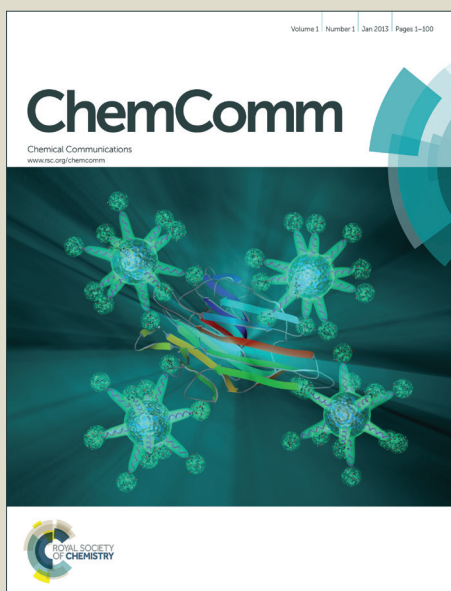


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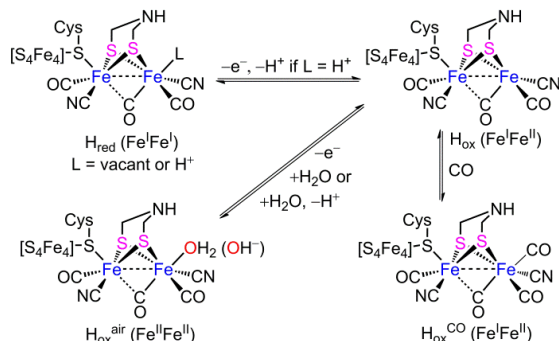
The influence of S-to-S bridge in diiron dithiolate models on the oxidation reaction: A mimic of the H_{ox}^{air} state of [FeFe]-hydrogenases†Dehua Zheng,^a Mei Wang,^{*a} Lin Chen,^a Ning Wang,^{a,b} Minglun Cheng^a and Licheng Sun^{a,c}

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Two-electron oxidation of a diiron complex (**1**) containing a bulky S-to-S bridge with an exocyclic carbonyl group affords $[1(OH)]^+$, which replicates the coordination structure and electronic configuration of H_{ox}^{air} , and the chemically reversible reaction between **1** and $[1(OH)]^+$ mimics the bioprocess of interconversion of the inactive H_{ox}^{air} and the active H_{red} state of the [FeFe]-hydrogenases.

Synthesis and chemistry of organometallic diiron dithiolate complexes have attracted extensive attention as such complexes structurally resemble the active site of [FeFe]-hydrogenases ([FeFe]-H₂ases), which reversibly catalyze the H₂ evolution and uptake with high activity in microorganism. Direct biophysical and spectroscopic evidence as well as theoretical studies suggests that the diiron core of [FeFe]-H₂ases exists in the following states, H_{red} ($Fe^I Fe^I$, L = H⁺ or $Fe^{II} Fe^{II}$, L = H⁻), H_{ox} ($Fe^I Fe^{II}$), H_{ox}^{CO} ($Fe^{II} Fe^I$), and H_{ox}^{air} ($Fe^{II} Fe^{II}$), which can interconvert with each other by redox and L_{ap}-association/dissociation reactions (Scheme 1).^{1–3}

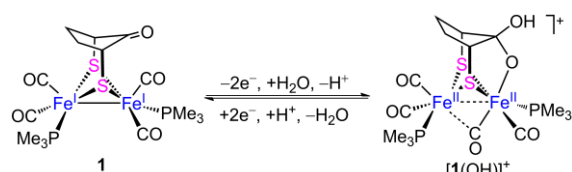


Scheme 1 Interconversion of different states of the [FeFe]-H₂ase active site.

