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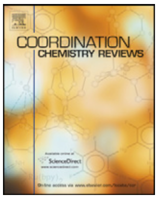

Review

Electron and proton transfers at diiron dithiolate sites relevant to the catalysis of proton reduction by the [FeFe]-hydrogenases

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ABSTRACT

This review focuses on electron and proton transfers involving hexacarbonyl and substituted {2Fe2S} complexes inspired from the active site of the [FeFe]-hydrogenases ([FeFe]H_2ases), and on different mechanisms by which the synthetic models catalyze the reduction of protons. Selected aspects of the mechanisms proposed for the biological process on the basis of DFT calculations are also briefly presented.

Abbreviations: E_p, peak potential of a redox process; $E_{1/2} = (E_p^a + E_p^c)/2$, peak-to-peak separation, $\Delta E_p = E_p^a - E_p^c$; E_p^a and E_p^c, potential of the anodic and of the cathodic peak of a reversible process; CV, cyclic voltammetry; an EC process consists of an electron transfer step (E) followed by a chemical reaction (C), in the text, schemes and figure, the complexes are identified by a number or, for analogous complexes that differ by the nature of the dithiolate bridge, by a number and a letter, the latter specifying the identity of the bridge, **a** for azadithiolate ($SCH_2N(R)CH_2S$), **b** for benzenedithiolate (SC_6H_4S), **e** for ethanedithiolate ($S(CH_2)_2S$), **p** for propanedithiolate ($S(CH_2)_3S$), and **t** for thiadithiolate (SCH_2SCH_2S).

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1. Introduction

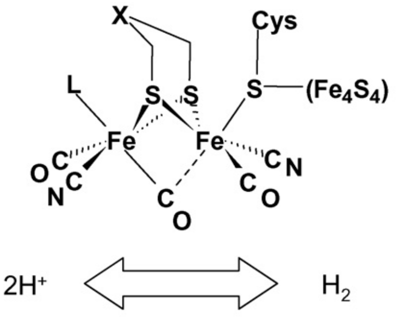
Crystallographic [1,2] and spectroscopic [3,4] studies of [FeFe]-hydrogenases ([FeFe]H_2ases) from *Clostridium pasteurianum* (Cp I) and *Desulfovibrio desulfuricans* (DdH) revealed the unique organometallic nature of their active sites, the so-called H-cluster (hydrogen-activating cluster). The H-cluster comprises two subunits, the $[2Fe]_H$ and the $[4Fe–4S]_H$ centres, that are linked by a cysteinyl bridge (Scheme 1). The $[2Fe]_H$ subsite, where the reversible reaction $2H^+ + 2e \leftrightarrow H_2$ is thought to take place, consists of a dithiolate-bridged diiron centre, the coordination sphere of the metal atoms being completed by two pairs of terminal CO and CN^- ligands, and by a carbonyl in a bridging or terminal (or semi-bridging) position (Scheme 1).

The nature of the X atom or group of atoms of the dithiolate bridge is not known with certainty. It was initially assigned as CH_2 [2] but the alternative that X = NH was later proposed as more likely [5]. However, a dithiomethylether bridge (X = O) is also a possibility [6]. The presence of the L ligand, a water molecule or a hydroxo group, at the distal iron atom (Fe_d; the other Fe atom, closest to the Fe_4S_4 cluster, is named proximal, Fe_p) of Cp I is one of the differences with respect to the crystal structure of the DdH hydrogenase, a second one being the bridging (Cp I) or essentially terminal (DdH) mode of coordination of the CO beneath the Fe–Fe vector. It has been suggested that these differences may arise from the fact that the H-cluster is in a more reduced state in the as-isolated DdH than in the as-isolated Cp I enzyme [5]. In the CO-inhibited form of the Cp I H_2ase, an exogenous CO group is found in place of the L ligand [7].

The high efficiency of dihydrogen production by the [FeFe]H_2ases [4], the need for new energy sources as an alternative to fossil fuels, and the striking structural resemblance of the $[2Fe]_H$ subsite with long-known synthetic molecules of formula $[Fe_2(CO)_6(\mu\text{-}SR)_2]$ [8,9], attracted the interest of organometallic chemists soon after the publication of the structure of the H-cluster [10]. Since then, the chemistry of diiron dithiolate complexes was subjected to a massive development with over one hundred publications in 2007–2008.

The synthetic models of the $[2Fe]_H$ centre are commonly based on {2Fe2S}, {2Fe2P} (Scheme 2) or {2Fe3S} cores [11], but an artificial model of the entire H-cluster has been synthesized [12].

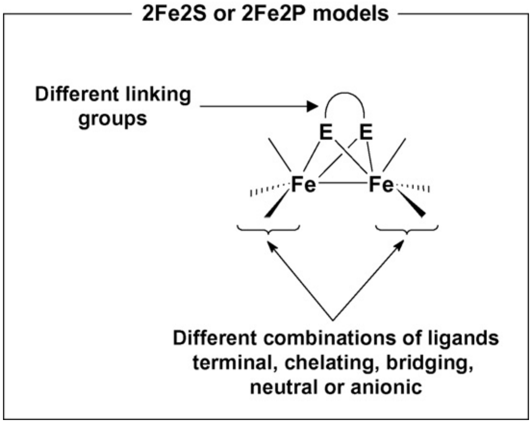
Most of the synthetic diiron dithiolate compounds are able to electrocatalyze the reduction of protons [11,13] but they are all much less efficient than the enzyme. One of the challenges that the chemists have to deal with in order to improve the performances of the chemical models is to gain a better understanding of the mechanisms by which they catalyze the reduction of protons and to identify the differences with respect to the way the enzymes function.



$X = CH_2$ or NH or O

$L = H_2O$ or OH^-, H_2, H^-, CO or vacant

Scheme 1. Schematic representation of the H-cluster, the active site of the [FeFe]H_2ases.



Scheme 2. Schematic representation of organometallic models of the $[2Fe]_H$ subsite.

This non-exhaustive review will focus on some aspects of the protonation of {2Fe2S} complexes, of their electrochemistry in the absence and in the presence of acid, and on the relevance of their chemistry to the mechanisms of the catalytic proton reduction by the H-cluster proposed on the basis of theoretical studies. The very active research fields devoted to [Ni–Fe]H_2ases and to their synthetic models [4,14–16], and to hydrogen production/uptake catalyzed by mononuclear complexes [15–19], will not be covered herein but the interested readers should be aware of recent studies in this domain.

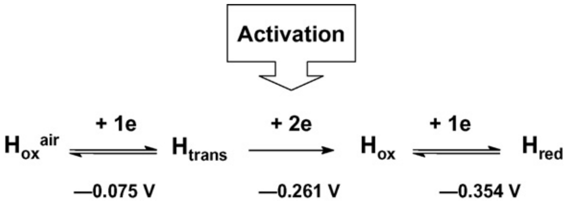
2. Mechanisms of the catalysis of proton reduction by the [FeFe]H_2ases proposed on the basis of theoretical studies

A number of theoretical studies have addressed the question of the redox states of the iron atoms in the different forms of the H-cluster, as well as possible mechanisms of the reduction of protons and oxidation of dihydrogen at the enzyme active site. These DFT calculations performed on models where the dithiolate ligand is either propanedithiolate or dithiomethylamine (that will be named azadithiolate in this paper), and where the Cys–S–Fe_4S_4 group is usually modeled as CH_3SH or CH_3S^-, have been reviewed [4c,15,16]. Only a few aspects of the mechanisms proposed for the activation of the enzyme and for hydrogen production will be presented herein.

2.1. The activation step

Several states of the H-cluster have been recognized. The $\mathbf{H}_{\mathbf{ox}}^{\mathbf{air}}$ (or $\mathbf{H}_{\mathbf{inact}}$) inactive form of the enzyme is converted to a transient $\mathbf{H}_{\mathbf{trans}}$ form by a reversible one-electron reduction. An irreversible two-electron reduction of the latter produces the $\mathbf{H}_{\mathbf{ox}}$ active state, the one-electron reduction of which affords the active $\mathbf{H}_{\mathbf{red}}$ state (Scheme 3) [20]. The fate of the two electrons involved in the $\mathbf{H}_{\mathbf{trans}} \rightarrow \mathbf{H}_{\mathbf{ox}}$ activation step, that apparently do not end up on any of the six iron centres of the H-cluster, has been discussed [4,20].

The L ligand present at the distal iron of the $\mathbf{H}_{\mathbf{ox}}^{\mathbf{air}}$ state is probably still present in $\mathbf{H}_{\mathbf{trans}}$, where it can be replaced by an exogenous CO [20]. Based on DFT calculations, the most likely redox state of the $\mathbf{H}_{\mathbf{ox}}^{\mathbf{air}}$ form consists of a Fe(II)Fe(II) core with L, proposed to be a water molecule [21,22] or a hydroxide ligand [23], bound to the distal iron centre. From their QM/MM calculations on an azadithiolate model of the H-cluster, De Gioia and coworkers [22] favoured a configuration with an aqua ligand and a non-protonated N bridgehead atom since the relative pK_as of the protonated amine and of a



Scheme 3. Redox states of the H-cluster; potentials (at pH 7) are in V vs. NHE (adapted from Ref. [20]).

bound water molecule are such that the OH ligand, rather than the N atom of the bridge, would be protonated at the physiological pH. The one-electron reduction of the Fe(II)Fe(II) core causes the loss of the aqua ligand and generates a Fe(II)Fe(I) species with a vacant coordination site at the distal iron centre (**H_{ox}**) (Scheme 4, path a). In pathway b, protonation of the OH ligand that first requires a reduction step is followed by the release of H_2O [23a]. Both redox-induced cleavage of M–L or M–X bonds [24,25] and redox-induced change of the pK_a of a ligand or of a metal centre [19e,19h,26,27] have ample chemical precedents.

The fact that the apical site liberated by the loss of H_2O (Scheme 4) is occupied by a CO ligand in the CO-inhibited enzyme (**H_{ox}–CO**) [7] strongly suggests that this position is central to the enzyme function.

2.2. *Proposed mechanisms for the catalytic reduction of protons by the H-cluster*

2.2.1. *Propanedithiolate-bridged models*

On the basis of DFT calculations on the activation of H_2 or on the reduction of H^+ by the H-cluster, the formation of a bridging hydride and the protonation of a S atom of the propanedithiolate bridge was proposed [28], although the occurrence of a terminal hydride at Fe_d was also reported [21]. Most recent calculations on a model including the $[4Fe–4S]_H$ subunit, that is the entire H-cluster, favoured the formation of a terminal hydride, and its protonation during the reduction process to a (η^2-H_2) ligand bound at Fe_d [29] (Scheme 5, steps 2 and 4). However, the species with a bridging hydride and all terminal CO ligands was more stable than the isomer with a terminal H at Fe_d and a bridging CO [21,29]. The stability order of the {Fe(μ-CO)Fe_d–H} vs. {Fe(μ-H)Fe_d–CO} entities might be reversed by an interaction of the H-cluster with the protein that was not taken into account in the DFT calculations. An alternative is that the formation of a terminal hydride at Fe_d is kinetically controlled [29].

Compounds with terminal hydride ligands have been obtained at low temperature upon protonation of Fe(I)Fe(I) complexes with a pdt bridge [30–32]. These terminal hydride complexes are unstable and rearrange to the bridging hydride isomers that are isolated at room temperature (Section 4.2.2).

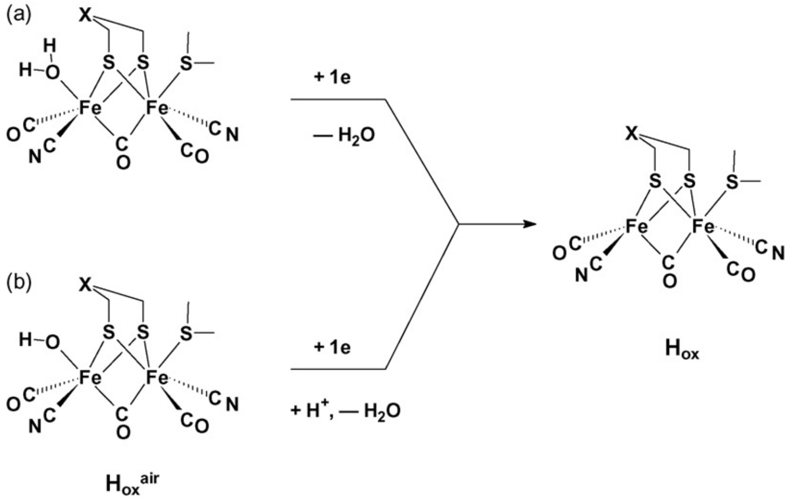
2.2.2. *Azadithiolate-bridged models*

Calculations performed on azadithiolate models showed that the presence of the amine function in the second coordination sphere of the metal centres provides a low energy path for the formation and cleavage of the H–H bond. The proton reduction cycle in Scheme 6 is adapted from the results reported by several groups [22,23,33] who arrived at similar conclusions regarding the catalytic cycle if one except the order of certain steps such as the proton and electron transfers in step 4 (Scheme 6) [22,23]. Liu et al [23b] proposed different routes for H_2 production and uptake, but in the most favourable pathway for H_2 production, the reduction of the Fe(II)Fe(II)-hydride precedes N-protonation while the opposite order was proposed by De Gioia and coworkers [22]. In both cases, the second {$1H^+/1e$} reduction is followed by the formation of a η^2-H_2 ligand, and subsequent H_2 loss regenerates **H_{ox}**, Scheme 6, steps 5 and 6. The calculations showed that the release of the H_2 ligand is spontaneous at the Fe(I)Fe(II) level of the $[2Fe]_H$ subsite, while a H_2 molecule bound to the Fe(II)Fe(II) core would undergo heterolytic H–H bond cleavage [22].

