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COMMUNICATION

Pentacoordinate iron complexes as functional models of the distal iron in [FeFe] hydrogenases†‡

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Mononuclear pentacoordinate iron complexes with a free coordination site were prepared as mimics of the distal Fe (Fe_d) in the active site of [FeFe] hydrogenases. The complexes catalyze the electrochemical reduction of protons at mild overpotential.

The development of renewable energy is nowadays one of the most important challenges as global energy consumption is rising significantly.[1] Molecular hydrogen is a carbon-free fuel that could become the energy carrier of the future, thus making the reversible inter-conversion of protons to molecular hydrogen a key process for future energy schemes. Nature is able to catalyze this process by a class of enzymes called hydrogenases (H_2ases), one of which being the [FeFe] H_2ases. The X-ray crystallographic structure determination of the enzymes[2] has revealed their active site (Chart 1a) and allowed the mechanistic understanding of the catalytic process.[3]

Inspired by these insights, many Fe_2 model complexes of the [FeFe] H_2ase active site have been synthesized.[4] However, the compounds often exhibit large overpotentials and low turnover rates for electrocatalytic proton reduction,[5] in part also because of their lack to mimic functionally important features of the active site. For example, the enzymatic process occurs when both iron centres are in the Fe(I) oxidation state,[6] in contrast to many catalytic Fe_2 mimics that involve a formal Fe(0) state. Second, nature employs terminal hydride intermediates that are formed at a free coordination site on the distal iron centre (Fe_d).[7] Synthetic Fe_2 model complexes are coordinatively saturated and often lack a free site for substrate binding. Also, the oxidative addition of protons is often slow in the model compounds,[8] and yields less reactive bridging hydrides.[9] Reductive ligand elimination (CO, NHR_2) can create open coordination sites on the dinuclear model complexes but the limited stability of the intermediates contributes to catalyst degradation.[10]

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† Electronic supplementary information (ESI) available: Synthesis, crystal data of **5**, electrochemistry data and details of overpotential calculation. CCDC 811891. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc14449a

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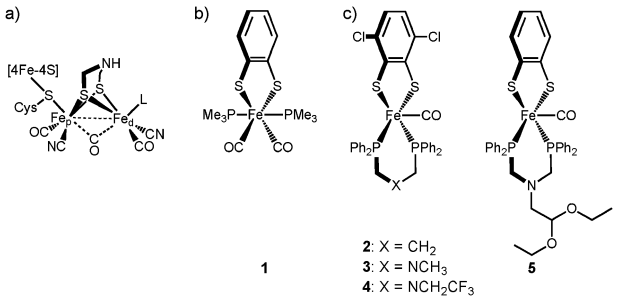


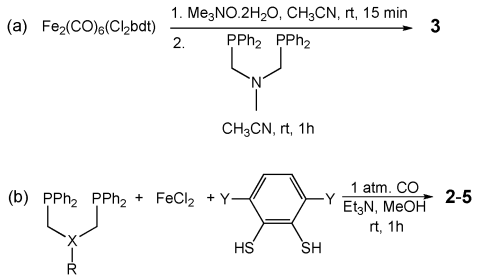
Chart 1 (a) The active site of the [FeFe] H_2ase; (b) hexacoordinate model complex **1** and (c) pentacoordinate Fe(II) complexes **2–5**.

Mononuclear complexes that mimic Fe_d naturally avoid the less reactive μ-H structures, and we have recently reported catalytic H_2 formation with the mononuclear Fe(II) complex **1**.[11] Although being also coordinatively saturated, Fe-hydride formation is enabled after reductive deligation of one sulfide of the bidendate benzene-1,2-dithiolate (bdt) ligand. This rearrangement from a hexacoordinate to a pentacoordinate Fe species compromises however the stability of the reduced catalyst and thereby limits total turnover numbers.

Herein, we report on stable pentacoordinate Fe(II) complexes **2–5** which provide an open site for substrate binding without the need for ligand dissociation (Chart 1).[12,13] The complexes catalyze H_2 formation from weak acids at low overpotentials and feature greatly improved stability under turnover conditions.