Studies of the [FeFe]-H₂ase mimicking were focused mainly on the H_{red} state in the early years of this century. Very recently, some $Fe^I Fe^I$ complexes with an unusual rotated geometry as that existing in the H_{red} state of [FeFe]-H₂ase active site were reported.⁴ The first experimental evidence for the formation of the $Fe^{II} Fe^I$ complex with a bridging CO was observed in situ from the one-electron oxidation of a diiron carbonyl cyanide precursor bearing a thioether group in 2002.⁵ The structurally characterized mixed-valence diiron models of H_{ox} were reported in 2007.⁶ In the following years, the diiron complexes of H_{ox} mimics, either

bearing special σ ligands IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and dppv (*cis*-1,2-C₂H₂(PPh₂)₂) or featuring a bulky bridge, dmpdt (2,2-dimethyl-1,3-propanedithiolate), successively appeared in the literatures.^{7–9} Further studies have clearly demonstrated that the open apical site in H_{ox} models is readily coordinated by CO to give H_{ox}^{CO} mimics.^{9,10} The $Fe^{II} Fe^{II}$ H_{ox}^{air} state has an ⁻OH or a H₂O coordinating to the open apical site of distal iron center.¹ The first structural models of H_{ox}^{air} are $[Fe_2(S_2C_nH_{2n})(\mu-CO)(CNMe)_6]^{2+}$ and its analogous where the open apical site is coordinated by CNMe ligand instead of oxygen-coordinating ligand.¹¹ The other synthetic diferrous models reported to date either have an acetonitrile or a phosphine ligand coordinating to the apical site of the rotated iron center.¹² To the best of our knowledge, no diferrous model bearing an ⁻OH or a H₂O ligand as that existing in the H_{ox}^{air} state has been reported in the literatures. Studies on the models of the different states of [FeFe]-H₂ases and their interconversion will help chemists and biologists to get a better understanding of the chemical reactivity of the [FeFe]-H₂ase active site and the mechanism for enzymatic H₂ generation and uptake. Although many electro- and photocatalytic systems with [FeFe]-H₂ase models as catalysts have been reported in recent 60 years, it should be noticed that the electro- and photocatalytic H₂ production by $Fe^I Fe^I$ [FeFe]-H₂ase mimics so far reported takes place via the mechanisms involving $Fe^0 Fe^I$, $Fe^0 Fe^0$, and $Fe^0 Fe^{II}$ intermediates, which are quite different from the mechanism proposed for the H₂ production at a natural [FeFe]-H₂ase active 65 site. To find the [FeFe]-H₂ase models that reduce protons to H₂ in a principally identical pathway with the enzymatic mechanism still remains a big challenge. Successful development of such models could lead to the creation of more efficient molecular catalysts for hydrogen generation.

Herein we describe the preparation of an diiron complex bearing a specially designed S-to-S bridge, $[(\mu-cpdt)\{Fe(CO)_2(PMe_3)\}_2]$ (**1**, cpdt = cyclopentanone-2,5-dithiolate), with a CO-monodisplaced complex $[(\mu-cpdt)\{Fe_2(CO)_5(PMe_3)\}]$ (**2**) as by-product. The electrochemical and chemical oxidation of the $Fe^I Fe^I$ complex **1** to an $Fe^{II} Fe^{II}$ model $[1(OH)]^+$ of H_{ox}^{air} as well as the molecular structures of **1** and $[1(OH)]^+ [Bar^F_4]$ were reported. The in situ generated $[1(OH)]^+ [Bar^F_4]$ can be readily reduced back to **1**. This reversible redox reaction between **1** and $[1(OH)]^+$ (Scheme 2) mimicks the 80 process of interconversion of the inactive H_{ox}^{air} and the active H_{red} state of the [FeFe]-H₂ase.^{1–3}



Scheme 2 Interconversion of $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ (**1**) and $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ ($[\mathbf{1}(\text{OH})]^+$) models.