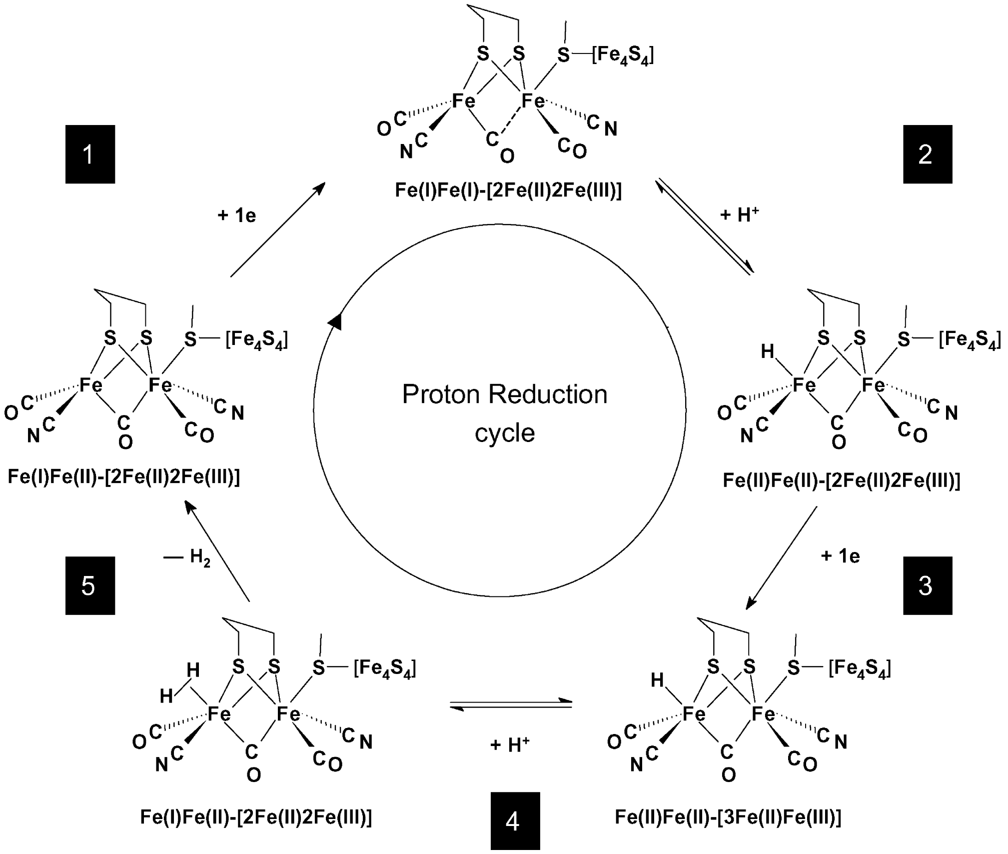
The activation barrier to the migration of the proton from the N atom to the distal iron centre (Scheme 6, step 3) is small [23]. The concomitant inversion of the amine function of the bridge allows H bonding of the remaining NH proton with the S atom of a neighbouring cysteine (Cys-178) as well as with the terminal hydride at the distal iron centre [22]. Proton migrations from N to Fe have recently been observed in synthetic Fe(I)Fe(I) models [31,34–36], see below.

3. General aspects of proton reduction processes at transition-metal centres

Despite the apparent simplicity of the H^+/H_2 conversion, the coupling of two protons and two electrons at a L_nM metal centre may follow a number of different routes, as illustrated in Scheme 7 in which possible coupled proton and electron transfers [37] (that is



Scheme 4. The proposed $H_{ox}^{air} \rightarrow H_{ox}$ activation step; the global charges are not indicated (adapted from Refs. [21–23]).



Scheme 5. A proposed mechanism for the reduction of protons by [FeFe]H_2ase based on DFT calculations on a model of the entire H-cluster; the global charges are not indicated (adapted from Ref. [29]).

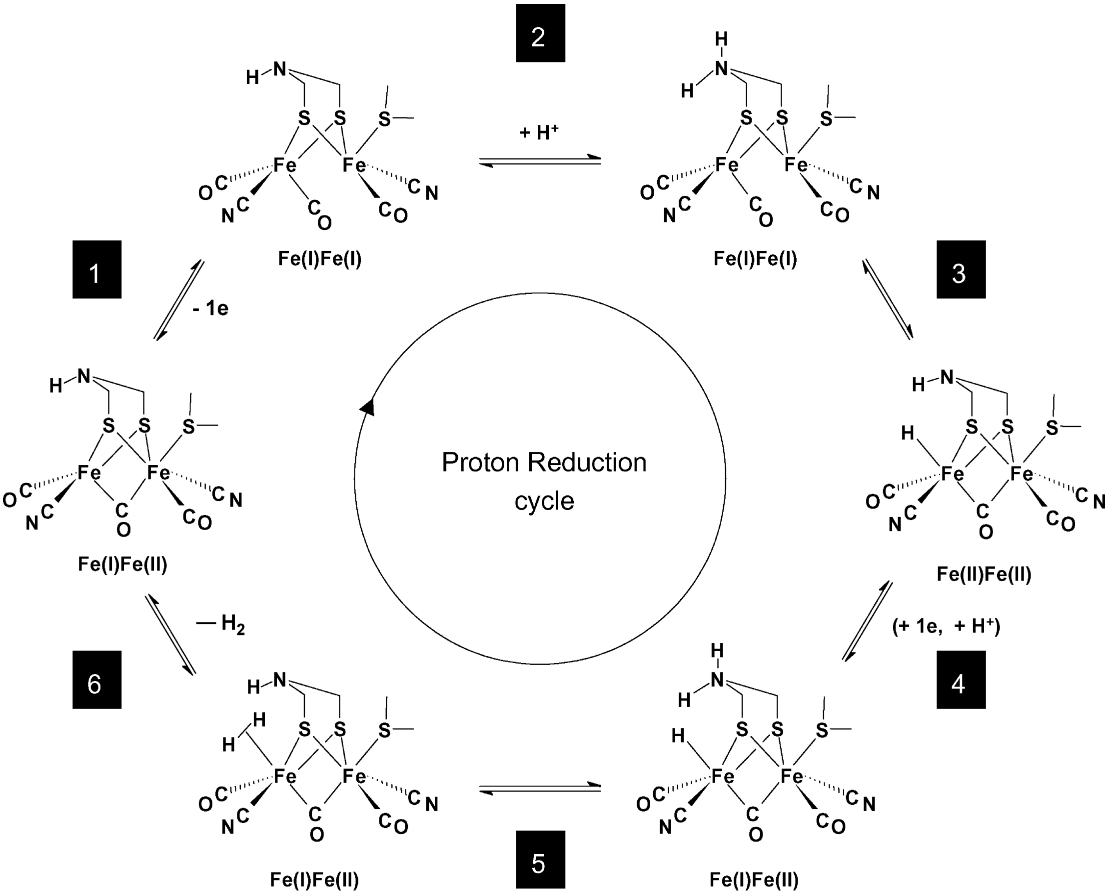
along the diagonal of the individual square schemes) are not taken into account.

Whether the first step of the process consists of the addition of a proton or that of an electron to L_nM depends on the pK_as of $[L_nM{-}H]^+$ and of HA, since the equilibrium constant of the first protonation step is $K_1 = K_a(\mathrm{HA})/K_a([L_nM{-}H]^+)$. Obviously, these options are not restricted to the initial step, and L_nMH_2 for example can also be accessed from $L_nM{-}H$ following two different pathways. The nature of the ligand set is thus important as to the orientation of the reactions since electron-releasing ligands that increase the basicity at the metal centre would promote its protonation. In the case of diiron dithiolate complexes (Section 4.2), hexacarbonyl derivatives cannot be protonated at the Fe–Fe bond in MeCN, even by strong acids such as $HBF_4{\cdot}Et_2O$ or HSO_3CF_3 (HOTf), while substituted analogues give rise to Fe(μ-H)Fe cations under similar conditions. Tuning the electronic properties of the ligands may thus divert the process from an initial electronation to an initial protonation. The ligands may also be used to introduce basic site(s) in the environment of the metal centre(s), which is an other way of switching from an initial electron transfer to an initial protonation step provided a sufficiently strong acid is used. This may be achieved via terminal or chelating ligands or, in the case of diiron models, via the S to S link (azadithiolate bridge).

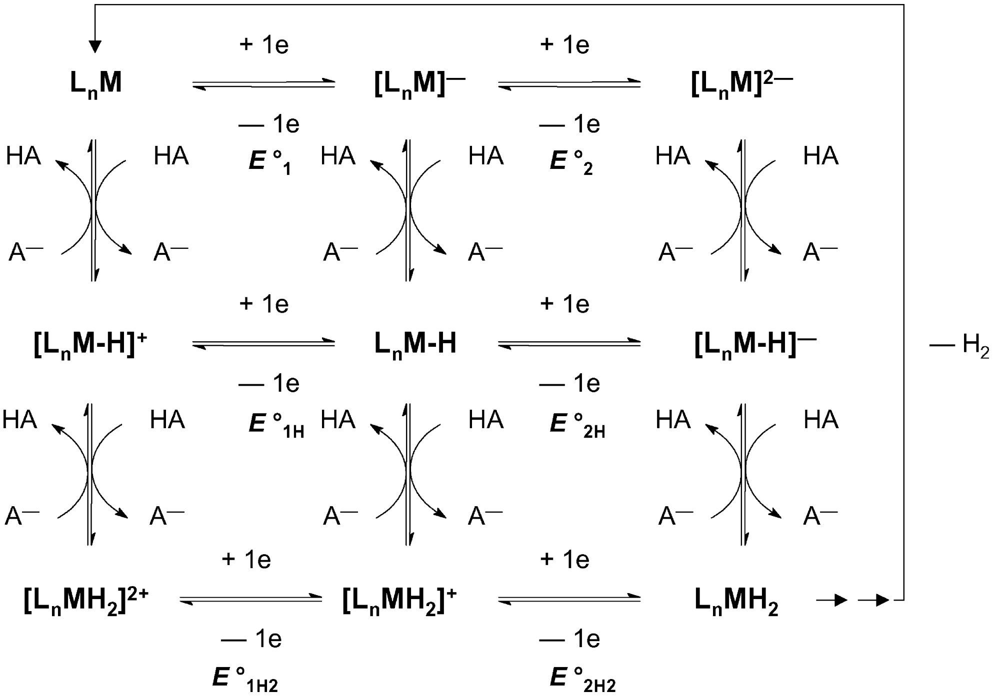
Protonation at a metal centre results in a positive shift of the redox potential of $L_nM{-}H^+$ relative to L_nM ($\Delta E^\circ = E^\circ_{1H} - E^\circ_1 > 0$, Scheme 7). From the thermodynamic cycles in Scheme 7 it can be seen that potentials and pK_as are interdependent, with $\Delta E^\circ = 0.059[\mathrm{p}K_a(L_nM{-}H) - \mathrm{p}K_a(L_nM{-}H^+)]$ for the top left square, assuming reversible redox steps. A potential shift thus means that electron transfers change the pK_a of a metal hydride [27]. Knowing that this change may be as much as 20 pK_a units in MeCN [27d], it is expected that the reduction of a non-protonatable metal centre to its anion will be followed by a protonation step when an acid is present.

