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Evidence for the Formation of Terminal Hydrides by Protonation of an Asymmetric Iron Hydrogenase Active Site Mimic

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Treatment of $[Fe_2(\mu\text{-pdt})(CO)_6]$ [pdt = $S(CH_2)_3S$] with dppe ($Ph_2PCH_2CH_2PPh_2$) in refluxing toluene affords the asymmetric complex $[Fe_2(\mu\text{-pdt})(CO)_4(dppe)]$ (**1**). Protonation of **1** with HBF_4–Et_2O in CH_2Cl_2 gives at room temperature the μ-hydrido derivative $[Fe_2(\mu\text{-pdt})(CO)_4(dppe)(\mu\text{-H})](BF_4)$ (**2**). Monitoring the reaction by ^1H, ^{31}P, and ^{13}C NMR at low temperature reveals unambiguously that the process of the protonation of **1** implies terminal hydride intermediates.

Synthetic organometallic diiron molecules incorporating some of the structural key features of the active site of the iron-only hydrogenases are intensively developed with the aim that a better understanding of the stereoelectronic control exerted by the active site on the catalytic processes should allow one to elaborate more efficient electrocatalysts. Some satisfactory, rudimentary or sophisticated, structural models with a combination of dithiolate or azadithiolate bridges and various sets of terminal ligands, involving CO, CN^-, RNC, or PR_3, have been synthesized, but few efficient catalysts of proton reduction have been obtained.[1] In this context, the question of the activation of protons is far from being trivial because it is the elementary step for a future efficient electrocatalyst.[2] The knowledge of the fate of the protons at such a diiron site is primordial to understanding the processes that must drive the formation of H_2 at the natural site or at those of new electrocatalysts based on the diiron core. Terminal hydride is proposed to be a major key intermediate in these processes, but until now the first and sole precedent of a terminal hydride had been obtained indirectly by the addition of $LiAlH_4$ to a bimetallic iron(II) complex.[3] It has been reported that the protonation of pdt ($S(CH_2)_3S$) or adt (SCH_2NRCH_2S) species gives μ-hydride or N-protonated derivatives.[4] Recently, theoretical studies have pointed out the interest in using asymmetric diiron systems as one of the key structural features of the natural site.[5] The use of chelating bidendate ligands such as diphosphine is a way to obtain such an asymmetry and to influence the basicity of the site.[6] The work reported here concerns new aspects of the protonation of asymmetric dithiolatodiiron systems. The appearance during the course of our writing of several "ASAP" papers devoted to asymmetric diiron compounds[7] prompted us to report our preliminary results on the study

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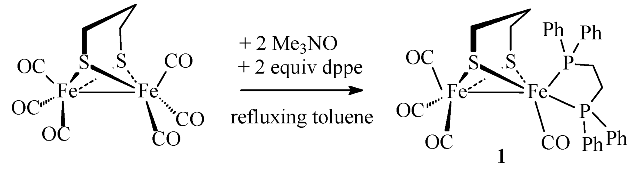
Scheme 1



of protonation of [$Fe_2(\mu\text{-pdt})(CO)_4(dppe)$] (**1**; dppe = $Ph_2PCH_2CH_2PPh_2$), which shows clearly for the first time the involvement of terminal hydride intermediates in this reaction.

Treatment of [$Fe_2(\mu\text{-pdt})(CO)_6$] with dppe in refluxing toluene for 5 h in the presence of Me_3NO afforded the asymmetric complex **1**, which was obtained in moderate yields (Scheme 1) after a subsequent purification workup.[8]

X-ray analysis of a single crystal of **1** obtained from a diethyl ether solution establishes without any ambiguity the asymmetric geometry of **1** and the binding mode of the bidendate diphosphine to one iron atom in a basal−apical position [Fe1−P1 2.231(1) Å, Fe1−P2 2.190(1) Å, and P1−Fe1−P2 87.7(4)°; Figure 1].[9] Distances and angles are unexceptional. **1** is structurally closely analogous to other known diiron(I) hexacarbonyl-pdt complexes.[4,7] Two {$Fe(CO)_3$} and {$Fe(CO)P_2$} units are eclipsed and linked by a direct Fe−Fe bond and a pdt group. The resulting coordination geometry around each iron atom is described as a distorted square pyramid supplemented by the Fe^I-Fe^I single bond required by the normal electron counting rule.

