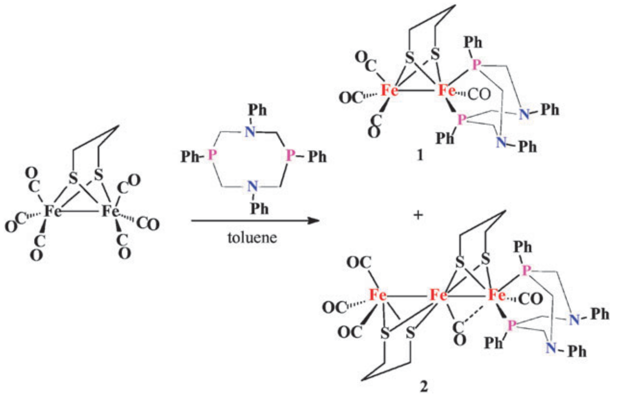
**A new dissymmetrically disubstituted diiron dithiolate species, $[Fe_2(CO)_4(\kappa^2\text{-}P^{Ph}{}_2N^{Ph}{}_2)(\mu\text{-pdt})]$ (pdt = $S(CH_2)_3S$), was prepared by using a flexible cyclic base-containing diphosphine, 1,3,5,7-tetraphenyl 1,5-diaza-3,7-diphosphacyclooctane ($P^{Ph}{}_2N^{Ph}{}_2$ = $\{PhPCH_2NPh\}_2$). Preliminary investigations of proton and electron transfers on the diiron system have been done.**

Despite the efforts of synthetic chemists to design diiron molecules with some of the key features of the H cluster, the organometallic active site of the [FeFe]-hydrogenase enzymes,[1,2] the activity (high turnover and low overpotential) of this natural system for building or breaking $H_2$ has still not been equalized by homogenous bioinspired [FeFe]-electrocatalysts.[3] The role of a proton relay in the second sphere of coordination of the active site is proposed to be essential in the catalytic functioning of the H cluster. Such a proton relay has been modeled by using azadithiolate bridges or base-containing phosphine and diphosphine ligands.[3,4] The introduction of a pendant base by using functionalized diphosphine has been widely developed by DuBois and Rakowski DuBois.[5] Their studies demonstrated great interest in using flexible base-containing diphosphine of the type PNP ($(R_2PCH_2)_2NR'$) or $P^R{}_2N^{R'}{}_2$ ($\{RPCH_2NR'\}_2$) that can be tuned by the choice of their substituents. Recently, we and others extended this approach to propanedithiolate (pdt) diiron compounds $[Fe_2(CO)_4(\kappa^2\text{-PNP})(\mu\text{-pdt})]$ in order to examine the influence of such a ligand on the proton and electron transfers at a diiron site.[6,7] Pursuing this approach, we have now combined diiron systems with a cyclic diphosphine $P^{Ph}{}_2N^{Ph}{}_2$. We report preliminary results concerning the formation of new dissymmetrically disubstituted diiron and triiron dithiolate species featuring cyclic base-containing diphosphine. Protonation and electrochemical behaviours of the bimetallic species have been investigated.



**Scheme 1** Synthesis of **1** and **2**.

The reaction of the hexacarbonyl precursor $[Fe_2(CO)_6(\mu\text{-pdt})]$ with $P^{Ph}{}_2N^{Ph}{}_2$ ($\{PhPCH_2NPh\}_2$),[8] in refluxing toluene, afforded a mixture of products which were separated by chromatography on a silica gel column (Scheme 1).§ The complex $[Fe_2(CO)_4(\kappa^2\text{-}P^{Ph}{}_2N^{Ph}{}_2)(\mu\text{-pdt})]$ (**1**) and two side-products, **2** and **3**, were obtained in *ca.* 49%, 6% and 2% yields, respectively. They were characterised by $^{31}P\{^1H\}$ NMR and IR spectroscopies, elemental analyses and by single crystal X-ray analyses. The structure of **1** was confirmed by an X-ray analysis¶[9] of a single crystal obtained from hexane–dichloromethane solution (Fig. 1). This indicated a basal–apical bidentate coordination of the diphosphine to one iron atom, thereby forming boat and chair FePCNCP rings. $^{31}P\{^1H\}$ NMR studies at low temperature indicated that typical fluxional processes (Fig. Sa, ESI‡), related to the cyclic diphosphine and to the dithiolate bridge, are operative in solution.[10]

X-Ray analysis[9] of a single crystal of a side product **3** revealed a typical structure of a monosubstituted dithiolate diiron complex $[Fe_2(CO)_5L(\mu\text{-pdt})]$ with a monodentate cyclic