The starting compound, $[(\mu\text{-cpdt})\text{Fe}_2(\text{CO})_6]$ was prepared from the reaction of *cis*-2,5-dibromocyclopentanone with a freshly prepared lithium salt $[(\text{LiS})_2\text{Fe}_2(\text{CO})_6]$.¹³ Treatment of $[(\mu\text{-cpdt})\text{Fe}_2(\text{CO})_6]$ with 4 equiv. of PMe_3 in refluxing toluene for 8 h afforded a diphosphine complex (**1**) in ~37% yield and a monophosphine complex (**2**) in about 52% yield. The CO-displacement of $[(\mu\text{-cpdt})\text{Fe}_2(\text{CO})_6]$ is more difficult than the analogous complex $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_6]$ (pdt = 1,3-propanedithiolate) due to the steric hindrance of the bulky cpdt bridge. Complex **1** exhibits three $\nu(\text{CO})$ absorptions at 1986, 1958, and 1913 cm^{-1} together with a weak ketonic $\nu(\text{C}=\text{O})$ absorption at 1713 cm^{-1} . Similarly, complex **2** displays three $\nu(\text{CO})$ bands at 2043, 1986, 1967 cm^{-1} and a keto-carbonyl absorption at 1715 cm^{-1} . The signals appearing in the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra as well as the elemental analysis data clearly indicate that **1** contains two PMe_3 ligands and **2** has only one PMe_3 (see ESI†).

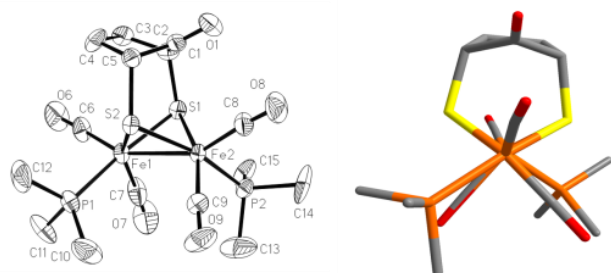


Fig. 1 (left) ORTEP diagrams for **1** with thermal ellipsoids drawn at the 30% probability level and (right) a twisted Newman projection viewing along Fe2–Fe1 bond as a capped-stick drawing. Hydrogen atoms and the counter ion BArF_4^- have been omitted for clarity.

The molecular structures of **1** and **2** were determined by single crystal X-ray analysis (Figs. 1(left) and S1†, Tables S1 and S2†). Crystallographic studies show that the shortest distance between the endo hydrogen atoms of the cpdt bridge and the oxygen of the apical CO ligand is 2.565 Å in **1**, which is close to the sum of the van der Waals' radii of oxygen and hydrogen atoms. The keto-carbonyl group and the apical CO in the same side are nearly parallel and the distance between O1 and C8 is about 3.0 Å. Because of the bulkiness of the S-to-S bridge, the two PMe_3 ligands are located at the basal position of each iron center in the opposite orientation. In comparison, the apical/basal geometry is a usual conformation in the crystal structures of products obtained from the CO-displacement of all-carbonyl diiron models by two PMe_3 ligands.^{8,15} Noticeably, the plot viewing along the Fe–Fe bond is an apparently twisted Newman projection with a torsional angle ($\angle C_{\text{ap}}\text{--Fe--Fe--C'_{ap}}$) of 34.1° (Fig. 1(right)) for the two apical CO ligands at each iron center of **1**. This torsional angle is between the values for the $[(\mu\text{-dmpdt})\{\text{Fe}(\text{CO})_2(\text{PMe}_3)_2\}_2]$ (28.9°) and $[(\mu\text{-depdt})\{\text{Fe}(\text{CO})_2(\text{PMe}_3)_2\}_2]$ (depdt (2,2-diethyl-1,3-propanedithiolate) (75.1°).¹⁵ The distance between two iron

atoms of **1** is 2.575 Å. The crystal structure of **2** is similar to **1** (Fig. S1†). The bond lengths and angles are given in Table S2†.