Where proton reduction is initiated by an electron transfer step, it is important to investigate the redox behaviour of L_nM in the absence of acid since electron transfers may cause bonds cleavage and generate new sites for proton attack. Furthermore, both electron transfers in the top line of Scheme 7 may occur at the same potential, particularly when dinuclear species are involved, due to an inversion of the potentials of the individual steps ($E^\circ_2 - E^\circ_1 > 0$). Typically, this situation arises when a structural rearrangement of the anion (in case of a reduction) makes the transfer of a second electron thermodynamically more favourable than the first [38–41]. This is often the case when the LUMO of the complex has strong σ antibonding character, which leads to substantial changes in bonds lengths through the reduction process. Numerous calculations have established that the LUMO in bimetallic complexes such as $[Fe_2(CO)_6(\mu\text{-dithiolate})]$ has dominant M–M σ* character.

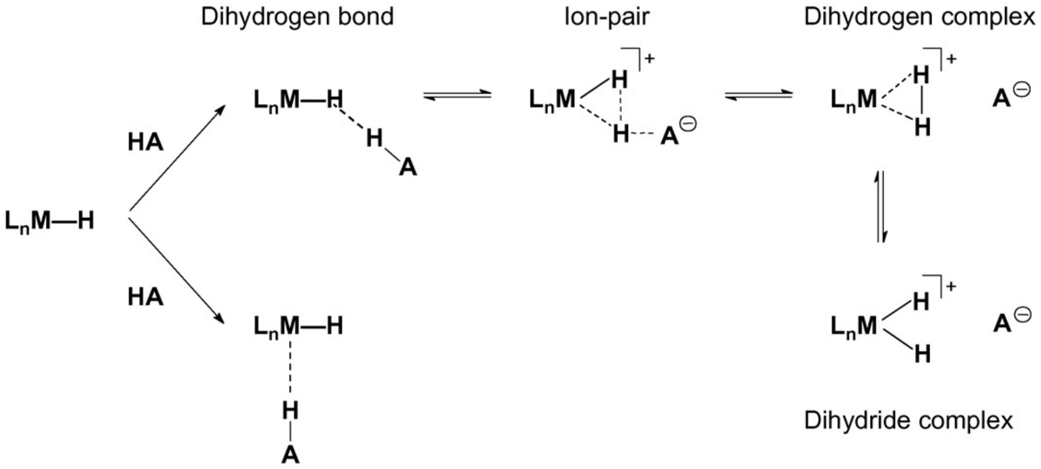
The final species in Scheme 7, namely L_nMH_2, may either be a dihydrogen complex $L_nM(\eta^2\text{-}H_2)$, or a dihydride $L_nM(H)_2$. Numerous studies of proton transfer to $L_nM{-}H$ complexes demonstrated that the kinetic protonation site is the hydride ligand although protonation at the metal may also be observed, and that the η^2-H_2 ligand is formed via dihydrogen bonded and ion-paired adducts [42–52] (Scheme 8). The effect of the metal centre and of the electronic properties of the ligands on the acidity of the dihydrogen ligand [53], and the effect of the solvent on the nature of the protonation product [54] were also investigated.



Scheme 6. Proton reduction cycle catalyzed by the H-cluster as proposed from DFT calculations; the global charges are not indicated; note the inversion at the N atom concomitant with the migration of the N–H proton in steps 3 and 5 (from Refs. [22,23,33]).



Scheme 7. Proton and electron transfers possibly involved in the H^+/H_2 conversion.



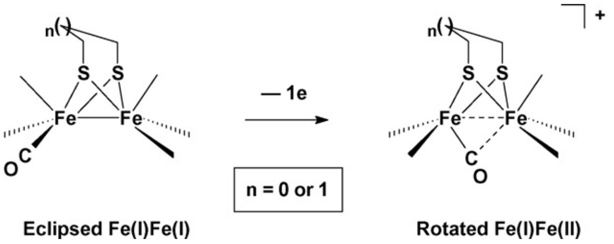
Scheme 8. Protonation of a metal–hydride complex.

When a basic site is available in the outer coordination sphere [55], as in azadithiolate-bridged diiron models or in complexes where a tertiary amine is introduced via diphosphine ligands [19], the side chain of a Cp ring [56,57], or as a mercaptopyridine [58], L_nMH_2 may carry both a proton and a hydride. Efficient proton–hydride coupling requires inter alia, a precise match of the pK_a of the dihydrogen ligand and of the protonated base and a precise positioning of the proton relay in order to avoid costly rearrangements of the coordination sphere [19].

4. Diiron dithiolate complexes: electrochemistry, protonation, proton reduction

4.1. *Electrochemical reduction of [$Fe_2(CO)_{6-n}(L)_n$(μ-dithiolate)] complexes*

The present survey of the electrochemistry of [$Fe_2(CO)_{6-n}(L)_n$(μ-dithiolate)] complexes is restricted to their reduction both in the absence and in the presence of acid. Their oxidation processes are not presented in this review. Nevertheless, several recent reports by the groups of Darensbourg and of Rauchfuss [59,60] revealed that the oxidation of such complexes opens a very exciting area since it induces a structure change from the eclipsed geometry of the Fe(I)Fe(I) species to the "rotated" structure at the Fe(I)Fe(II) level (Scheme 9), more closely ressembling that of the $\mathbf{H_{ox}}$ state of the H-cluster. An earlier report by Pickett and coworkers also showed that the one-electron oxidation of a dicyanide Fe(I)Fe(I) complex with the {2Fe3S} core produced a Fe(I)Fe(II) transient species whose spectral characteristics were close to those of the CO-inhibited form of the H-cluster ($\mathbf{H_{ox}}$**–CO**) [61].



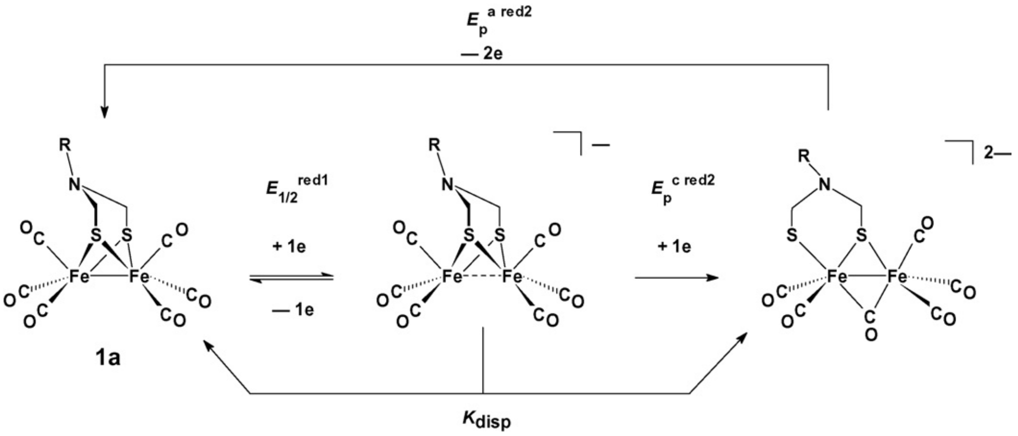
Scheme 9. Oxidatively induced structure change in [$Fe_2(CO)_{6-n}(L)_n$(μ-dithiolate)] complexes. The coordination sphere of the iron centres is purposely left incomplete (see Refs. [59,60]).

4.1.1. *Hexacarbonyl complexes*

As mentioned in Section 3, it is important to examine, in acid-free media, the electrochemistry of complexes for which the proton reduction process is initiated by a reduction step. Indeed, the reduction of dinuclear thiolate-bridged species may lead to bonds cleavage [13,24] so that, depending on the strength of the acid used, the catalytically active species for proton reduction may have little or no resemblance with the initial complex [62]. Besides, the redox processes of dinuclear species may involve the transfer of two electrons in a single step due to the inversion of the potentials of the individual one-electron processes ($E_2^\circ - E_1^\circ > 0$) [24,38–41].

Cyclic voltammetry (CV) studies of [$Fe_2(CO)_6$(μ-dithiolate)] complexes (**1**) established that the reduction processes and the products formed are somewhat dependent on the nature of the dithiolate bridge. The complexes where the bridge is an azadithiolate (adt, $SCH_2N(R)CH_2S$, R = iPr or CH_2CH_2OMe; **1a**) [63], benzenedithiolate (bdt, SC_6H_4S; **1b**) [64,65] or thiadithiolate (tdt, SCH_2SCH_2S; **1t**) [66], as well as complexes with a metalladithiolate bridge (mdt, $SPt(L_2)S$, L_2 = (bis)diphenylphosphinoethane (dppe), (bis)diphenylphosphinoferrocene (dppf) or cyclooctadiene (cod); **1m**) [67], undergo an overall, reversible or quasi-reversible two-electron reduction. DFT studies on the adt- and bdt-bridged analogues **1a** and **1b** showed that the potential inversion (($E_2^\circ - E_1^\circ > 0$); see above) results from a rearrangement that consists of the cleavage of a Fe–S bond and the move of a CO from a terminal to a bridging position. The structure change is either distributed over the two one-electron steps, with a significant lengthening of one Fe—S bond in the anion (**1b**) [65], or concomitant with the transfer of the second electron (**1a**, R = iPr or CH_2CH_2OMe) [63] (Scheme 10). In the latter case, this results in a slow second electron transfer, and in a large peak-to-peak separation at fast scan rate ($\Delta E_p = E_p^a - E_p^c = 490$ mV for a scan rate $v = 20\,V\,s^{-1}$, R = iPr), with the consequence that the oxidation of the dianion at a less negative potential than that of the anion produces directly the neutral complex (Scheme 10).

Bis(phosphido)- and diphosphido-bridged hexacarbonyl diiron derivatives also undergo a partially reversible, single-step, two-electron reduction [68]. The effect of the electronic properties of the bridge on the reduction process is particularly striking in the case of the recently reported [$Fe_2(CO)_6$(μ-SRS)] complex where R is *o*-carborane (1,2-closo-$C_2B_{10}H_{10}$) [69], since this is the only hexacarbonyl dithiolate-bridged compound known to-date for which cyclic voltammetry at moderate scan rate shows two sequential reversible or quasi-reversible one-electron steps with $E_{1/2}(2) - E_{1/2}(1) < 0$ ($\Delta E_{1/2} = -0.25$ V). The fact that no struc-



Scheme 10. Simplified reduction scheme of azadithiolate complexes (R = iPr, CH_2CH_2OMe) [63].

ture change is coupled with the electron transfer(s) was assigned to the contribution of the R group to dissipate the excess charge resulting from the reduction [69]. The electrochemical reduction of the $[Fe_2(CO)_6(\mu\text{-xdt})]$ complexes [xdt = propanedithiolate, pdt: $S(CH_2)_3S$, **1p**, or ethanedithiolate, edt: $S(CH_2)_2S$, **1e**] was also studied in great detail [62,70–73], in particular by infrared spectroelectrochemistry. These studies revealed that the chemical reactivity of the one-electron reduced species resulted in extremely complex processes, with the formation of different tetranuclear entities [72,73], whose crystal structure was obtained in the case of the pdt complex [74]. Importantly, the peaks observed at potentials more negative than the primary reduction were shown to arise from daughter products rather than from the $\mathbf{1x}^- \rightarrow \mathbf{1x}^{2-}$ process (**x** = **e**, **p**) [62,72,73]. A similar conclusion was reached in the case of the adt-bridged analogue **1a** [63]. The reduction of **1p** is obviously much simplified when a short timescale, allowed by fast scan cyclic voltammetry ($v \geq 5\,V\,s^{-1}$), is used to isolate the electron transfer steps from the follow-up chemistry. Under these conditions, the electrochemical reduction of **1p** occurs in two one-electron steps, with the first one faster than the second that is coupled with the same kind of rearrangement as above (see Scheme 10) [63].

These electrochemical studies thus showed that the reduction of several $[Fe_2(CO)_6(\mu\text{-dithiolate})]$ complexes involves two one-electron processes that may appear sequentially or in a single two-electron step, depending on the nature of the bridge. In order to assess this effect more clearly, it would be of interest to check whether the electrochemical reduction of several azadithiolate-bridged species, that was reported to consist in an irreversible one-electron process (R = $CH_2C_6H_4$-4-Br [75]; R = C_6H_5-4-NH_2 [76]; R = CH_2CH_2OH [77]), would appear differently under different experimental conditions.

The studies summarized above also clearly illustrate the interest of using acids that are strong enough to rapidly protonate the anion, $[Fe_2(CO)_6(\mu\text{-dithiolate})]^-$, when studying the proton reduction processes catalyzed by non-protonatable complexes (dithiolate = pdt, edt). When weak acids are used, it may be difficult to identify the actual catalyst with certainty which complicates the analysis of the reaction mechanisms [62].