Compound **1** was also characterized by elemental analyses and IR and NMR spectroscopies. Strong bands at 2019 and 1949 cm^{-1} are observed in the carbonyl region of the IR spectrum of a CH_2Cl_2 solution of **1**. Expected shifts of the ν(CO) absorptions to lower frequencies relative to those of the precursor [$Fe_2(\mu\text{-pdt})(CO)_6$] have also been pointed out.[10] At 298 K, solutions of **1** contain two isomeric species with relative abundances depending on the solvent. The $^{31}P\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 shows two singlets at 89.6 and 75.0 ppm with relative 5:1 intensities. In toluene-d_8, this ratio is 2.5:1 and the two isomers do not interconvert readily between 293 and 335 K. The ^1H NMR spectrum of **1** confirms the ^{31}P NMR one; it displays two sets of resonances expected for two isomeric forms of the μ-pdt and dppe groups. $^{31}P\{^1H\}$ NMR studies at low temperature reveal that fluxional processes,[11] related to the dppe group and to the μ-pdt, are operative in solution (Scheme 2). The results of these experiments can be explained by the presence of four isomers of **1** in solution: two isomers ($\mathbf{1}_{\mathbf{ba-ap}}$ and $\mathbf{1'}_{\mathbf{ba-ap}}$) having the dppe group in a basal−apical (major) position and two isomers ($\mathbf{1}_{\mathbf{ba-ba}}$ and $\mathbf{1'}_{\mathbf{ba-ba}}$) having this ligand in a basal−basal (minor) position, as depicted in Scheme 2.

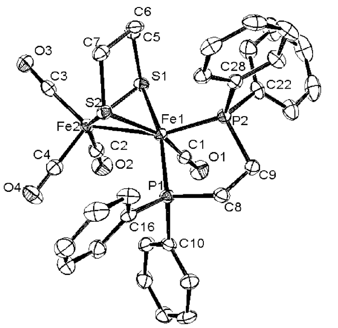
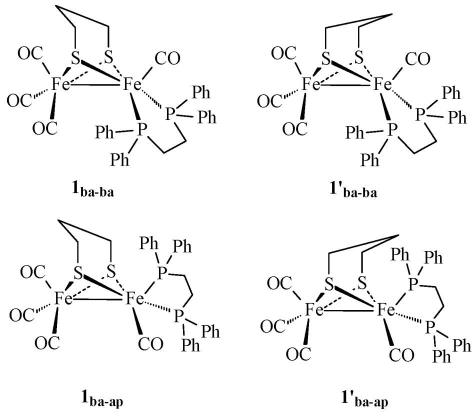


Figure 1. Structure of **1** showing 50% thermal ellipsoids. Selected distances (Å) and angle (deg): Fe1−Fe2, 2.547(7); Fe1−P1, 2.231(1); Fe1−P2, 2.190(1); P1−Fe1−P2, 87.7(4).

Scheme 2



The $^{31}P\{^1H\}$ NMR spectrum at 190 K in toluene-d_8 displays two different patterns of resonances for each type of isomer. One of these patterns consists of two unresolved AB signals of equal intensity, which are related to those of two inequivalent phosphorus atoms; these are consistent with boat and chair forms of the iron−dithiocyclohexane rings of basal−apical isomers. The other pattern contains two singlets of different intensity (2:1), in agreement with the corresponding boat and chair forms of the basal−basal isomers, having a symmetrically bonded dppe ligand (see Figure a in the Supporting Information).