The cyclic voltammogram (CV) of **1** in CH_2Cl_2 , which was freshly distilled over P_2O_5 , displays a quasi-reversible oxidation event at $E_{\text{pa}} = +0.04$ V (All potentials given in this paper are versus $\text{Fc}^{+/0}$) with an onset potential of -0.25 V for the $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ couple and an irreversible oxidation peak at $E_{\text{pa}} = +0.29$ V for the $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ process (Fig. 2). The second peak immediately follows the first one and the two oxidation events are partially overlapped. After electrolysis of the CH_2Cl_2 solution of **1** at -30 °C with an applied potential of 0.4 V for 30 s, the DPV of the resulting solution scanned in cathodic direction exhibits two reduction peaks at +0.24 V and 0.0 V for the $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}/\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$ and $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ couple (Inset of Fig. 2), respectively. The intensity of reduction peak of the $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ species considerably lower than that for the reduction of the $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$ intermediate, due to some rapid chemical reaction and/or decomposition of the $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ species. It is noteworthy that a weak reduction peak appears at -0.71 V in the second run of the CV of **1**, which is not observed in the first run scanned in cathodic direction. When the anodic scan returned before 0.1 V to avoid the second oxidation process, the reversibility of the first oxidation event was apparently improved and the reduction peak at -0.71 V did not appear in the subsequent cathodic scan. This evidence indicates that some chemical reaction occurs during or after the $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ oxidation process. The intensity of the newly appeared reduction event apparently increased when a small amount (~ 10 μL) of water was added to the CH_2Cl_2 solution of **1**, implicating that water is involved in the further reaction of the two-electron oxidized species. The redox event at -0.71 V was observed even when a strictly dried CH_2Cl_2 was used as solvent, indicating that the in situ generated $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ species is very sensitive towards a trace amount of water.

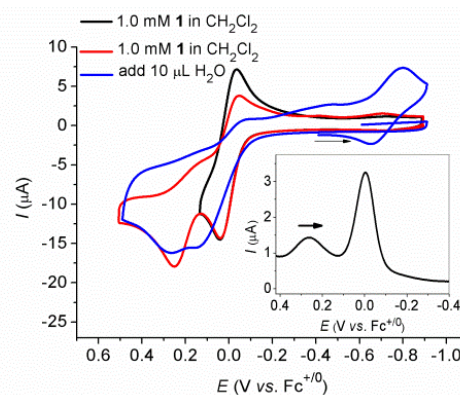


Fig. 2 Cyclic voltammograms of **1** (1.0 mM) in the freshly distilled CH_2Cl_2 (black and red lines) and with addition of about 10 μL water into the CH_2Cl_2 solution of **1** (blue line); Inset: DPV of the CH_2Cl_2 solution of **1** (1.0 mM) after electrolyzed at an applied potential of 0.4 V at -30 °C for 30 s; using 0.1 M $n\text{Bu}_4\text{NPF}_6$ as electrolyte at a scan rate of 100 mV s^{-1} .

In the light of electrochemical results, chemical oxidation of **1** was carried out in CH_2Cl_2 by using FcBArF_4 as oxidant, to figure out the product related to the reduction peak at -0.71 V. When two equiv of FcBArF_4 and 10 μL of water were added to the CH_2Cl_2 solution of **1**, the color of the solution changed instantly from red to purple. The product was isolated from the resulting solution as purple crystalline solid in 88% yields, which is

denoted as $[\mathbf{1}(\text{OH})]\text{BAR}^{\text{F}}_4$. This oxidized product was characterized by HR-MS, IR, and NMR spectroscopy. The $[\text{M}]^+$ peak found at $m/z = 538.9282$ is in good agreement with the calculated m/z value for the formula weight of $[\mathbf{1}+\text{OH}]^+$ (calcd for $\text{C}_{15}\text{H}_{25}\text{O}_6\text{S}_2\text{P}_2\text{Fe}_2$, $m/z = 538.9267$). Compared to $\mathbf{1}$, the $\nu(\text{CO})$ absorptions of $[\mathbf{1}(\text{OH})]^+$ shift largely to high wavenumbers (Fig. 3b). The $[\mathbf{1}(\text{OH})]^+$ displays three $\nu(\text{CO})$ absorptions at 2053, 2014, and 1959 cm^{-1} . In addition, two $^{31}\text{P}\{\text{H}\}$ NMR signals are observed at δ 31.07 and 11.54 for $[\mathbf{1}(\text{OH})]^+$ (Fig. 4), suggesting that the two PMe_3 ligands have different chemical environments. The CV of $[\mathbf{1}(\text{OH})]^+$ in CH_2Cl_2 shows a reversible reduction potential at -0.71 V (Fig. S2a†), which is identical with the weak event appearing in the second run of the CV of $\mathbf{1}$ (Fig. 2). In the presence of CF_3COOH , the reduction potential of $[\mathbf{1}(\text{OH})]^+$ is positively shifted from -0.71 V to -0.38 V due to the protonation of $[\mathbf{1}(\text{OH})]^+$ (Fig. S2b†).