4.1.2. Substituted complexes

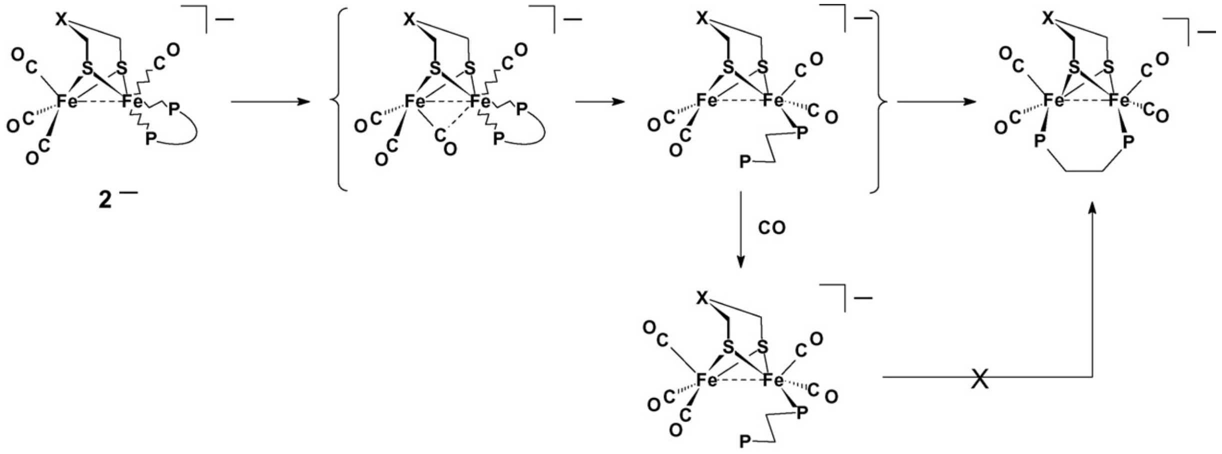
The reductive electrochemistry of $[Fe_2(CO)_{6-n}(L)_n(\mu\text{-dithiolate})]$ complexes in the absence of acid has been comparatively less investigated than that of the hexacarbonyl parents. As expected, the substitution of donor ligands L (CN^-, PR_3, RNC) for CO shifts the reduction potential of the complexes to more negative values, but the reduction mechanisms were not investigated thoroughly except for unsymmetrically disubstituted $[Fe_2(CO)_4(\kappa^2\text{-dppe})(\mu\text{-dithiolate})]$ compounds (dithiolate = adt (**2a**) or pdt (**2p**)) whose reduction produced the (μ-dppe) isomers according to an electron transfer catalyzed (ETC) process [78]. This kind of complexes with a chelating ligand were synthesized after theoretical calculations [79] concluded that an unsymmetrical disubstitution at the Fe(I)Fe(I) level may favour the rotated geometry observed in the $[2Fe]_H$ subsite (Scheme 1). This was confirmed by a DFT analysis of the substitution of PMe_3 for CO in $[Fe_2(CO)_4(\kappa^2\text{-dppv})(\mu\text{-dithiolate})]$ (**4**) that showed that the electron-richness of the $\{Fe(CO)(\kappa^2\text{-dppv})\}$ centre favours the rotation of the $\{Fe(CO)_3\}$ fragment and the formation of a bridging CO in the transition state [80]. Such a rotation might also be facilitated by reduction, so the mechanism in Scheme 11 was proposed to rationalize the ETC isomerization of $[Fe_2(CO)_4(\kappa^2\text{-dppe})(\mu\text{-dithiolate})]$ and the inhibition of the catalytic process by CO [78].

The isomerization was thus proposed to be initiated by the rotation of the $\{Fe(CO)_3\}$ centre, possibly assisted by the weakening of the Fe–Fe bond, in the anion $\mathbf{2}^-$. Such an isomerization was not observed however upon reduction of other $[Fe_2(CO)_4(\kappa^2\text{-LL})(\mu\text{-pdt})]$ complexes where LL is dmpe ($Me_2PCH_2CH_2PMe_2$) (**3**), phenanthroline (**5**), or the (bis)N-heterocyclic carbene (NHC) I_{Me}–CH_2–I_{Me} (**6**; I_{Me} = 1-methylimidazol-2-ylidene). This does not mean that the $\{Fe(CO)_3\}$ fragment does not rotate in these compounds but that (at least) one step of the overall ETC isomerization process does not take place. It is conceivable that the formation of intermediate(s) with a dangling ligand might be prevented by a lower hemilability of dmpe, phen or I_{Me}–CH_2–I_{Me} as compared to dppe. An other example of a κ^2-LL → μ-LL isomerization has been reported recently for LL = $(EtO)_2PN(Me)P(OEt)_2$ (PNP) [81]. In this case, the isomerization was not triggered by reduction but by the binding of a PR_3 ligand (R = Me, OEt) and intermediates with the partially decoordinated PNP were isolated and fully characterized [81].

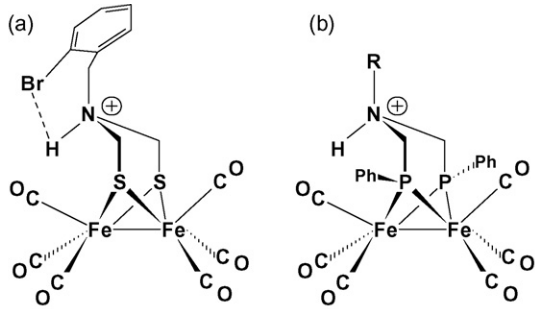
4.2. Protonation of $[Fe_2(CO)_{6-n}(L)_n(\mu\text{-dithiolate})]$ complexes

4.2.1. Hexacarbonyl complexes

The possibility to protonate hexacarbonyl diiron dithiolate-bridged complexes is restricted to the $[Fe_2(CO)_6\{\mu\text{-}SCH_2N(R)CH_2S\}]$ derivatives, provided the acid used is sufficiently strong to protonate the amine function (in MeCN, pK_a = 8.1 for R = Me; pK_a ca. 8 for R = H [35]). Although a number of such protonated complexes have been prepared in situ, they could not be isolated unless the NH proton was stabilized by an interaction



Scheme 11. Mechanism and intermediates proposed for the ETC catalyzed isomerization of [$Fe_2(CO)_4(\kappa^2$-dppe)(μ-dithiolate)] and for its inhibition by CO (adapted from Ref. [78]).



Scheme 12. Representation of the only two [$Fe_2(CO)_6${μ-$ECH_2NH(R)CH_2E$}]$^+$ complexes characterized by X-ray crystallography (a) [82b,c]; (b) R = CH_2CH_2OMe [83].

with a heteroatom of the R substituent [82] or by substitution of the S atom of the bridge by P(Ph) groups [83], Scheme 12.

Protonation at the N bridgehead atom results in a shift of the carbonyl bands to higher energy by ca. 15–20 cm^{-1} [34,35,75,82–87]. Even when the NH proton is not detected by ^1H NMR spectroscopy, the 15–20 cm^{-1} magnitude of the shift of the ν(CO) bands in the infrared spectrum is used to diagnose protonation at the amine function of the bridge, and more generally at a ligand [36,88,89], rather than at the Fe–Fe site, which occurs for substituted complexes. In this case, larger shifts of the ν(CO) bands are observed [30,32,34,82c,88–90]. As it can be seen from Table 1, protonation at the N atom of the bridge also causes a shift of the reduction towards less negative potentials by ca. 0.4 V. The reduction of the protonated complex **1aH⁺** (R = iPr or CH_2CH_2OMe) is an irreversible one-electron process for scan rates up to 60 V s^{-1}, that regenerates the parent complex **1a** through the formal loss of a hydrogen atom. However, in spite of this fast follow-up reaction, **1aH** can be trapped by acid [86] (Section 4.3.3).

Table 1
Reduction potentials of [$Fe_2(CO)_6$(μ-$SCH_2N(R)CH_2S$)] and [$Fe_2(CO)_6$(μ-$SCH_2NH(R)CH_2S$)]$^+$ complexes in MeCN (V vs. Fc^+/Fc).

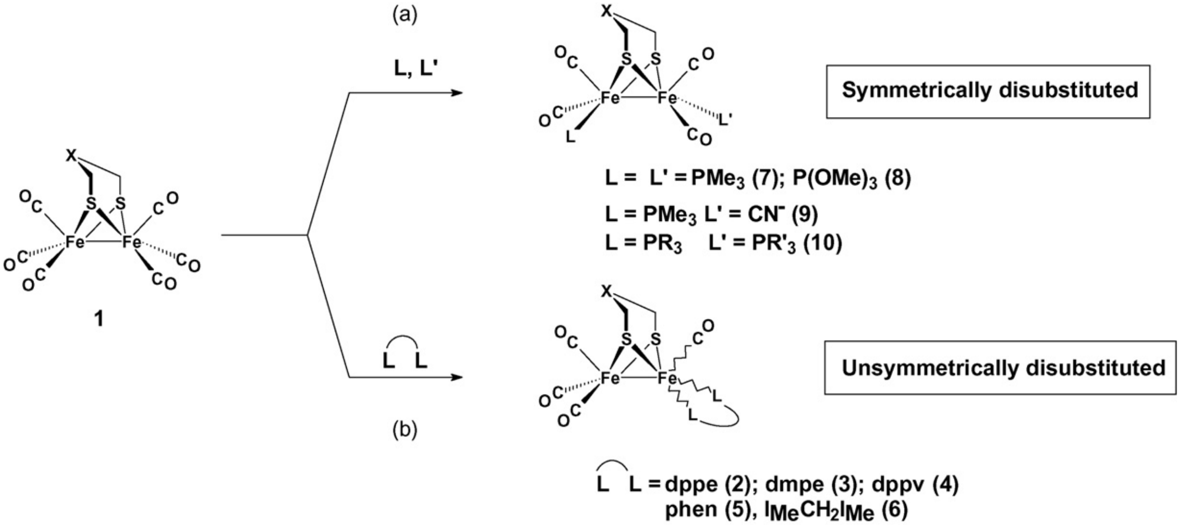
R	$E^{red}_{1/2}$ neutral	E^{red}_{p} N-protonated	Reference
$CH_2C_6H_4$-4-Br	−1.56	−1.18	[75]
$CH_2C_6H_4$-2-Br	−1.48	−1.01	[82c]
$CH_2C_4H_3O$	−1.55	−1.13	[82a]
CH_2CH_2OMe	−1.56	−1.19	[63,86]
iPr	−1.58	−1.17	[63,86]
$CH_2C_4H_3S$	−1.64	−1.20	[82d]
$CH_2C_4H_2SBr$	−1.54	−1.09	[82d]

4.2.2. *Substituted complexes*

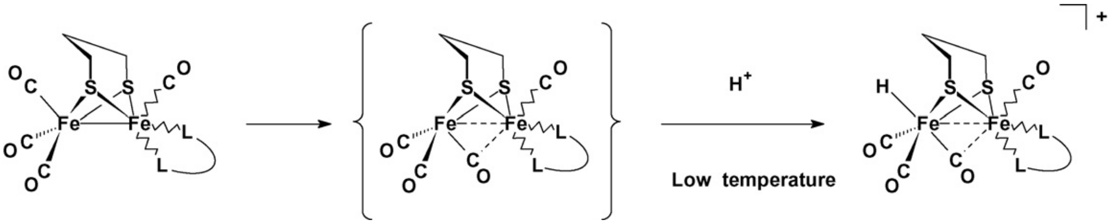
Although numerous singly substituted [$Fe_2(CO)_5$(L)(μ-dithiolate)] complexes have been reported [91], we will focus here on the protonation of di- or more highly substituted derivatives. The objective of the synthesis of such complexes was to both reinforce their basicity so that they can be protonated, and model more closely the ligand set at the $[2Fe]_H$ subsite. The first disubstituted complexes to be reported were the dicyanide derivatives [10]. Later, phosphines or NHCs have been widely used as alternatives to the CN^- ligand. As mentioned in Section 4.1.2, the substitution of donor ligands for CO shifts the reduction of the complexes towards more negative potentials. However, when acid is present, this negative shift is compensated by a positive one that is due to the fact that the hydride derivatives are easier to reduce than the parent complexes. From the reduction potentials of different disubstituted complexes and of their protonation products (bridging hydride species), and from a thermodynamic cycle such as shown in Scheme 7, it can be estimated that the one-electron reduction of the parent increases the basicity of the Fe–Fe site by 15 ± 2 pK_a units in MeCN [13].