Protonation of **1** with $HBF_4 \cdot Et_2O$ in CH_2Cl_2 at 298 K was carried out; it gave a red solution of the μ-hydride derivative [$Fe_2(\mu\text{-pdt})(CO)_4(dppe)(\mu\text{-H})$]($BF_4$) ($\mathbf{2}_{\mathbf{ba-ba}}$). Compound $\mathbf{2}_{\mathbf{ba-ba}}$ was precipitated from the solution by the addition of diethyl ether and recovered as a red powder (Scheme 3).[8]

The carbonyl absorptions in the IR spectrum of $\mathbf{2}_{\mathbf{ba-ba}}$ are logically shifted to higher energy [2097 (s), 2050 (s), 2036 (s), and 1971 (s) cm^{-1}] relative to those of **1**. The ^1H NMR spectrum of **2** in CD_2Cl_2 confirms that protonation occurs at the Fe−Fe site with a characteristic high-field signal for a $Fe_2(\mu\text{-H})$ group that appears as a triplet at −14.1 ppm with

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(8) Full details of the synthesis and characterization of compounds **1** and **2** are provided as Supporting Information.

(9) Crystal data for **1**: $C_{33}H_{30}Fe_2O_4P_2S_2 \cdot CH_2Cl_2$, fw = 813.26, T = 170 K, monoclinic, space group $P2_1/c$, a = 10.7135(5) Å, b = 10.7968(5) Å, c = 30.9134(15) Å, β = 100.229(4)°, V = 3519.0(3) Å^3, Z = 4. Refinement of 415 parameters gave R1 = 0.0474, wR2 = 0.0896, and $|\Delta\rho| < 0.621$ e·Å^{-3} for all 7171 unique reflections. Crystal data for $\mathbf{2}_{\mathbf{ba-ba}}$: $C_{33}H_{31}BF_4Fe_2O_4P_2S_2 \cdot 0.5CH_2Cl_2$, fw = 858.61, T = 170 K, monoclinic, space group $P2_1$, a = 11.9437(4) Å, b = 9.6134(3) Å, c = 31.1947(10) Å, β = 95.608(3)°, V = 3564.6(2) Å^3, Z = 4. Refinement of 497 parameters gave R1 = 0.0386, wR2 = 0.0881, and $|\Delta\rho| < 0.482$ e·Å^{-3} for all 7334 unique reflections. Further crystallographic data for **1** and $\mathbf{2}_{\mathbf{ba-ba}}$ are provided as Supporting Information.

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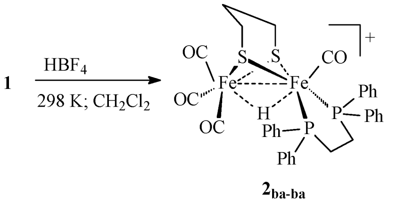
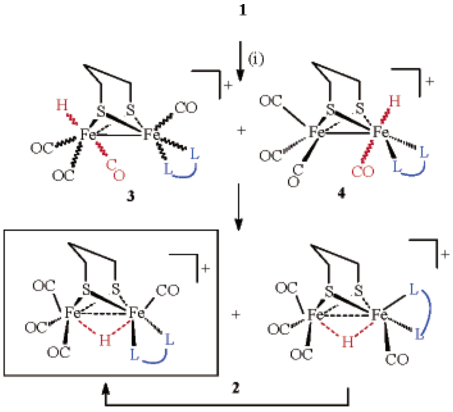
Scheme 3



Scheme 4



L_2 = dppe; (i) + HBF_4

a coupling constant of 21.0 Hz, consistent with the symmetrical and cis position of the two phosphorus atoms relative to the μ-hydride in a basal−basal isomer. The $^{31}P\{^1H\}$ NMR spectrum displays a signal at 78.7 ppm. An X-ray analysis of $\mathbf{2_{ba-ba}}$ (Figure 2) confirms that protonation of **1** induces the slippage of the chelated dppe to a basal−basal coordination in the protonated form.[9]

Protonation experiments at low temperature shed a particularly important insight into the process of formation of **2**. Treatment of **1** (5 mg) with an excess (2−3 equiv) of $[(HOEt_2)BF_4]$ in a CD_2Cl_2 solution at 203 K resulted in the very slow apparition of a signal at −4.33 ppm corresponding to the formation of a terminal hydride at the distal iron atom (**3**; which does not bind the dppe group; Figure 3).