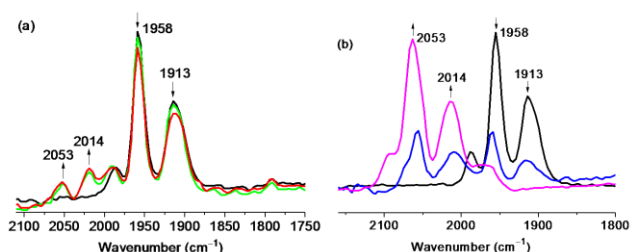


Fig. 3 Selected regions of (a) in situ IR spectra of $\mathbf{1}$ in CH_2Cl_2 (black), addition of an equiv. of $\text{FcBAR}^{\text{F}}_4$ and 10 μL H_2O (green), and addition of one more equiv. of $\text{FcBAR}^{\text{F}}_4$ (red) at -50 $^\circ\text{C}$; (b) $\mathbf{1}$ in CH_2Cl_2 (black), addition of 2 equiv. of $\text{FcBAR}^{\text{F}}_4$ and 10 μL H_2O at -20 $^\circ\text{C}$ (blue) and 20 $^\circ\text{C}$ (pink).

The molecular structure of $[\mathbf{1}(\text{OH})]\text{BAR}^{\text{F}}_4$ was determined by single crystal X-ray analysis (Fig. 4, Tables S1 and S2†). The crystallographic study confirms that a OH group is added to the carbon of keto-carbonyl in the cpdt bridge of $\mathbf{1}$ and the oxygen atom of the keto-carbonyl is coordinated to the rotated iron center. The rotation of $\text{Fe}(\text{CO})_2\text{PMe}_3$ unit happens at the less crowded side of the S-to-S bridge. The unrotated $\text{Fe}(\text{CO})_2\text{PMe}_3$ unit of $[\mathbf{1}(\text{OH})]^+$ has a square pyramidal configuration identical with that of $\mathbf{1}$, while the coordination configuration of the rotated $\text{Fe}(\text{CO})_2\text{PMe}_3$ unit alters from square pyramid in $\mathbf{1}$ to octahedron in $[\mathbf{1}(\text{OH})]^+$. The nonlinear manner of $\text{Fe}2-\text{C}9-\text{O}9$ angle (170.6°) and the different bond lengths of $\text{Fe}2-\text{C}9$ (1.769 Å) and $\text{Fe}1-\text{C}9$ (2.609 Å) clearly indicate the semibridging character of C9 in $[\mathbf{1}(\text{OH})]^+$. The $\text{Fe}-\text{Fe}$ distance of $[\mathbf{1}(\text{OH})]^+$ is $2.6202(18)$ Å, being longer than that of $\mathbf{1}$ ($\text{Fe}-\text{Fe}$, $2.5748(18)$ Å) while close to the $\text{Fe}-\text{Fe}$ distance of the $[\text{FeFe}]-\text{H}_2\text{ase}$ active site (ca. 2.60 Å).¹⁶ In the crystal state, two molecules of $[\mathbf{1}(\text{OH})]^+$ combine together through H-bonds between the OH group of the bridge and the coordinated oxygen atom (Fig. S3†). The $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ complex $[\mathbf{1}(\text{OH})]^+$ with an OR coordinating to the apical site of the rotated iron center has a similar coordination structure and the same d^6-d^6 electronic configuration of the $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ $\text{H}_{\text{ox}}^{\text{air}}$ state, which has an ^-OH or a H_2O occupying the apical position of rotated Fe^{II} ion.¹