Several types of disubstituted complexes may be distinguished depending on their geometry and on the number of protonation site(s) they possess. [$Fe_2(CO)_6$(μ-dithiolate)] complexes undergo disubstitution of CO by monodentate ligands (L) in a symmetrical manner. These reactions, studied in detail for L = CN^- in {2Fe2S} and {2Fe3S} complexes [11j,11k,92,93], produce [{$Fe(CO)_2L$}$_2$(μ-dithiolate)] derivatives with one substituent on each iron centre (Scheme 13(a)). These compounds will be considered herein as *symmetrically* disubstituted even though they may carry different substituents L and L′ [88,92,94] as shown in Scheme 13(a). The only way to obtain {2Fe2S} derivatives with the two substituents on the same metal centre, which we will name *unsymmetrically* disubstituted complexes, is to react the precursor with a bidentate ligand that can adopt a chelating mode of coordination [30,32,36,78,80,81,95–97] (Scheme 13(b)).

One of the major differences between the [$Fe_2(CO)_4(\kappa^2$-LL)(μ-pdt)] complexes and the symmetrical [{$Fe(CO)_2L$}$_2$(μ-pdt)] analogues lies in their protonation. While the latter produce exclusively the bridging hydride complex [{$Fe(CO)_2L$}$_2$(μ-pdt)(μ-H)]$^+$ (L = PMe_3 [88,90], tBuNC [98]; L/L′ = PMe_3/CN^- [88]) upon treatment with an appropriate acid, intermediates with a terminal hydride could be detected when the protonation of [$Fe_2(CO)_4(\kappa^2$-LL)(μ-pdt)] was run at low temperature [30,32]. It has been verified that the difference does not arise from different experimental conditions by studying the protonation of [{$Fe(CO)_2PR_3$}$_2$(μ-pdt)]



Scheme 13. Representation of symmetrically and unsymmetrically disubstituted complexes.

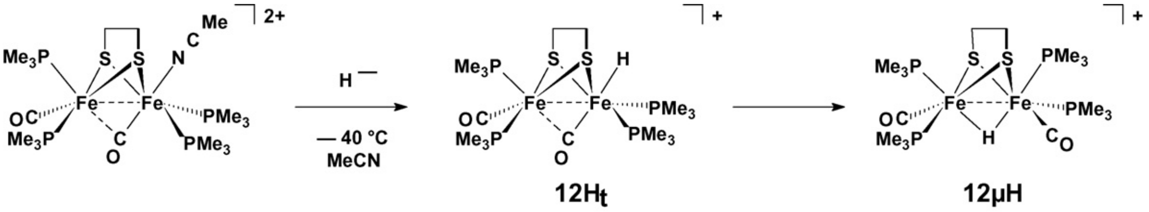


Scheme 14. Low temperature protonation of $[Fe_2(CO)_4(\kappa^2\text{-LL})(\mu\text{-pdt})]$ derivatives.

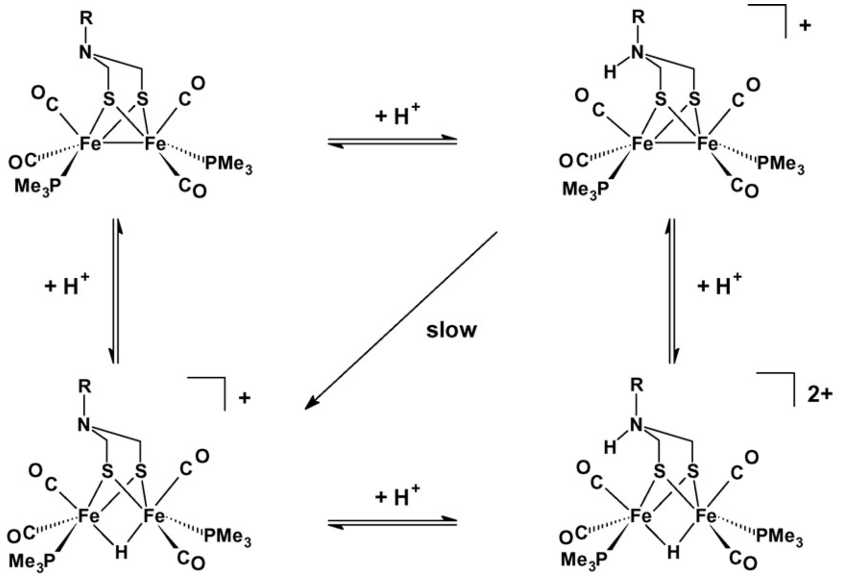
(R = Me (**7p**), OMe (**8p**)) at the same temperatures and with the same acid as for $[Fe_2(CO)_4(\kappa^2\text{-LL})(\mu\text{-pdt})]$. No evidence for the formation of a terminal hydride could be obtained in the case of **7p** and **8p** [30d]. Therefore, it appears that the unsymmetrical arrangement of the ligands is central to the formation of a terminal Fe–H species (Scheme 14). This may arise from an easier access to the rotated geometry [79] in the case of $[Fe_2(CO)_4(\kappa^2\text{-LL})(\mu\text{-pdt})]$ derivatives.

However, the uneven substitution is not the only key to the formation of terminal hydrides. The formation of a terminal Fe–H bond upon protonation of the tetrasubstituted complex $[Fe_2(CO)_2(\kappa^2\text{-dppv})_2(\mu\text{-pdt})]$ (**11p**) at low temperature strongly suggests that the basicity of the diiron centre is also a critical factor [31]. Moreover, the stability of the {Fe–Fe–H} form towards isomerization to {Fe(μ-H)Fe} is increased considerably in the case of the tetrasubstituted complex **11p**, with $t_{1/2} \sim 10$ min at 20 °C [31]. Another example of a tetrasubstituted complex with a terminal hydride ligand (**12H$_t$**, Scheme 15) has been reported [99]. In this case, the terminal Fe–H bond was obtained by substitution of hydride for a labile MeCN ligand in the Fe(II)Fe(II) precursor, rather than by protonation of a Fe(I)Fe(I) derivative. Although **12H$_t$** converts to its bridging isomer **12μH**, it could be isolated and characterized by X-ray crystallography [99]. To date, **12H$_t$** is still the only crystallographically characterized example of a terminal hydride at the {2Fe2S} core. Importantly, treatment of **12H$_t$** with acid was shown to produce dihydrogen while no such reaction was detected with **12μH**, which showed that a terminal hydride is more reactive than a bridging one towards formation of H_2 in a Fe(II)Fe(II) complex [99].

The other distinction between disubstituted complexes relates to the number of their available protonation sites. Disubstituted azadithiolate-bridged complexes may be protonated at the metal and/or at the bridgehead atom. The same is true for $[Fe_2(CO)_4(\kappa^2\text{-LL})(\mu\text{-pdt})]$ and $[\{Fe(CO)_2L\}_2(\mu\text{-pdt})]$ derivatives where the κ²-LL or L ligand possesses a basic function. It has been recently demonstrated that three different protonated species formed in the reaction of $[\{Fe(CO)_2(PMe_3)\}_2\{\mu\text{-SCH}_2N(R)CH_2S\}]$ (**7a**) with appropriate acids in MeCN ($R = CH_2Ph$ [34]; $R = CH_2C_6H_4\text{-2-Br}$ [82c]). Furthermore, the slow migration of the proton from the nitrogen atom to the Fe–Fe site (pK_a $\{Fe(\mu\text{-H})Fe\}^+ = 15$ [34]) was observed when $R = CH_2Ph$ (pK_a $\{RNH\}^+ = 12$ [34]) (Scheme 16) and when R = H (pK_a $\{NH_2\}^+ = 10.1$ [35]).



Scheme 15. Synthesis of the only crystallographically characterized {2Fe2S} complex with a terminal Fe-H bond (Ref. [99]).

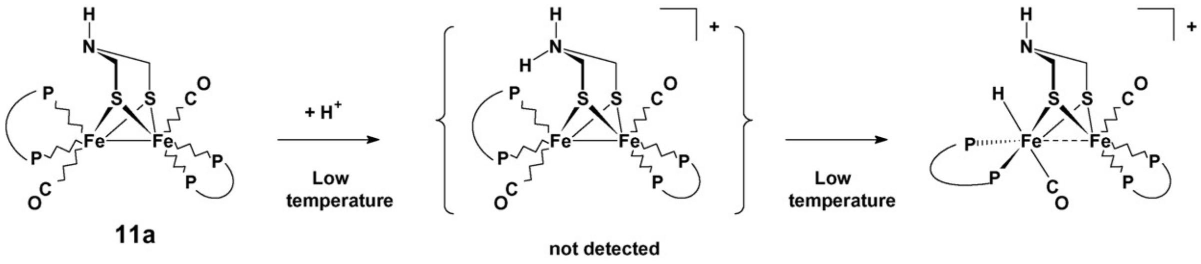


Scheme 16. Protonation pathways of [{Fe(CO)$_2$(PMe$_3$)}$_2${μ-SCH$_2$N(R)CH$_2$S}] (R = CH$_2$Ph) in MeCN (from Ref. [34]).

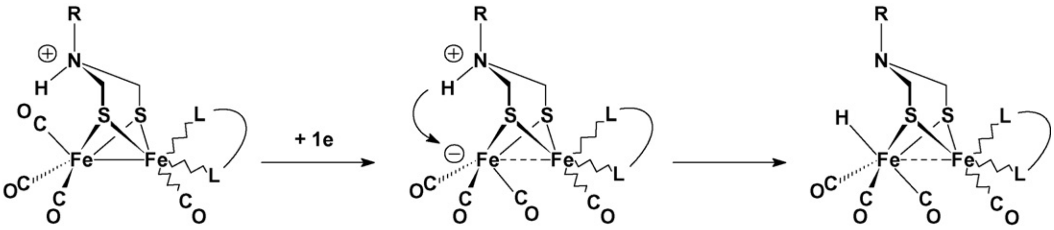
In sharp contrast, the unsymmetrical complex [Fe$_2$(CO)$_4$(κ^2-LL){μ-SCH$_2$N(iPr)CH$_2$S}] (LL = dppe (**2a**), phen (**5a**)) was protonated exclusively at the N atom by a strong acid (HBF$_4$·Et$_2$O) in MeCN under any condition of temperature, and no tautomerization was detected [87]. This is rather surprising since the ligand set was shown to provide enough basicity for the diiron centre of the pdt-bridged analogues to be protonated in a terminal fashion at low temperature [30a,c] (Scheme 14). The presence of two chelating diphosphines instead of only one makes a spectacular difference since the protonation of [Fe$_2$(CO)$_2$(κ^2-dppv)$_2${μ-SCH$_2$NHCH$_2$S}] (**11a**) in MeCN at low temperature afforded the complex with a terminal H ligand, characterized by ^{1}H and ^{31}P NMR spectroscopies [31] (Scheme 17).

The transient formation of the N-protonated species was assumed from the fact that azadithiolate complexes are known to protonate readily at the N bridgehead atom. These results suggest that the tautomerization, that is not observed for [Fe$_2$(CO)$_4$(κ^2-LL){μ-SCH$_2$NH(iPr)CH$_2$S}]$^+$ (LL = dppe or phen) [87], is driven by the stronger basicity of the tetrasubstituted metal site as compared to the disubstituted one. On this basis, one may reasonably assume that the migration of the proton from the N atom of the bridge to a metal centre may be induced by an electron transfer that would increase the basicity of the metal site in case of a metal-centered reduction [86], keeping in mind that the pK_a change may be of ca. 15 units in MeCN (Scheme 18).

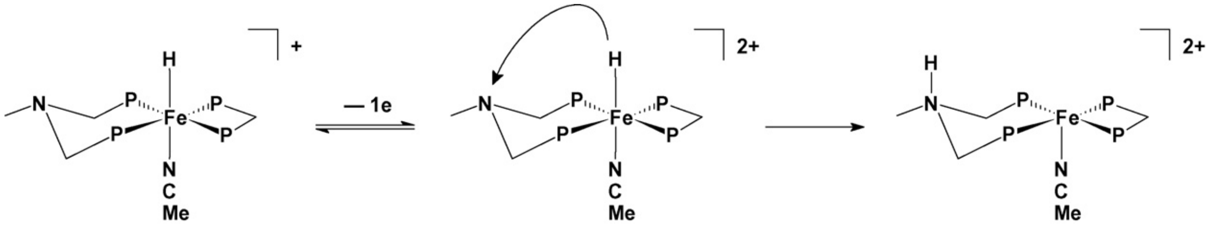
The redox-induced pK_a change of a protonated site has been observed in mononuclear complexes. In these cases, the migration of a proton from the metal centre to the nitrogen atom of a PNP ligand was shown to occur upon one-electron oxidation of the Fe(II) hydride [HFe(PNP)(dmpm)(MeCN)]$^+$ in MeCN-[NBu$_4$][BF$_4$] (PNP = Et$_2$PCH$_2$N(Me)CH$_2$PEt$_2$; dmpm = Me$_2$PCH$_2$PMe$_2$) [19e] (Scheme 19). A similar follow-up proton migration was also detected upon oxidation of [HNi(PNP)$_2$]$^+$ to [Ni(PNHP)(PNP)]$^{2+}$, via the Ni(III) hydride complex [HNi(PNP)$_2$]$^{2+}$. This arises from the



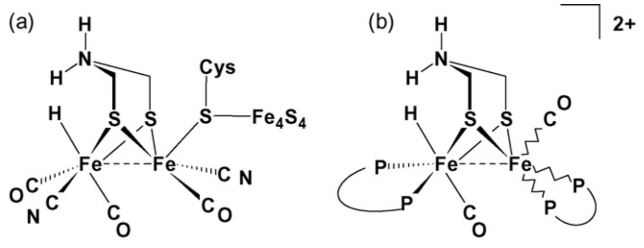
Scheme 17. Protonation of [Fe$_2$(CO)$_2$(κ^2-dppv)$_2${μ-SCH$_2$NHCH$_2$S}] (**11a**) (adapted from Ref. [31]).



