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Influence of a Pendant Amine in the Second Coordination Sphere on Proton Transfer at a Dissymmetrically Disubstituted Diiron System Related to the $[2Fe]_H$ Subsite of $[FeFe]H_2$ase

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Studies of the protonation of $[Fe_2(CO)_4(\kappa^2\text{-PNP})(\mu\text{-pdt})]$ (**1**; PNP $= (Ph_2PCH_2)_2NCH_3$) by $HBF_4 \cdot Et_2O$ showed that the nature of the reaction product depends on whether the reaction is conducted in acetone or in dichloromethane. In acetone, an N-protonated form, **2**, is isolated. Tautomerization of **2** in CH_2Cl_2 gives rise to a μ-hydride species **3**. Variable-temperature NMR experiments have been performed to clarify the processes involved.

Recent progress in the chemistry of organometallic diiron molecules related to the active site of the iron-only hydrogenases has shown that the use of chelating ligands such as diphosphine,[1] N-heterocyclic carbene,[2] and phenanthroline[3] favors the formation of terminal hydride species at a single iron atom of bimetallic propanedithiolate (pdt) complexes $[Fe_2(CO)_{6-2x}(\kappa^2\text{-}L_2)_x(\mu\text{-pdt})]$ ($x = 1, 2$). Among the mechanisms that have been proposed for the uptake/production of hydrogen by $[FeFe]H_2$ase, one of the most attractive involves the formation of a key intermediate featuring hydrido−proton interaction. The amine of an azadithiolate bridge would act as a proton relay in such a model,[4] which has led to the study of more sophisticated azadithiolate (adt) mimics $[Fe_2(CO)_{6-2x}(\kappa^2\text{-}L_2)_x(\mu\text{-adt})]$ in order to combine the effect of a chelating diphosphine with that of a pendant amine in symmetrical or unsymmetrical substituted diiron compounds.[1b,5] Another powerful strategy for introducing a pendant base in the second coordination sphere of a metal center has been successfully developed by DuBois et al.[6] by using base-containing diphosphines (PNP $=$ $(Et_2PCH_2)NR$; R $=$ Me, ^{t}Bu). We have extended this approach to Fe_2pdt compounds in order to examine the influence of such a ligand on the proton and electron transfer at a diiron site. Recently, works on $[Fe_2(CO)_4(\kappa^2\text{-PNP})(\mu\text{-pdt})]$ species[7] and other diiron molecules featuring nitrogen bases have appeared in the literature.[8] More, during the review process of the present work, a study by Sun and coworkers concerning the protonation of $[Fe_2(CO)_4(\kappa^2\text{-PNP})(\mu\text{-}$

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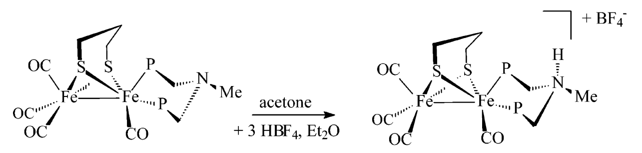
10.1021/ic801369u CCC: $40.75

Scheme 1[a]



1

2

[a] Phenyl groups are omitted for clarity.

pdt)] (PNP = $(Ph_2CH_2)_2N^nPr$) has appeared as a communication.[9] Herein, we report our preliminay results on the protonation of $[Fe_2(CO)_4(\kappa^2\text{-PNP})(\mu\text{-pdt})]$ (**1**; PNP = $(Ph_2CH_2)_2NMe$), which show clearly the influence of a pendant base lying in the outer coordination sphere of a dissymmetrically disubstituted diiron core on proton transfer. Our data give new and complementary insights into the functioning of such molecules.