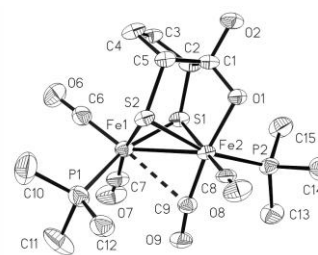


Fig. 4 ORTEP diagrams for $[\mathbf{1}(\text{OH})]\text{BAR}^{\text{F}}_4$ with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and the counter ion $\text{BAR}^{\text{F}}_4^-$ have been omitted for clarity.

The chemical oxidation process of $\mathbf{1}$ by $\text{FcBAR}^{\text{F}}_4$ in the presence of a trace of water was further studied by in situ IR spectroscopy. Two new bands at higher energy appeared upon addition of an equiv. of $\text{FcBAR}^{\text{F}}_4$ and 10 μL H_2O to the CH_2Cl_2 solution of $\mathbf{1}$ at -50 $^\circ\text{C}$ (Fig. 3a). The weak absorptions at 2053 and 2016 cm^{-1} are close to the typical $\nu(\text{CO})$ absorptions of $[\mathbf{1}(\text{OH})]^+$, indicating that only a small part of $\mathbf{1}$ was oxidized to $[\mathbf{1}(\text{OH})]^+$ at -50 $^\circ\text{C}$. The intensities of these new bands did not grow with addition of another equiv. of $\text{FcBAR}^{\text{F}}_4$ at -50 $^\circ\text{C}$. As the temperature was enhanced from -50 $^\circ\text{C}$ to -20 $^\circ\text{C}$ and then to 20 $^\circ\text{C}$, the $\nu(\text{CO})$ absorptions of $\mathbf{1}$ completely disappeared and simultaneously, the typical $\nu(\text{CO})$ absorptions of $[\mathbf{1}(\text{OH})]^+$ went up apparently (Fig. 3b). The one-electron oxidized species $[\mathbf{1}]^+$ could not be detected by in situ IR spectroscopy even in the presence of one equivalent of Fc^+ in a dried CH_2Cl_2 solution at -50 $^\circ\text{C}$ due to the close oxidation potentials for the $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$ and $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}/\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ couples. Accordingly, the ^{31}P NMR spectroscopic evidence (Fig. 4) shows that a $\sim 1:1$ mixture of unreacted starting complex $\mathbf{1}$ ($^{31}\text{P}\{\text{H}\}$ NMR: δ 24.20 and 27.78) and $[\mathbf{1}(\text{OH})]^+$ ($^{31}\text{P}\{\text{H}\}$ NMR: δ 11.60 and 31.13) was formed upon addition of an equiv. of $\text{FcBAR}^{\text{F}}_4$ to the CD_2Cl_2 solution of $\mathbf{1}$ (the CD_2Cl_2 solvent was not treated and contains a trace amount of water). With further addition of one more equiv. of $\text{FcBAR}^{\text{F}}_4$, the intensities of the new ^{31}P NMR signals increased, accompanied by the disappearance of the original ^{31}P NMR signals of $\mathbf{1}$. No extra ^{31}P NMR signal was observed. Interestingly, the in situ generated $[\mathbf{1}(\text{OH})]^+$ could be rapid and quantitatively reduced back to $\mathbf{1}$ by addition of two equiv. of Cp_2Co to the resulting CH_2Cl_2 solution (Fig. S4†), indicative of the good chemical reversibility of the reaction, which is reminiscent of the fact that the inactive $\text{H}_{\text{ox}}^{\text{air}}$ state can be converted to the active states, H_{ox} and H_{red} , by reduction.