Pentacoordinate complexes **2–5** are accessible through the use of bidendate bis-phosphane ligands that reside *trans* to the bdt ligand, in contrast to hexa-coordinated **1** with monodendate phosphanes in a *cis* relationship to the bdt. Compounds **2–5** differ in their second coordination sphere of the bis-phosphane and/or chloride substituents at the bdt. Complexes **3–5** contain an amine functionality in the bis-phosphane as a potential protonation site. Additional ether chains at the amine provide increased solubility in polar aprotic solvents and render **5** most suitable for electrocatalysis investigations.

The N-containing bis-phosphane ligands were obtained by reaction of two equivalents of Ph_2PCH_2OH (readily preformed from equimolar amounts of $(CH_2O)_n$ and Ph_2PH) with the appropriate primary amine in refluxing MeOH.[14] With the bis-phosphanes in hand, complexes **2–5** can be obtained by two different routes: starting from dinuclear $[Fe_2(CO)_6(Cl_2bdt)]$[15] (**6**)



Scheme 1 (a) Formation of **3** from a dinuclear Fe precursor; (b) synthesis of complexes **2–5** from $FeCl_2$.

in the presence of decarbonylation agent Me_3NO (Scheme 1a), addition of the bis-phosphane led to a disproportionation and the formation of mononuclear complexes in a reaction similar to that described of **6** with CN^- or PMe_3.[12,16] Following this route, complex **3** was isolated in 36% yield. Complexes **2–5** can however also be obtained directly from $FeCl_2$, Cl_2bdt or bdt and the appropriate bis-phosphane in MeOH under a CO atmosphere (Scheme 1b). Using this more direct approach, the yield of **3** could for example be increased to 63%. It is noteworthy that the reaction is unique for a chelating dithiolate as the same reaction of bis-phosphanes with two equivalents of thiolate (RS^-) affords hexacoordinate *cis,cis,cis*-$[Fe(RS)_2(PPh_2(CH_2)_3PPh_2)(CO)_2]$.[17]

The molecular structure of **5** could be resolved by X-ray crystallography (Fig. 1) which confirms that the Fe centre is pentacoordinated.† It has a square pyramidal geometry with the apical carbonyl ligand *trans* to the free coordination site.

The IR spectra of all complexes show a single ν_{CO} band in the same spectral range (1917, 1919, 1921 and 1912 cm^{-1} for **2–5** in CH_2Cl_2).† The difference between **2–4** and **5** can be attributed to the effect of the electron-withdrawing chloride substituents while the different phosphanes have a similar electronic impact on the Fe centre.

Protonation studies were performed on **2–5**. When one equivalent of triflic acid was added to a solution of **2** or **4** in CH_2Cl_2, no changes in the IR frequencies of the CO band were observed. The lack of reactivity is explained by the absence of an amine in **2**, while the amine in **4** seems to be insufficiently basic for *N*-protonation due to the electron withdrawing CH_2CF_3 substituent.[18] In contrast, exposing **3** or **5** to equivalent conditions led to significant shifts of the respective ν_{CO} bands. Upon protonation of **5** with stoichiometric amounts of triflic acid (pK_a = 2.6 in acetonitrile) or excess of *p*-toluenesulfonic acid (TsOH, pK_a = 8.3 in acetonitrile) a shift of 20 cm^{-1} of the CO

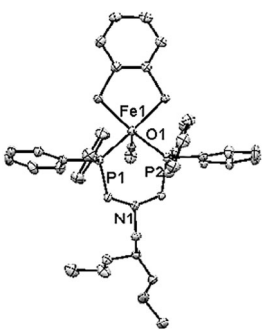


Fig. 1 ORTEP view with thermal ellipsoids at 50% probability level of complex **5**. The hydrogen atoms are omitted for clarity.