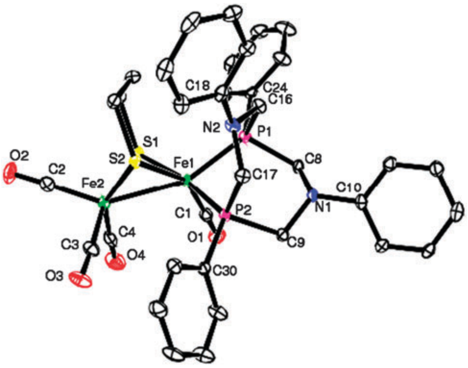


**Fig. 1** Ortep view (ellipsoids at 30% of probability level) of $[Fe_2(CO)_4(\kappa^2\text{-}P^{Ph}{}_2N^{Ph}{}_2)(\mu\text{-pdt})]$ (**1**). Selected bond lengths (Å) and angles (°): Fe(1)–Fe(2), 2.5655(9); Fe(1)–P(1), 2.1862(13); Fe(1)–P(2), 2.1833(14); P(1)–Fe(1)–P(2), 82.41(5).

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‡ Electronic supplementary information (ESI) available: Experimental details, NMR and ORTEP figures, acid-dependence of the reduction current for **1**. CDCC 789266 (**1**), 789267 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc03295f

diphosphine sulfide (L) (Fig. Sb, ESI‡). The formation of this product could arise from partial decomposition of dithiolate diiron compounds.[11]

Unfortunately, until now, only very small single crystals of **2** were obtained. For this reason, **2** could not be identified without any ambiguity. A very poor X-ray analysis suggested that the molecular structure of **2**, proposed in Scheme 1, is a trinuclear iron cluster $[Fe_3(CO)_4(\kappa^2\text{-}P^{Ph}{}_2N^{Ph}{}_2)(\mu\text{-}CO)(\mu\text{-pdt})_2]$ that is structurally analogous to $[Fe_3(CO)_6(\mu\text{-}CO)(\mu\text{-edt})_2]$ (edt = ethane dithiolate).[12] Electron-counting rules suggest a diamagnetic structure with two Fe–Fe bonds and a formal Fe(I)Fe(II)Fe(I) unit bridged by two dithiolate groups. A diphosphine ligand is chelated at one iron center and a semi-bridging carbonyl group links two iron atoms. It is worth noting that few examples of oligomeric Fe—SR–CO species have been reported.[13–15] Such a structure is also reminiscent of mixed valent Fe(I)–Fe(II) systems, with a pyramidal inversion of one iron atom, that have been recently reported in the literature.[16] The structure of **2** can also be structurally viewed as a mixed valent Fe(I)–Fe(II) assembly linked to a $\{Fe(CO)_3\}$ group through a metal–metal bond and the sulfur atoms of a dithiolate bridge. The overall structure of **2** accords with its elemental analysis and spectroscopic data.‡ In particular, the $^{31}P\{^1H\}$ NMR spectrum of **2** presents a doublet of doublets with a coupling constant of 80 Hz (Fig. Sc, ESI‡) which accords with a bidentate diphosphine in basal–apical position.

The reactivity of $[Fe_2(CO)_4(\kappa^2\text{-}P^{Ph}{}_2N^{Ph}{}_2)(\mu\text{-pdt})]$ (**1**) with protons was investigated in order to compare its activity with that of the $[Fe_2(CO)_4(\kappa^2\text{-}PNP^{Me})(\mu\text{-pdt})]$ analogue ($PNP^{Me} = \{Ph_2PCH_2\}_2NMe$).[6]

The reactions of $[Fe_2(CO)_4(\kappa^2\text{-}P^{Ph}{}_2N_2{}^{Ph})(\mu\text{-pdt})]$ (**1**) with acid were monitored by cyclic voltammetry (CV) in $CH_2Cl_2$–$[NBu_4][PF_6]$ and by $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopy at room temperature. The $^1H$ NMR spectrum of **1**, in $CD_2Cl_2$ at 298 K, in the presence of 1 equiv. of $CH_3SO_3H$ or $CF_3SO_3H$ shows a doublet at −13.5 ppm ($J_{PH}$ = 17.5 Hz) and a triplet at −13.6 ppm ($J_{PH}$ = 20.0 Hz) with relative 3 : 1 intensities which are characteristic of the formation of μ-hydride species with basal–apical and dibasal diphosphine.[10] The $^{31}P\{^1H\}$ NMR spectrum of this solution exhibits expected signals: a singlet at 51.8 ppm and two doublets of equal intensities at 64.5 ppm (d, $J_{PP}$ = 97 Hz) and 47.8 ppm (d, $J_{PP}$ = 97 Hz).[10] Two-dimensional heteronuclear multiple-bond $^1H$–$^{31}P$ NMR experiments confirmed assignments of these signals.