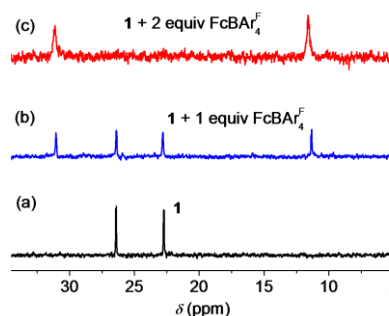
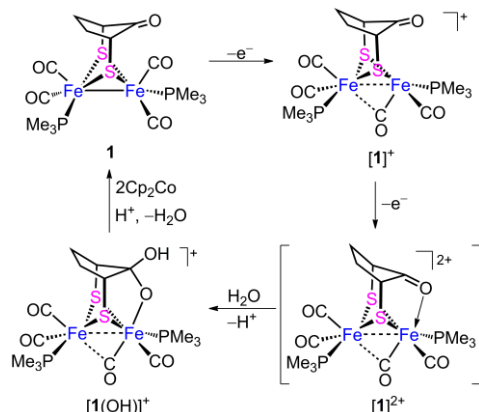


Fig. 4 Selected regions of in situ $^{31}\text{P}\{\text{H}\}$ NMR spectra of (a) $\mathbf{1}$, (b) $\mathbf{1}$ + an equiv. of $\text{FcBAR}^{\text{F}}_4$, and (c) $\mathbf{1}$ + 2 equiv. of $\text{FcBAR}^{\text{F}}_4$ in CD_2Cl_2 .

On the basis of CVs of **1** (Fig. 2), the chemical reaction happens during or immediately after the second oxidation of **1**. It is assumed that during the further oxidation process of $[1]^+$ the cpdt bridge bows its keto-carbonyl head, resulting in the coordination of the oxygen atom to the open apical site of the rotated Fe^{II} ion to form an active intermediate $[1(\text{O})]^{2+}$ (Scheme 3). In this case, the keto-carbonyl carbon is strongly electron deficient and very sensitive toward nucleophile. An intramolecular metal-assisted hydration of the keto-carbonyl takes place facily. The starting complex **1** can be recovered by the reductive dehydration of $[1(\text{OH})]^+$ in the presence of Cp_2Co and Lewis acid.



Scheme 3 Proposed mechanism for oxidative hydration and reductive dehydration of the cpdt-bridged diiron model.

In summary, diiron dithiolate complexes (**1** and **2**) bearing a bulky S-to-S bridge were prepared. The crystal structures of **1** and **2** show that the introduction of sterically hindered bridge enforces an unusual twisted conformation of the two Fe^{II} units in the molecule. The S-to-S bridge with an exocyclic carbonyl in the second coordination sphere considerably influences the redox reaction of **1**. Unlike the edt- (ethane-1,2-dithiolato), pdt-, and adt- (2-azapropene-1,3-dithiolato) bridged $[\text{FeFe}]\text{-H}_2\text{ase}$ models, the second oxidation event is very close to the first one due to the involvement of the exocyclic carbonyl in the oxidation reaction. Consequently, the two-electron oxidation of **1** affords a diiron complex $[1(\text{OH})]^+$ with an intramolecular OR group coordinating to the open apical site of the rotated Fe^{II} center. The coordination structure and $\text{d}^6\text{-d}^6$ electronic configuration of $[1(\text{OH})]^+$ closely replicates that in the $\text{H}_{\text{ox}}^{\text{air}}$ state. More interestingly, the in situ generated $[1(\text{OH})]^+$ is readily reduced back to the starting $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ complex **1** by Cp_2Co . This redox reaction mimics the bioprocess of interconversion of the inactive $\text{H}_{\text{ox}}^{\text{air}}$ and the active H_{red} state of the $[\text{FeFe}]\text{-H}_2\text{ases}$.

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Notes and references

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⁵⁰ † Electronic Supplementary Information (ESI) available: Procedures for synthetic, spectroscopic and electrochemical experiments. CCDC 798239, 798238 and 926091. For ESI and crystallographic data in CIF or electronic format see DOI: 10.1039/b000000x.

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