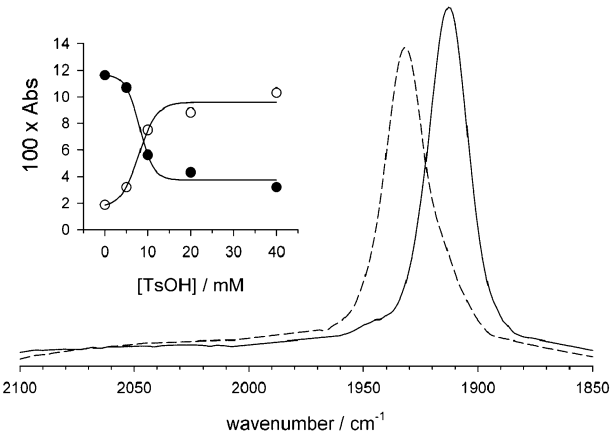


Fig. 2 IR spectra in CH_3CN solution of **5** (2 mM) before (—) and after addition of 40 mM TsOH (---). Inset: Absorbance at 1912 cm^{-1} (●) and 1932 cm^{-1} (○) as a function of acid concentration.

band was observed and a pK_a of about 7.3 could be estimated for $\mathbf{5H}^+$ from titration experiments in CH_3CN (Fig. 2).

The ^1H NMR spectrum of $\mathbf{5H}^+$ shows no signal in the hydride region but a new signal at 9.44 ppm. The signal in the ^{31}P NMR is only slightly downfield shifted by $\Delta\delta$ = 5.1 ppm.† These data are consistent with protonation on the nitrogen of the bis-phosphane ligand, similar to Fe_d in the oxidized form of the [FeFe] H_2ase active site which also carries a proton in the second coordination sphere and not metal-bound as a hydride.[6]

The redox behaviour of **5** and its catalytic activity were studied by cyclic voltammetry and controlled potential electrolysis in CH_3CN solution. In the absence of acid, voltammograms of **5** show a reversible one-electron reduction wave at $E_{1/2}$ = −1.66 V *vs.* $Fc^{+/0}$ that can be attributed to the formal $Fe^{II/I}$ couple. In contrast, hexacoordinate complex **1** with two strongly donating PMe_3 ligands undergoes irreversible reductions with

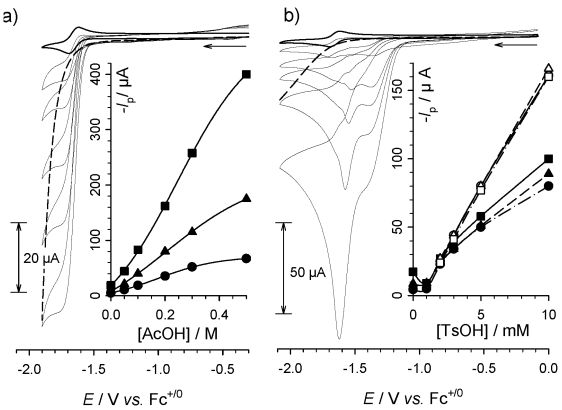


Fig. 3 Electrochemistry of **5** in CH_3CN solution with $[(C_4H_9)_4N][PF_6]$ (0.10 M) as a supporting electrolyte. (a) Cyclic voltammetry (v = 0.100 V s^{-1}) of **5** (0.25 mM) with 0, 0.05, 0.10, 0.20, 0.30, 0.50 M AcOH and background current on the glassy carbon electrode for 0.50 M AcOH without catalyst (---). Inset: Peak/plateau current as a function of [AcOH] with 0.25 mM **5** (●), 0.50 mM **5** (▲), and 1.0 mM **5** (■). (b) Cyclic voltammetry (v = 0.100 V s^{-1}) of **5** (0.25 mM) with 0, 1, 2, 3, 5, 10 mM TsOH and background current on the glassy carbon electrode for 10 mM TsOH without catalyst (---). Inset: Peak/plateau current as a function of [TsOH] with 0.25 mM **5** (●), 0.50 mM **5** (▲), and 1.0 mM **5** (■) at −1.4 V (−1.69 V for [TsOH] = 0) and at −1.53 to −1.63 V (open symbols).

cathodic peak potentials at E_{pc} = −2.21 V and E_{pc} = −2.45 V.[11] The structural dissimilarities between **1** and **5** hence result in a greatly improved stability of the one-electron reduction product of the latter complex.