Scheme 18. Possible reductively induced tautomerization in [Fe$_2$(CO)$_4$(κ^2-LL){μ-SCH$_2$NH(R)CH$_2$S}]$^+$ (from Ref. [86]).



Scheme 19. Oxidatively induced proton migration in $[HFe(PNP)(dmpm)(MeCN)]^+$; the Et and Me substituents of the P atoms were omitted (adapted from Ref. [19e]).



Scheme 20. A possible intermediate involved in proton reduction by the $[FeFe]H_2$ase [5] (a), and the synthetic structural analogue **11a-2H^{2+}**(b) [31].

lowering of the pK_a of the Ni–H entity by more than 14 units upon one-electron oxidation of the metal [19h].

The proton migration in Scheme 17 is reminiscent of a reaction proposed to take part in the proton reduction catalyzed by the H-cluster (see step 3 in Scheme 6). Furthermore, ^1H, ^{31}P NMR, and infrared spectroscopies showed that **11a** can be protonated at the metal and at the N atom to **11a-2H^{2+}** [31], which provides a close synthetic structural analogue of an intermediate that was proposed to occur as the H-cluster (assuming an azadithiolate bridge [5]) is turning over (Scheme 20).

$[Fe_2(CO)_4(\kappa^2\text{-LL})(\mu\text{-pdt})]$ and $[\{Fe(CO)_2L\}_2(\mu\text{-pdt})]$ derivatives also offer several potential sites for protonation when the κ^2-LL or L ligand possesses a basic function. This is the case of the PTA complexes $[\{Fe(CO)_2(PTA)\}_2(\mu\text{-xdt})]$ (xdt = pdt (**13p**) [89], or adt (**13a**) [100]; PTA = 1,3,5,-triaza-7-phosphaadamantane) and of the κ^2-PNP and μ-PNP derivatives $[Fe_2(CO)_4(\kappa^2\text{-PNP})(\mu\text{-pdt})]$ (PNP = $Ph_2PCH_2N(Me)CH_2PPh_2$ (**14**) [36] or $(EtO)_2PN(Me)P(OEt)_2$ (**15**) [81] or $Ph_2PN(R)PPh_2$, R = iPr (**16**), allyl (**17**) [95a]) and $[Fe_2(CO)_4(\mu\text{-PNP})(\mu\text{-pdt})]$ (PNP = $Ph_2PN(R)PPh_2$, R = nPr, nBu (**18**) [101]). While **13a** was protonated only at the N atom of the bridge by various acids [100], protonation of the PTA ligands of **13p** resulted in a ca. 0.4 V positive shift of the reduction compared to that of the neutral parent [89]. The magnitude of the potential shift is thus quite similar to that observed upon protonation of $[Fe_2(CO)_6(\mu\text{-adt})]$ complexes at the N atom of the bridge (Table 1). The reaction of **14** with 1 equiv $HBF_4{\cdot}Et_2O$ gave rise to the interesting situation where the site that is protonated depends on the solvent (Scheme 21).

In dichloromethane, the final product is the bridging hydride complex (**14μH$^+$**) formed via the N-protonated intermediate (**14$_N$H$^+$**) detected by low temperature ^1H and ^{31}P NMR spectroscopy. When the reaction is performed in acetone but under otherwise identical conditions (concentration, temperature, acid), the stable isomer is **14$_N$H$^+$** that was isolated and characterized crystallographically [36] (Scheme 21). This example illustrates the fact that the role of the solvent in acid–base reactions must not be underestimated. The crystallographic characterization of a diprotonated form of a close analogue of **14** where PNP is $Ph_2PCH_2N(nPr)CH_2PPh_2$ has been recently reported [102].

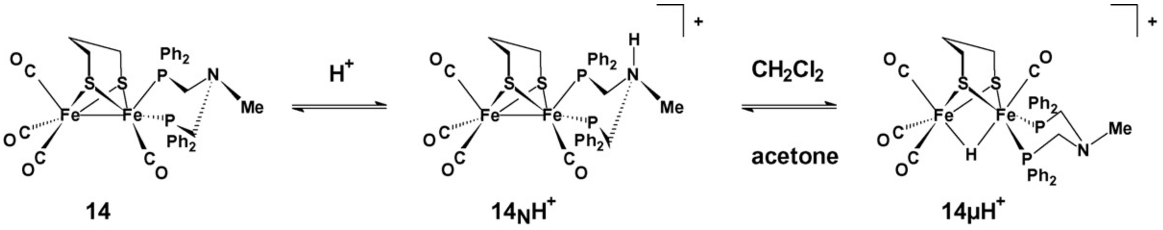
4.3. Proton reduction processes

Most of the diiron dithiolate complexes cited therein have been electrochemically investigated in the presence of acids, however the mechanisms proposed for the catalysis of proton reduction will not all be presented in this section. Instead, we will try to illustrate the diversity of the possible pathways involving hexacarbonyl complexes with different kinds of bridges (dithiolate or diphosphide) in the presence of different acids by focusing on the mechanisms that have been described in most detail. Similarly, only a few recent aspects of proton reduction catalyzed by di- and tetrasubstituted complexes will be presented.

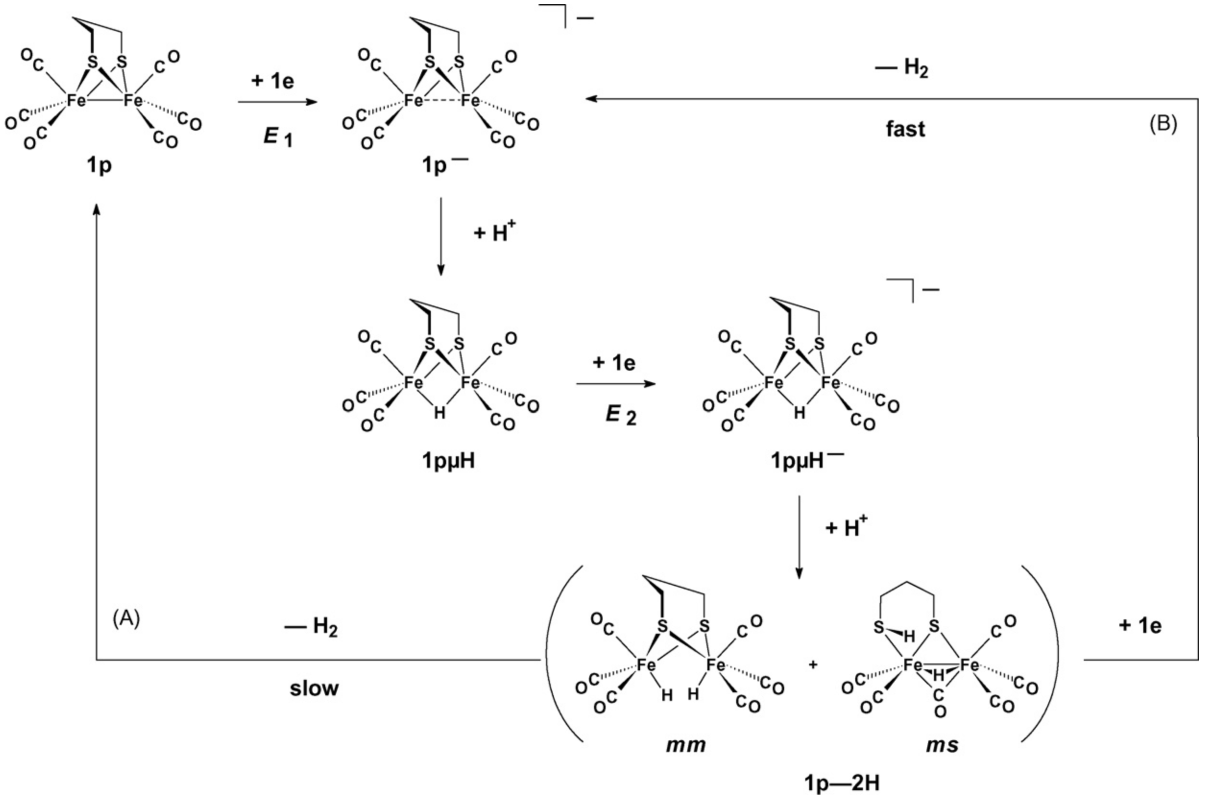
*4.3.1. Proton reduction catalyzed by $[Fe_2(CO)_6(\mu\text{-pdt})]$, **1p***

The reduction of proton catalyzed by $[Fe_2(CO)_6(\mu\text{-pdt})]$ (**1p**) has been investigated in the presence of a weak acid (CH_3CO_2H, pK_a = 22.3 in MeCN [103]) and of a moderately strong acid (HOTs, pK_a ~ 8.3 in MeCN [104]) [71,72]. Since **1p** does not protonate, the catalysis is initiated by the reduction of the complex at a potential around −1.7 V (vs. Fc^+/Fc) in thf [72], which generates **1p$^-$**, a much stronger base than **1p**. While **1p$^-$** is not protonated by acetic acid in MeCN [71], the current increase at −1.7 V in the presence of HOTs in thf is due to the fact that the electrogenerated **1p$^-$** is protonated to **1pμH**, that is easier to reduce than **1p** ($E_2 - E_1 > 0$; ECE process) [72]. The resulting **1pμH$^-$** is in turn protonated to **1p-2H** that slowly releases H_2 (k ca. 5 s^{-1} from digital CV simulations [72]) (Scheme 22, process A).

The second catalytic process (Scheme 22, path B) observed at a potential more negative than process A by ca. 0.25 V is due to the reduction of **1p-2H**. The corresponding anion releases H_2 at a much faster rate and regenerates **1p$^-$** that is the catalytically active species in process B. The different steps were examined by DFT



Scheme 21. Protonation of $[Fe_2(CO)_4(\kappa^2\text{-}Ph_2PCH_2N(Me)CH_2PPh_2(\mu\text{-pdt})]$ (**14**) (from Ref. [36]).



Scheme 22. Proposed mechanisms of proton reduction catalyzed by [$Fe_2(CO)_6$(μ-pdt)] (adapted from Refs. [72,105]).

[105], which confirmed that the release of H_2 by the {$2H^+/2e$}-reduced product **1p-2H** is a slow reaction, while the reduced form of the latter releases H_2 rapidly. The DFT analysis of the second protonation step showed that an initially formed η^2-H_2 ligand would split, which might produce two isomers, one with both protons on the metal centres (*mm* in Scheme 22), and the other with a bridging hydride and a protonated sulfur atom (*ms* in Scheme 22) [105]. Isomers *mm* and *ms* are the twice-protonated forms of the isomers of **1p^{2-}** [63] so that the reduction of **1pμH** and that of **1p$^-$** appear to induce similar structure changes. The chemical reactivity of **1p$^-$** [72] (and that of the ethanedithiolate analogue **1e$^-$** [73]) are responsible for extremely complex reduction processes in the absence of acid (Section 4.1.1). It is clear that in order to prevent this complicated chemistry to occur in acidic medium, the **1p$^-$** anion must be rapidly trapped by proton, which requires that the acid used is sufficiently strong. If it were not the case, as when acetic acid is used, the catalytic process would be supported by product(s) arising from the decay of **1p$^-$**. A detailed analysis of this situation has been recently reported [62].