The clean transformation of **1** into the intermediate **3** (Scheme 4) was complete within 5 h; this can be monitored by ^{31}P NMR by the disappearance of signals of **1** and the appearance of a singlet at 60.1 ppm. An increase of the temperature to 243 K induced the formation of μ-hydride species with basal−basal ($\mathbf{2_{ba-ba}}$) and basal−apical ($\mathbf{2_{ba-ap}}$) diphosphine forms, which were detected in the ^1H NMR spectrum, at this temperature, as a triplet at −14.23 ppm (J_{PH} = 21 Hz) and a doublet at −14.50 ppm (J_{PH} = 26 Hz). The ^{31}P NMR spectrum displayed a singlet at 77.7 ppm and an AB pattern at 87.1 ppm (d, J_{PP} = 24.3 Hz) and 81.5 ppm (d, J_{PP} = 24.3 Hz) (Figure b in the Supporting Information). The two-dimensional heteronuclear multiple-bond correlation $^1H-^{31}P$ NMR spectrum shows a correlation between the hydride observed as a triplet and the ^{31}P singlet and between the doublet at −14.50 ppm and the ^{31}P AB system. This mixture was stable at 243 K, and the complete transformation of $\mathbf{2_{ba-ap}}$ into $\mathbf{2_{ba-ba}}$ was observed when the temperature increased by 298 K (overnight). When the protonation was performed at 223 K in addition to the formation of the three previous species (**3**, $\mathbf{2_{ba-ap}}$, and $\mathbf{2_{ba-ba}}$), an additionnal intermediate **4** was detected (Figure c in the Supporting Information). The identification of **4** with a terminal hydride species resulting from the protonation of **1** at the proximal iron atom, the one which supports the dppe ligand in a basal−basal position, is strongly suggested by NMR data. Indeed, a triplet is observed at −2.47 ppm with a coupling constant J_{PH} of 69 Hz in the ^1H NMR spectrum of the reaction mixture. The $^{31}P\{^1H]$ NMR spectrum reveals an additional singlet at 83.3 ppm.

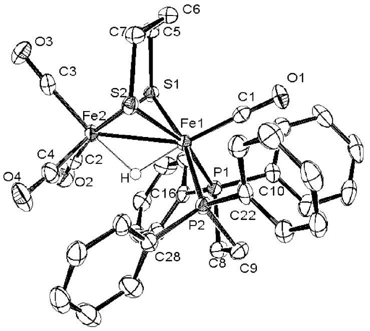


Figure 2. View of the cation $[Fe_2(\mu\text{-pdt})(CO)_4(dppe)(\mu\text{-H})]^+$ ($\mathbf{2_{ba-ba}}$) (50% ellipsoids). Selected distance (Å) and angle (deg): Fe1−Fe2, 2.581(5); Fe1−H, 1.627(3); Fe2−H, 1.640(4); Fe1−P1, 2.234(1); Fe1−P2, 2.238(1); P1−Fe1−P2, 87.2(3).

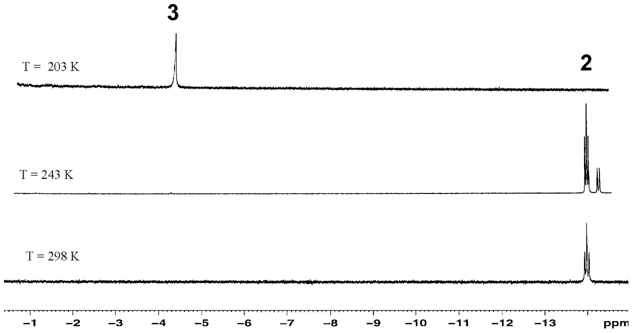


Figure 3. Protonation of **1** at 203 K and a variable-temperature study of the reaction.

In summary, we show in this work the first NMR evidence for the formation of terminal hydride intermediates by protonation of an asymmetric model of the natural site of iron-only hydrogenase. An IR study of these processes should allow the determination in species **3** and **4** of whether the CO group opposite the dithiolate bridging group is bridging or terminally bound. Further experiments on protonation of other asymmetric diiron complexes are in progress.

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Supporting Information Available: Synthetic, spectroscopic, crystallographic, and analytical data for **1** and **2**, NMR spectra, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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