Treatment of $[Fe_2(CO)_6(\mu\text{-pdt})]$ with $(Ph_2PCH_2)_2NMe$,[6c] following reported procedures,[1a] afforded moderate yields (55%) of **1**. Expected IR and ^1H NMR data were observed.[10] The comparable electron-releasing properties of the PNP and dppe ligands are shown by the similar potentials for the reversible one-electron oxidation of **1** and of $[Fe_2(CO)_4(\kappa^2\text{-dppe})(\mu\text{-pdt})]$ in a CH_2Cl_2 electrolyte [$E_{1/2} = -0.21$ and -0.25 V (vs Fc^+/Fc), respectively]. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 displayed a singlet at 53.2 ppm that is assigned on the basis of variable-temperature (VT) $^{31}P\{^1H\}$ NMR experiments to a species having a basal−apical arrangement of the diphosphine.[10,11] Indeed, the $^{31}P\{^1H\}$ NMR of **1** at 183 K evidenced the presence of an AB signal ($J_{PP} = 29$ Hz). A coalescence process was noted at 213 K, for which $\Delta G^{\neq}$ of 41 kJ mol^{-1} was calculated.[12] An X-ray crystal structure of **1** showed a basal−apical coordination of the diphosphine.[10] The FeP_2C_2N metallacycle adopts a chair conformation, with the methyl substituent of N1 in an equatorial position. The Fe−Fe distance [2.564(4)Å] is comparable to that found in similar complexes[1−3,7] and the P1−Fe1−P2 angle [93.38(18)°] is very close to that measured for an analogue where the diphosphine is $Ph_2P(CH_2)_3PPh_2$.[7b]

Our investigation on the protonation of **1** by $HBF_4\cdot Et_2O$ revealed that the nature of the reaction product depends on whether the reaction is conducted in acetone or in dichloromethane. IR monitoring of the addition of 1 equiv of $HBF_4\cdot Et_2O$ to a solution of **1** in acetone showed the immediate replacement of the ν(CO) bands of the starting material by three new bands at higher energy [ν(CO) = 2028(s), 1957(s), and 1907(w) cm^{-1}]. The resulting product $[Fe_2(CO)_4(\kappa^2\text{-PN(H)P})(\mu\text{-pdt})]^+$ (**2**) was isolated as a powder by the addition of Et_2O to the acetone solution. The shift of the carbonyl bands by ca. 10 cm^{-1} is consistent with protonation occurring at a ligand rather than at the Fe−Fe site (Scheme 1).[13] The $^{31}P\{^1H\}$ NMR in $(CD_3)_2CO$ showed a singlet at 60.0 ppm. Neither ^1H nor 2D ($^1H-^{15}N$ or $^1H-^1H$) NMR experiments allowed the detection of the signal of the added proton. **2** is involved in a fluxional process that exchanges the basal and apical positions of the phosphorus atoms of the ligand.[10]

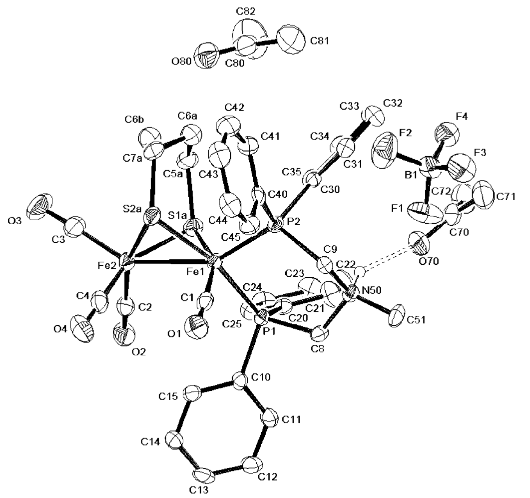


Figure 1. ORTEP of the cation $\mathbf{2}\cdot 2CH_3COCH_3$ (the counterion BF_4^- was omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe1−P2, 2.1812(10); Fe1−P1, 2.2101(9); Fe1−Fe2, 2.5687(7); C8−N50, 1.510(4); C8−P1, 1.867(3); C9−N50, 1.500(4); C9−P2, 1.852(3); P2−Fe1−P1, 94.05(4); C9−N50−C51, 109.4(2); C9−N50−C8, 113.1(2); C51−N50−C8, 109.2(2).