The transformation of **1** into a doubly protonated species, in the presence of an excess of sufficiently strong acid, was suggested by NMR experiments (Fig. Sd, ESI‡). Indeed, the treatment of **1** with two equivalents of $CF_3SO_3H$ in a $CD_2Cl_2$ solution resulted in the formation of two other bridging hydride species with dibasal and basal–apical diphosphine. The $^{31}P\{^1H\}$ NMR spectrum in $CD_2Cl_2$ revealed a singlet at 29.4 ppm and two doublets at 37.0 ppm (d, $J_{PP}$ = 91 Hz) and 26.6 ppm (d, $J_{PP}$ = 91 Hz). Two typical signals, a triplet at −15.0 ppm ($J_{PH}$ = 21.0 Hz) and a doublet at −13.9 ppm ($J_{PH}$ = 16.5 Hz), with relative 1 : 2 intensities were detected in the $^1H$ NMR spectrum.

VT $^1H$ and $^{31}P\{^1H\}$ NMR experiments in the presence of an excess of $CF_3SO_3H$ or $HBF_4{\cdot}OEt_2$ indicated the formation, at low temperature, of an intermediate species for which $^1H$ NMR spectra do not display any hydride signal, which is transformed upon warming into a doubly protonated species at both diiron and nitrogen atoms (Fig. Se, ESI‡). By comparison with the protonation studies of the $[Fe_2(CO)_4(\kappa^2\text{-}PNP^{Me})(\mu\text{-pdt})]$ analogue ($PNP^{Me} = \{Ph_2PCH_2\}_2NMe$),[6] the above result suggests that the initial protonation at an amine function of the $P_2N_2$ ligand is followed by a N–H → Fe(μ-H)Fe migration.

Upon addition of 1 equiv. of trifluoromethanesulfonic ($CF_3SO_3H$, $pK_a$ = 2.6 in MeCN)[17] or methanesulfonic acid ($CH_3SO_3H$, $pK_a$ = 8.36;[17] 10.0 in MeCN[18]), the redox systems of the initial complex ($E_p{}^{red}$ = −2.35 V, $E_{1/2}{}^{ox}$ = −0.10 V; potentials referred to the $Fc/Fc^+$ couple) were replaced by a reduction at −1.34 V, assigned to the bridging hydride derivative by comparison with the reduction potential of an authentic sample of this compound (see in ESI‡). Further additions of $CH_3SO_3H$ (Fig. 2a) resulted in an increase of the reduction current around −1.4 V, which suggests that catalytic proton reduction occurred. In contrast, the addition of the stronger $CF_3SO_3H$ acid that first produced the bridging hydride derivative led to the formation of the doubly protonated $[Fe_2(CO)_4(\kappa^2\text{-}HP^{Ph}{}_2N_2{}^{Ph})(\mu\text{-pdt})(\mu\text{-}H)]^{2+}$, characterised by a reduction at −1.2 V (Fig. 2b). However, the increase of the

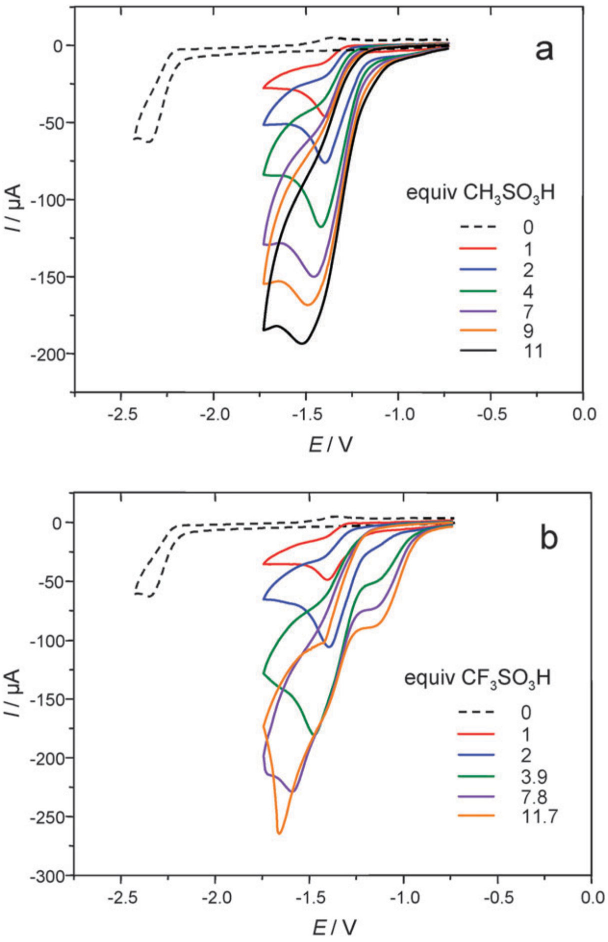

**Fig. 2** Cyclic voltammetry of $[Fe_2(CO)_4(\kappa^2\text{-}P^{Ph}{}_2N^{Ph}{}_2)(\mu\text{-pdt})]$ 1.86 mM (a) in the absence and in the presence of $CH_3SO_3H$ and (b) in the absence and in the presence of $CF_3SO_3H$ ($CH_2Cl_2$–$[NBu_4][PF_6]$; vitreous carbon electrode; $v$ = 0.2 V $s^{-1}$; potentials are in V *vs.* $Fc^+/Fc$).