4.3.2. Proton reduction catalyzed by [$Fe_2(CO)_6${μ-$PhP(CH_2)_3PPh$}], **19**

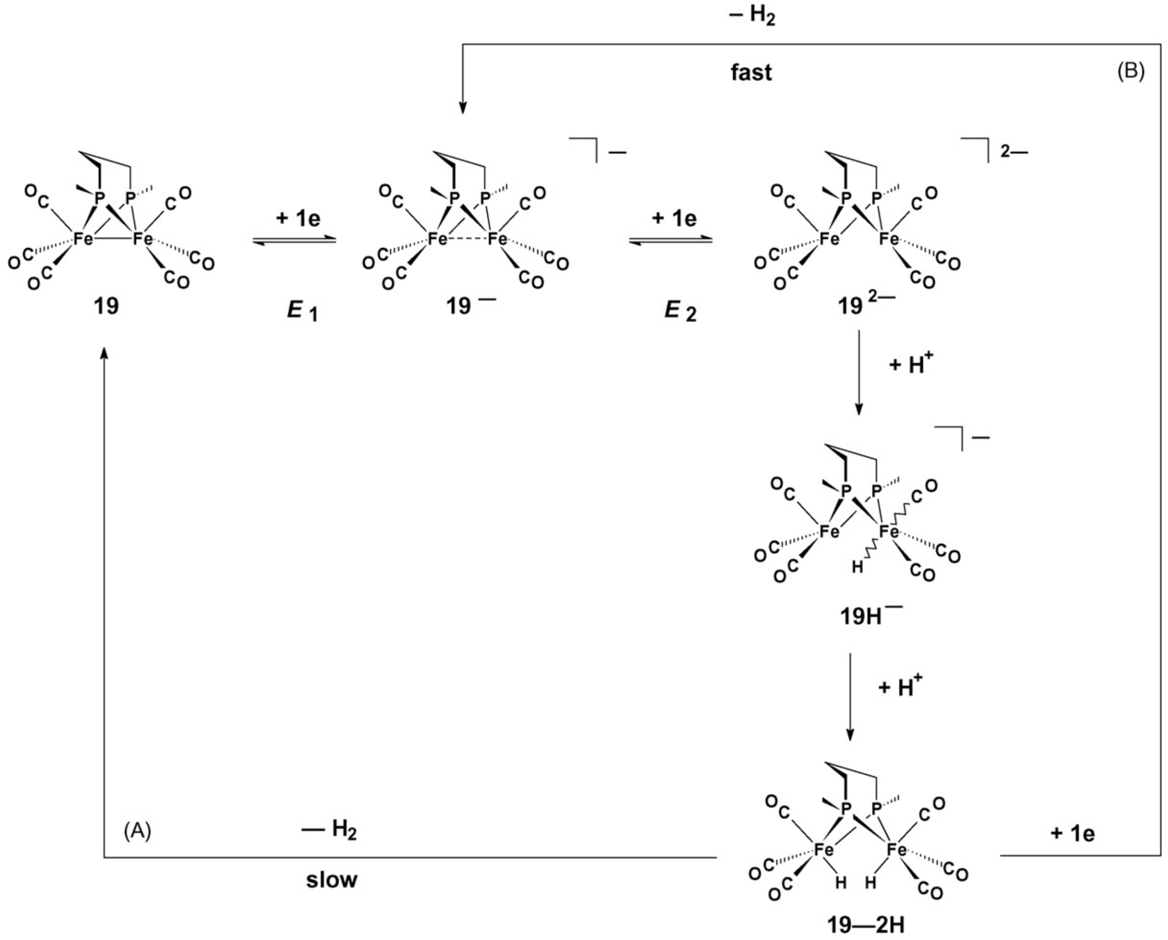
The cyclic voltammetry of the diphosphido-bridged complex **19** in the presence of acid (HOTs) in thf also showed the occurrence of two different catalytic processes around −2 and −2.4 V (vs. Fc^+/Fc). However, the mechanism of the least negative one (Scheme 23, process A) is markedly different from that involved in the case of **1p**, since the reduction of **19** occurs in a single step two-electron process in the presence of HOTs as in acid-free media ($E_2 - E_1 > 0$) [68a]. This results in a mechanism where the two electron transfers are followed by two protonation steps in an EECC process leading to **19-2H** that releases H_2 slowly (path A, Scheme 23) [68a]. DFT calculations on **19-2H** and **1p-2H** indicated that the slower rate of dihydrogen elimination by the former is related to a larger H...H distance in the dihydride [68a]. As for **1p**, the second catalytic process for **19** arises from the reduction of the {$2H^+/2e$}-reduced product (Scheme 23, process B).

A mechanism similar to that of process A (Scheme 23) applies to the catalytic reduction of HOTs by [$Fe_2(CO)_6$(μ-bdt)] (**1b**) at ca. −1.3 V (vs. Fc^+/Fc) in MeCN [106]. In the presence of the substantially weaker acetic acid, a catalytic process is observed around −2 V (vs. Fc^+/Fc) [65]. The difference arises from the fact that in contrast with HOTs, CH_3CO_2H is too weak to protonate the **1bH$^-$** intermediate. The latter must first be reduced to **1bH^{2-}** (around −2 V) before protonation by acetic acid can occur. The release of H_2 upon reaction of **1bH^{2-}** with acid regenerates **1b$^-$** that is the catalytically active species for the reduction of acetic acid [65].

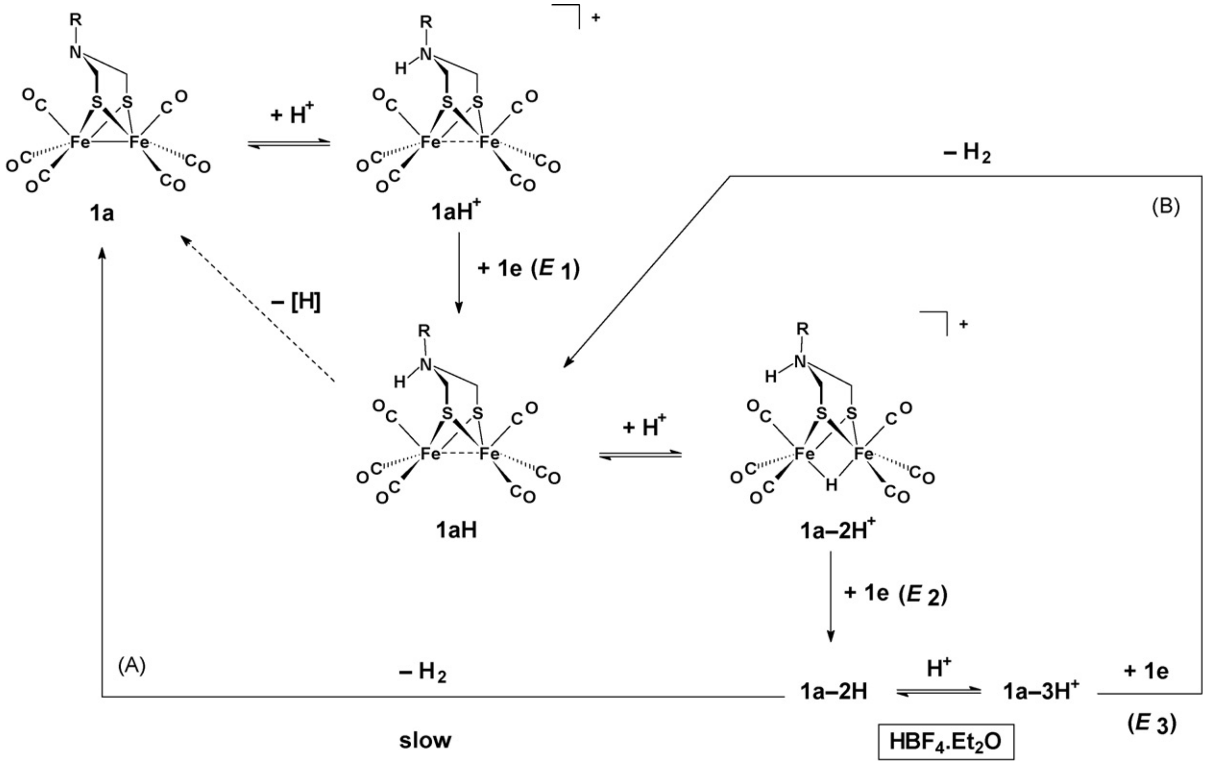
4.3.3. Proton reduction catalyzed by [$Fe_2(CO)_6$(μ-adt)], **1a**

The reduction of protons catalyzed by [$Fe_2(CO)_6${μ-$SCH_2NH(R)CH_2S$}] derivatives was investigated with complexes differing by the nature of the R substituent (R = $CH_2C_6H_4$-4-Br [75]; R = CH_2CH_2OMe, iPr [86]) and divergent conclusions ensued.

Provided a sufficiently strong acid is used (Section 4.2.1), the first step of the catalytic proton reduction in MeCN is the protonation of the amine function. The first electron transfer thus occurs at the potential of the reduction of **1aH$^+$**, that is around $E_1 = -1.2$ V (vs. Fc^+/Fc) (Scheme 24, Table 1). While **1aH** (R = iPr, CH_2CH_2OMe) regenerated **1a** in the absence of acid, it is protonated to **1a-2H$^+$** by $HBF_4 \cdot Et_2O$ or HOTs [86]. The fact that the reduction of **1aH$^+$** followed an ECE process when $HBF_4 \cdot Et_2O$ or HOTs is present demonstrated that **1a-2H$^+$** (R = iPr, CH_2CH_2OMe) reduces at a potential E_2 that is less negative than E_1 ($E_2 - E_1 \geq 0$) [86] (Scheme 24). In contrast, the reduction of the analogue with R = $CH_2C_6H_4$-4-Br was proposed to occur at a more negative potential (ca. −1.4 V) [75]. A second catalytic process is also observed at



Scheme 23. Proposed mechanisms of proton reduction catalyzed by [$Fe_2(CO)_6\{\mu\text{-}PhP(CH_2)_3PPh\}$]; the Ph substituents of the P atoms were omitted (adapted from Ref. [68a]).



Scheme 24. Proposed mechanisms of proton reduction catalyzed by [$Fe_2(CO)_6\{\mu\text{-}SCH_2N(R)CH_2S\}$] complexes **1a** (R = iPr, CH_2CH_2OMe) in MeCN (from Ref. [86]).

-1.4 V for the complex with R = iPr or CH_2CH_2OMe (Scheme 24, process B, $E_3 = -1.4$ V). However, it arises from the reduction of the **1a-3H⁺** complex that is formed only when the strongest acid ($HBF_4{\cdot}Et_2O$) is used. While the conditions for catalytic proton reduction at -1.2 V are met, catalysis is limited to the low concentrations in acid. When the rate of protonation of **1a-2H** by $HBF_4{\cdot}Et_2O$ exceeds the rate of H_2 loss by this species ([acid]/[**1a**] $\geq \sim 3$), process A is superseded by process B [86].

The influence of the acid strength was shown to occur at two different stages. First, the N atom of the bridge was not protonated by CF_3CO_2H (pK_a = 12.65 in MeCN [103]) so that the catalytic reduction of this acid necessitated that complex **1a** be first reduced [86]. Under these conditions the catalytic process observed around -1.55 V is likely to follow mechanisms similar to those shown in Scheme 22 for **1p**. Secondly, HOTs is not sufficiently strong to protonate **1a-2H** efficiently so that no catalysis occurred at -1.4 V for this acid. The second catalytic process in the presence of HOTs was observed at -1.6 V, at which potential the reduction of **1a-2H** was proposed to take place [86]. A recent report on the reduction of protons by hexacarbonyl azadithiolate complexes where the substituent of the N bridgehead atom is C_6H_4I-4 or $C_6H_4C{\equiv}CC_6H_4R$-4 (R = NO_2, NH_2, NMe_2, CHO, CO_2H, CO_2Et, OMe, H, F) showed that these derivatives are not protonated by acetic acid, and provided evidence that the nature of the R group (NO_2, CHO) may influence the reduction steps in acidic media [107].

The above examples illustrate different pathways that are available for proton reduction by hexacarbonyl diiron complexes. These selected examples underline that the nature of the dithiolate or diphosphide bridge affects the potential and mechanisms of the catalytic processes that are also critically dependent on the strength of the proton source.