The X-ray crystal structure of $\mathbf{2}\cdot 2CH_3COCH_3$ confirms that protonation occurred at the nitrogen atom of the diphosphine (Figure 1).[10] The diphosphine ligand occupies basal−apical coordination sites, and the FeP_2C_2N metallacycle retains a chair conformation. The Fe−Fe distance, 2.5687(7) Å, is quite the same as that in **1**, which is consistent with protonation at a remote site. It should be noted that there is an interaction between the proton on the nitrogen atom of the PNP ligand and the oxygen atom (O70) of one of the acetone molecules (N50−O70 = 2.815 Å).

Upon recording IR spectra of the isolated powder of **2** in CH_2Cl_2, **2** underwent a transformation in this solvent. After about 1 h, the CO bands of **2** were replaced by a new set of strong bands at higher energy [ν(CO) = 2099, 2052, 2036, and 1961 cm^{-1}], which suggested the formation of a hydride species.[13] This was confirmed by ^1H NMR of a sample prepared by solubilization of an isolated sample of **2** in CD_2Cl_2. The ^1H NMR spectrum showing a new ill-resolved triplet at −13.1 ppm evidenced that the N-protonated complex **2** was totally converted into a new product $[Fe_2(CO)_4(\kappa^2\text{-PNP})(\mu\text{-pdt})(\mu\text{-H})]^+$ (**3**) possessing a bridging hydride and where the PNP ligand likely adopts a dibasal coordination position (Scheme 2). This observation led us to investigate the protonation of **1** in CH_2Cl_2 at RT. The

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(10) Full details of the synthesis and characterization including crystal data of compounds **1**−**3** and supplementary figures (NMR and electrochemistry) are provided as Supporting Information.

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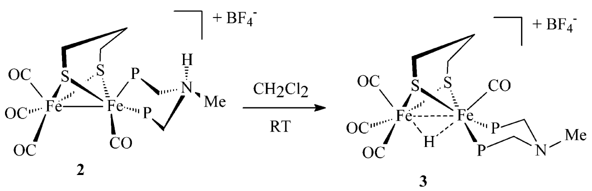
Scheme 2[a]



[a] Phenyl groups are omitted for clarity.

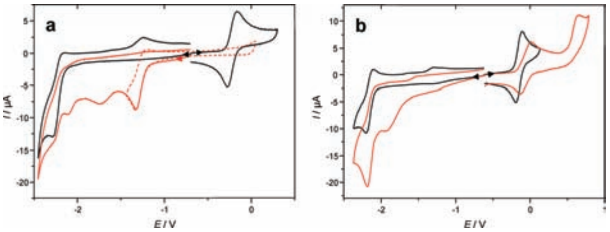


Figure 2. CV of **1** in (a) $CH_2Cl_2[NBu_4][PF_6]$ and (b) $(CH_3)_2CO[NBu_4][PF_6]$ before (black line) and after (red line) the addition of 1 equiv of $HBF_4 \cdot Et_2O$ (vitreous carbon electrode, $\upsilon = 0.2$ V s^{-1}, potentials in V vs Fc^+/Fc).

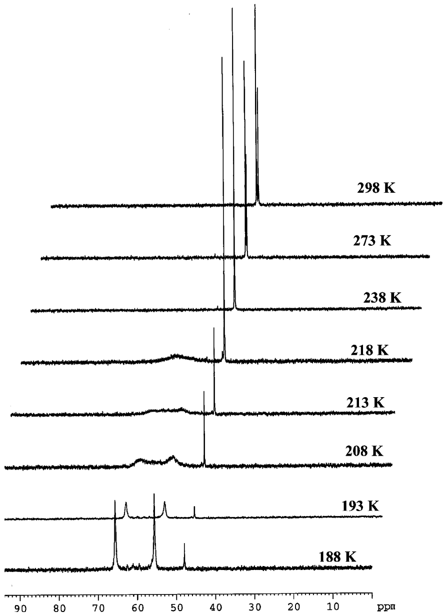


Figure 3. Protonation of **1** with 3 equiv of $HBF_4 \cdot Et_2O$ in CD_2Cl_2 at 188 K and a VT $^{31}P\{^1H\}$ NMR study of the reaction.

reaction of **1** with 1 equiv of $HBF_4 \cdot Et_2O$ in CH_2Cl_2, monitored by IR, allows to isolate **3**.