reduction current around −1.2 V upon addition of acid is very limited, which shows that essentially no proton reduction catalysis occurred on the CV time scale at this potential. It should be noted that as far as reduction of $CH_3SO_3H$ is concerned, the efficiency of **1** is not much different from that of the analogue $[Fe_2(CO)_4(\kappa^2\text{-PNP}^{Ph})(\mu\text{-pdt})]$ (see in ESI‡, Fig. Sg).

Comparison of the activities of PNP and $P_2N_2$ complexes require now further full electrochemical and theoretical studies. Further studies are now in progress in order to compare and to understand the effect of various cyclic diphosphines $P^R{}_2N^R{}_2$ on the proton and electron transfers at a dithiolate-bridged diiron site as well as to obtain novel linear triiron clusters.

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## Notes and references

§ *Reaction of* $[Fe_2(CO)_6(\mu\text{-pdt})]$ *with* $P^{Ph}{}_2N^{Ph}{}_2$: in a 100 mL round-bottom flask, 0.6 g ($1.55 \times 10^{-3}$ mol) of $[Fe_2(CO)_6(\mu\text{-pdt})]$ were reacted with $P^{Ph}{}_2N^{Ph}{}_2$ (0.633 g, $1.4 \times 10^{-3}$ mol) in the presence of 2 equiv. (0.344 g, $3.1 \times 10^{-3}$ mol) of $Me_3NO$, $2H_2O$. The mixture was refluxed in toluene for 18 h, after which time it was evaporated to dryness under vacuum. The solid residue was chromatographed on a silica gel column. Complexes **1–3** were eluted with hexane–dichloromethane and dichloromethane–diethyl ether mixtures. They were obtained as powders after evaporation of the solvent. Data for **1**: yield 0.537 g, 49%; anal. calcd for $C_{35}H_{34}Fe_2N_2O_4P_2S_2$: C, 53.59; H, 4.37; N, 3.57%; found: C, 53.65; H, 4.68; N, 3.31%; IR ($CH_2Cl_2$, $cm^{-1}$): $\nu_{CO}$ 2021(s), 1945(s), 1898(w); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 55.2(br). Data for **2**: yield 0.082 g, 6%; anal. calcd for $C_{39}H_{40}Fe_3N_2O_5P_2S_4$: C, 48.07; H, 4.14; N, 2.87%; found: C, 47.77; H, 4.23; N, 2.77%; IR ($CH_2Cl_2$, $cm^{-1}$): $\nu_{CO}$ 2020(s), 1949(s), 1820(w); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 56.4 (d, 80.0 Hz), 40.4(d, 80.0 Hz). Data for **3**: yield 0.024 g, 2%; anal. calcd for $C_{36}H_{34}Fe_2N_2O_5P_2S_3\cdot O(CH_2CH_3)_2$ C, 52.30; H, 4.83; N, 3.05%; found: C, 52.45; H, 4.56; N, 3.45%; IR ($CH_2Cl_2$, $cm^{-1}$): $\nu_{CO}$ 2042(s), 1983(vs), 1961(sh), 1923(w); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 25 °C): $\delta$ 55.7 (d, 13.0 Hz), 32.8 (d, 13.0 Hz).

¶ Crystal data for **1**: $C_{71}H_{70}Cl_2Fe_4N_4O_8P_4S_4$. $M$ 1653.73, triclinic, $P{-}1$, $a = 10.6550(7)$, $b = 12.7551(9)$, $c = 14.3432(10)$ Å, $\alpha = 103.409(6)°$, $\beta = 99.559(6)°$, $\gamma = 99.746(6)°$, $Z = 1$, $V = 1825.5(2)$ Å$^3$; $\rho_{cal} = 1.504$ g cm$^{-3}$; $\mu$(Mo-K$_\alpha$) = 1.149 mm$^{-1}$; $\lambda = 0.71073$ Å, $T = 170(2)$ K. 14 161 reflections measured, 7431 unique ($R_{int} = 0.0634$) used in refinement. $R_1$ [7431 with $I > 2\sigma(I)$] = 0.0659, w$R_2$ (all data) = 0.1392. CCDC 789266.

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