Addition of increasing amounts of acetic acid to **5** ($pK_{A\ (AcOH,\ CH_3CN)}$ = 22.3) renders the reduction wave irreversible and results in increasing anodic currents at the potential of the **5/5**$^-$ wave. This behaviour is indicative for electrocatalytic reduction of protons from acetic acid as direct proton reduction at the glassy carbon electrode is negligible at this potential (Fig. 3a). The catalytic current reaches its half-maximum value at a potential of −1.65 V, *i.e.* only 0.17–0.24 V more negative than the half-wave potential obtained for the reduction of acetic acid (0.1–0.5 M in acetonitrile) on a Pt electrode.† The catalytic current increases linearly with catalyst concentration over the investigated range of catalyst (0.25–1.0 mM) and acetic acid (0.05–0.50 M) concentrations (inset of Fig. 3a). At the highest acid concentrations, plots of catalytic plateau currents are approximately linear with $[AcOH]^{1/2}$ and a bimolecular catalytic rate constant of $1 \times 10^3\ M^{-1}\ s^{-1}$ can be estimated from the slope, giving rise to a turnover frequency of 500 s^{-1} at [AcOH] of 0.5 M.[19] †

Formation of H_2 during controlled potential electrolysis was evidenced by gas chromatography,† and, after 30 turnovers, IR analysis of the reaction mixture did not indicate any degradation of **5**. The mechanism of proton reduction from acetic acid starts with one-electron reduction to **5**$^-$ which presumably renders the metal sufficiently basic to add a proton as a hydride ligand to the open coordination site. Attack of a proton on a reduced hydride species could then result in formation and release of H_2.

With stronger acids like TsOH, **5** can be protonated on the ligand and reduction of **5H**$^+$ is observed as an irreversible wave at E_{pc} = −1.32 V. With increasing excess of TsOH two catalytic waves emerge at −1.34 to −1.37 V and at −1.53 to −1.63 V, respectively (1–10 mM TsOH) (Fig. 3b).

However, due to the strong acid required for formation of **5H**$^+$, the half wave potential of the first wave is already 0.65–0.79 V more negative than the corresponding potentials on a Pt electrode.† It can be anticipated that reduction of **5H**$^+$ is also metal-centred and triggers the formation of a hydride intermediate that forms H_2 by reaction with acid. The second catalytic peak is tentatively attributed to a mechanism that is initiated by one-electron reduction of **5** to **5**$^-$. For both peaks, the catalytic currents are largely independent of catalyst concentration (0.25–1.0 mM) and depend linearly on [TsOH], at higher concentrations also for the first peak that relies on the protonation of **5**. These features are indicative of a "total catalysis" situation where the acid substrate is rapidly consumed in the vicinity of the electrode and the current is limited by substrate diffusion from the bulk rather than catalytic turnover frequency.[19] From the anodic shift of the second catalytic peak relative to $E_{1/2}$ of the **5/5**$^-$ couple a catalytic rate constant on the order of $10^6\ M^{-1}\ s^{-1}$ can be estimated for the reduction of TsOH with pseudo first order rate constants of $10^4\ s^{-1}$ at [TsOH] = 0.01 M.

In summary, we have shown that chelating bis-phosphane ligands favour the formation of pentacoordinate ferrous complexes with a bidentate bdt ligand and a single CO ligand. In contrast to the first mononuclear models of Fe_d in the [FeFe] H_2ases active site, the complexes are characterized by an open coordination site that allows for substrate binding without potentially destabilizing ligand dissociation. Catalytic H_2 formation from weak acids like AcOH at low overpotential could be demonstrated with promising results with regard to catalytic rate constants and catalyst stability. The reaction with AcOH occurs *via* initial metal-based reduction, and with stronger acids *via* initial ligand protonation. Both mechanisms thus mimic the enzymatic reaction in the sense that hydride formation at Fe_d also only occurs after preceding reduction to the formal $Fe_d(I)$–$Fe_p(I)$ oxidation level.[6] Spectroscopic characterization of catalytic intermediates and computational investigations are currently in progress.

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