The cyclic voltammetry (CV) of **1** was also examined in $(CH_3)_2CO$ and CH_2Cl_2 at room temperature in the presence of $HBF_4.Et_2O$. Upon the addition of 1 equiv of $HBF_4 \cdot Et_2O$ to a $CH_2Cl_2[NBu_4][PF_6]$ solution of **1**, new reductions are observed at −1.26, −1.75, and −2.11 V, while the oxidation is removed (Figure 2a), showing that **1** is quantitatively protonated. The quasi-reversible system with $E_{1/2}{}^{red} = -1.26$ V is due to the one-electron reduction of **3**, as shown by a comparison with the CV of an authentic sample of this species under similar conditions.[10] It should be noted that the reduction of **3** also occurs at a potential very similar to that of the hydrogen-bridged dppe analogue ($E_{1/2}{}^{red} = -1.27$ V in CH_2Cl_2),[14] which confirms that the presence of the amine in the backbone of the chelating ligand does not affect the redox potentials in a significant way.

The addition of $HBF_4 \cdot Et_2O$ to a $(CH_3)_2CO[NBu_4][PF_6]$ solution of **1** also gives rise to changes in the CV (Figure 2b). However, no peak is observed at a potential suggesting the formation of a significant amount of **3**. Instead, both the irreversible reduction detected around −1.9 V and the quasi-reversible one-electron oxidation at $E_{1/2} = -0.05$ V are also present in the CV of a fully characterized sample of **2** under similar conditions.[10] It can therefore be concluded that treatment of **1** with 1 equiv of $HBF_4 \cdot Et_2O$ in acetone afforded the N-protonated species **2**. The fact that the stable protonated form of **1** depends on the solvent was confirmed by the following CV experiment. When a sample of the isolated N-protonated complex **2** was dissolved in $CH_2Cl_2[NBu_4][PF_6]$, CV revealed a fast conversion (within the time of dissolution) into the μ-hydride isomer **3**.[10]

VT $^{31}P\{^1H\}$ NMR experiments were performed in CD_2Cl_2. The spectrum obtained at 188 K from a CD_2Cl_2 solution of **1** and $HBF_4 \cdot Et_2O$ (3 equiv) prepared at this temperature revealed without any ambiguity that the protonation of **1** at this temperature gives the N-protonated form **2** as the major product of the reaction (~84%). A minor product (~16%) displays a singlet at 48.0 ppm that correlates with a triplet at −14.4 ppm in the ^1H NMR spectrum (2D $^1H-^{31}P$ HMBC NMR). This indicates that the minor product possesses a bridging hydride. The spectra obtained by warming the NMR sample show both the fluxional process of **2** and its consumption. A new singlet at 46.5 ppm, correlating with a triplet at −14.0 ppm in the ^1H NMR spectrum, appears at 243 K. The observation of two μ-hydride species in the presence of an excess of acid in our experiments suggests the formation of doubly protonated species featuring endo and exo orientation of the NH bond.[9]

Finally, our preliminary results suggest that the amine group of the diphosphine in **1** may act as a proton relay and direct the transfer of protons. CV experiments also showed that the formation of the $[Fe_2(CO)_4(\kappa^2\text{-LL})(\mu\text{-pdt})(\mu\text{-H})]^+$ complex is much faster when LL = PNP than when LL = dppe.[10] This is not likely to arise from a different basicity of the Fe−Fe site in the complexes because the electron-releasing properties of both LL ligands are similar. Therefore, the higher protonation rate of **1** as compared to that of the dppe analogue suggests a fast protonation at the nitrogen atom, followed by a rapid N → Fe proton migration. Further experiments are in progress in order to clarify the proton exchange processes in such systems.

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Supporting Information Available: Synthetic, spectroscopic, crystallographic, and analytical data for **1**−**3**, CV and NMR figures, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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