Process A in Scheme 24 is specific to hexacarbonyl azadithiolate derivatives since it involves the proton on the amine function. On the contrary, the NH proton is probably only a spectator in path B (Scheme 24) that is thus analogous to the processes catalyzed by non-protonatable complexes such as **1p**. When comparing the features of process A for **1a**, **1p** and **19**, there is a thermodynamic advantage to the azadithiolate species but no substantial kinetic difference. For these complexes, the rate of the catalytic process A was proposed to be limited by the slow elimination of H_2 from **1a-2H**, **1p-2H**, and **19-2H** [68a,72,86]. Whether this arises from geometric or electronic reasons is unclear. Numerous studies have shown that the balance between the dihydrogen- and dihydride isomers of mononuclear complexes is subtly dependent on the electronic properties of the metal and co-ligands [42] (see Section 3). On the other hand, the formation of the dihydrogen ligand may be promoted by a structure change when the proton and the hydride are unsuitably disposed, as it may be the case in **1a-2H**. The rate enhancement in process B may then be due to an electron-induced rearrangement that would bring the proton and the hydride in a closer proximity and thus facilitate H. . .H coupling. Both the electronic and geometric problems are susceptible to be solved, at least to some extent, by using substituted complexes that are electron-richer and expected to favour the rotated geometry and the formation of terminal hydrides.

4.3.4. Proton reduction catalyzed by substituted diiron dithiolate complexes

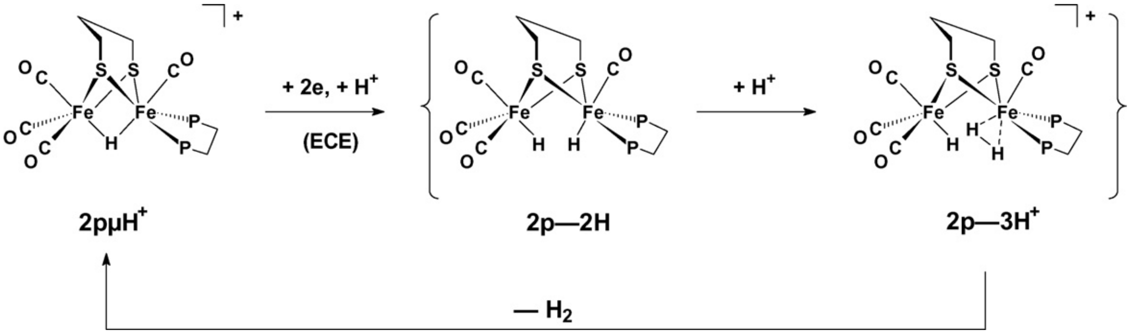
The ability of symmetrically disubstituted adt- or pdt-bridged complexes to catalyze the reduction of both strong and weak acids has been reported [34,82c,88,89,108]. In contrast to the pdt-bridged hexacarbonyl parent, the disubstituted complexes can be protonated by appropriate acids. The pK_a of the Fe–Fe bond in $[Fe(CO)_4(PMe_3)(CN)(\mu\text{-pdt})]^-$ (**9p**) was estimated to sit in the 10.4–11.3 range in MeCN [88a]. The first step of the reduction of a strong acid by **9p** or by $[\{Fe(CO)_2(PMe_3)\}_2(\mu\text{-pdt})]$ (**7p**) is thus the formation of the bridging hydride **9pμH⁺** or **7pμH⁺** [88–90]. In contrast, the reduction of **7p** precedes the protonation by acetic acid (pK_a = 22.3 in MeCN [103]), with the consequence that in this case, catalysis occurs at the potential of the reduction of **7p**, substantially more negative (about 0.75 V) than that of **7pμH⁺** [89]. The reduction of $[\{Fe(CO)_2(PMe_3)\}_2\{\mu\text{-}SCH_2N(R)CH_2S\}]$ (**7a**) was also studied in the presence of a weak or of a strong acid [34,82c,108]. The reduction of acetic acid probably follows the same mechanism as when the pdt analogue **7p** is used [89] since CH_3CO_2H does not protonate **7a** at the amine function nor at the Fe–Fe site [82c,108]. When a stronger acid (HOTf, pK_a = 2.6 in MeCN [103]) is used, cyclic voltammetry showed that catalysis occurred around -1.5 V (vs. Fc^+/Fc), that is a potential assigned to the reduction of the N-protonated species (R = CH_2Ph [34]) or of the bridging hydride (R = $CH_2C_6H_4$-2-Br [82c]). When R = CH_2Ph, no catalysis was noted at the reduction potentials of the Fe(μ-H)Fe isomer (-1.1 V) or of the diprotonated species (-1.0 V) on the timescale of cyclic voltammetry [34]. Nevertheless, slow catalysis was observed at these potentials on the longer timescale of controlled-potential electrolysis [34].

Still little is known on the mechanisms of proton reduction by $[Fe_2(CO)_4(\kappa^2\text{-dppe})(\mu\text{-adt})]$ (**2a**) in MeCN [87]. In the presence of HOTs, two catalytic processes are detected around -1.5 V (vs. Fc^+/Fc), that is the reduction potential of the N-protonated complex **2aH⁺** (process A), and -2.0 V (process B). The substitution of two COs by the chelating dppe that leads to faster kinetics of process A [87] has however a thermodynamic cost since this catalytic process is negatively shifted by ca. 0.3 V upon substitution (**1aH⁺** → **2aH⁺**). Whether the kinetic improvement derives from a better disposition of the proton and the hydride that would result from the proton migration in the one-electron reduced complex **2aH** (see Scheme 18), or arises from a stronger basicity of the substituted complex is not presently known. A recent study of the reduction of the protonated pdt analogue $[Fe_2(CO)_4(\kappa^2\text{-dppe})(\mu\text{-pdt})(\mu\text{-H})]^+$ (**2pμH⁺**) in the presence of HOTs or $HBF_4{\cdot}Et_2O$ showed that the least negative proton reduction process (ca -1.3 V vs. Fc^+/Fc) is actually catalyzed by the μ-hydride cation itself [109]. This was suggested to occur via the protonation of a dihydride intermediate, **2p-2H**, arising from the fact that the reduction of **2pμH⁺** occurs according to an ECE mechanism when acid is present (Scheme 25).

The postulated **2p-3H⁺** species is an analogue of the D_2 intermediate invoked to explain H/D exchange by $[\{Fe(CO)_2L\}_2(\mu\text{-pdt})(\mu\text{-H})]^+$ (L = PMe_3 [90], tBuNC [98]) under irradiation.

It is delicate to draw conclusions concerning the effects of the substitution of two COs by a chelating dppe on the proton reduction processes in this case, since the least negative process is catalyzed by different types of species, that is **1p** [72] (Scheme 22) or **2pμH⁺** [109] (Scheme 25). Nevertheless, the net result of the substitution was to allow both kinetic and thermodynamic (ca. 0. 3 V) improvements [109].

If one now compare the performances of the $[Fe_2(CO)_4(\kappa^2\text{-dppe})(\mu\text{-xdt})]$ derivatives (xdt = adt, **2a** or pdt, **2p**) towards proton reduction, it appears that the least negative catalytic process in MeCN occurs at the reduction potential of the protonated species, that is the N-protonated **2aH⁺** ($E_p^{red} = -1.53$ V vs. Fc^+/Fc [87]) or of the Fe–Fe protonated **2pμH⁺** ($E_{1/2}^{red} = -1.23$ V vs. Fc^+/Fc [109]), respectively. Although the mechanisms are probably different and may proceed at different rates, the proton reduction catalyzed by **2pμH⁺** is thermodynamically more favourable by 0.3 V. On the other hand, N-protonation of **2a** that requires little bond adjustment is faster [110] than the formation of the H-bridged complex **2pμH⁺**, as it has been reported for [{Fe(CO)$_2$(PMe$_3$)}$_2${μ-



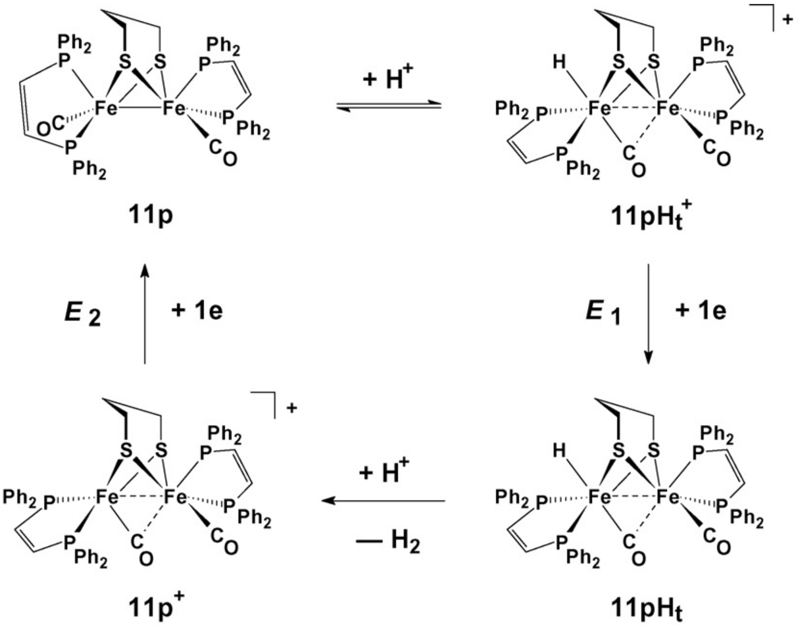
Scheme 25. Proposed intermediates of proton reduction catalyzed by [$Fe_2(CO)_4(\kappa^2$-dppe)(μ-pdt)(μ-H)]$^+$ (**2pμH$^+$**) in CH_3CN (from Ref. [109]).

$SCH_2N(R)CH_2S$}] (**7a**) [34,82c] (Scheme 16). One can thus expect that a complex where an internal base would rapidly trap a proton and rapidly forward it to the metal centre(s) would be both kinetically and thermodynamically profitable [19]. Such appears to be the case of [$Fe_2(CO)_2(\kappa^2$-dppv$)_2${μ-SCH_2NHCH_2S}] (**11a**) [31] (Scheme 17) and [$Fe_2(CO)_4(\kappa^2$-$Ph_2PCH_2N(Me)CH_2PPh_2$] (**14**) in dichloromethane [36] (Scheme 21).

The tetrasubstituted complex [$Fe_2(CO)_2(\kappa^2$-dppv$)_2$(μ-xdt)] (xdt = adt, **11a** or pdt, **11p**) is indeed very promising since its protonation produces a terminal hydride species that is sufficiently long-lived to be studied by cyclic voltammetry in CH_2Cl_2 at mild temperature (0 °C) [31]. Thus, CV of the protonated pdt complex **11pH$_t^+$** (terminal hydride) in the presence of acid showed that the catalytic reduction of protons occurs at a potential (ca. −1.7 V vs. Fc^+/Fc) that is 0.2 V less negative than when the H-bridged isomer (**11pμH$^+$**) is present. The proposed mechanism of proton reduction (Scheme 26) indicates that dihydrogen is released upon protonation of the one-electron reduced intermediate (**11pH$_t$**), which generates the rotated cation **11p$^+$**. The final electron transfer, investigated independently [60b,c], occurs at a potential less negative than the first one by ca. 0.8 V and regenerates the parent complex in the eclipsed geometry (Scheme 26).

The potentials of the reduction of strong or moderately strong acids catalyzed by different [$Fe_2(CO)_{6-n}(L)_n$(μ-dithiolate)] complexes are shown in Fig. 1, and the mechanisms in Schemes 22–26 illustrate the variety of the pathways that can be followed. The mechanism of the reduction of HOTs by **19** (Scheme 23) and also by [$Fe_2(CO)_6$(μ-bdt)] (**1b**) is different from the others since it involves the transfer of two electrons prior to the protonation steps [68a,106]. The other four mechanisms present a common feature, which is that the protonation of the one-electron reduced intermediate shifts the reduction positively so that an ECE mechanism is observed ($E_2 - E_1 \geq 0$) [72,86,109]. A notable difference between the processes catalyzed by **1a**, **1p** and **2pμH$^+$** (Schemes 22, 24 and 25) and that catalyzed by **11p** (Scheme 26) is that the release of H_2 follows the transfer of the second electron in the former three while it precedes the second electron transfer step in the latter [31]. There is here a close analogy with the mechanism of proton reduction catalyzed by the H-cluster (pdt bridge) as proposed from DFT calculations (see Schemes 5 and 26).

The differences observed between the mechanisms in which **2pμH$^+$** and **11pH$_t^+$** take part may be due, at least partly, to the higher reactivity of terminal compared to bridging hydrides towards H_2 formation in acidic media [31,99]. A comparison of the mechanisms of proton reduction by the isomers **11pH$_t^+$** and **11pμH$^+$** would be informative on this question. The reduction of protons by [$Fe_2(CO)_2(\kappa^2$-dppv$)_2${μ-SCH_2NHCH_2S}] (**11a**) has not been detailed so far, but **11a** was reported to be kinetically and



Scheme 26. Proposed mechanisms of proton reduction catalyzed by [$Fe_2(CO)_2(\kappa^2$-dppv$)_2$(μ-pdt)] (**11p**) in CH_2Cl_2 (from Ref. [31]).

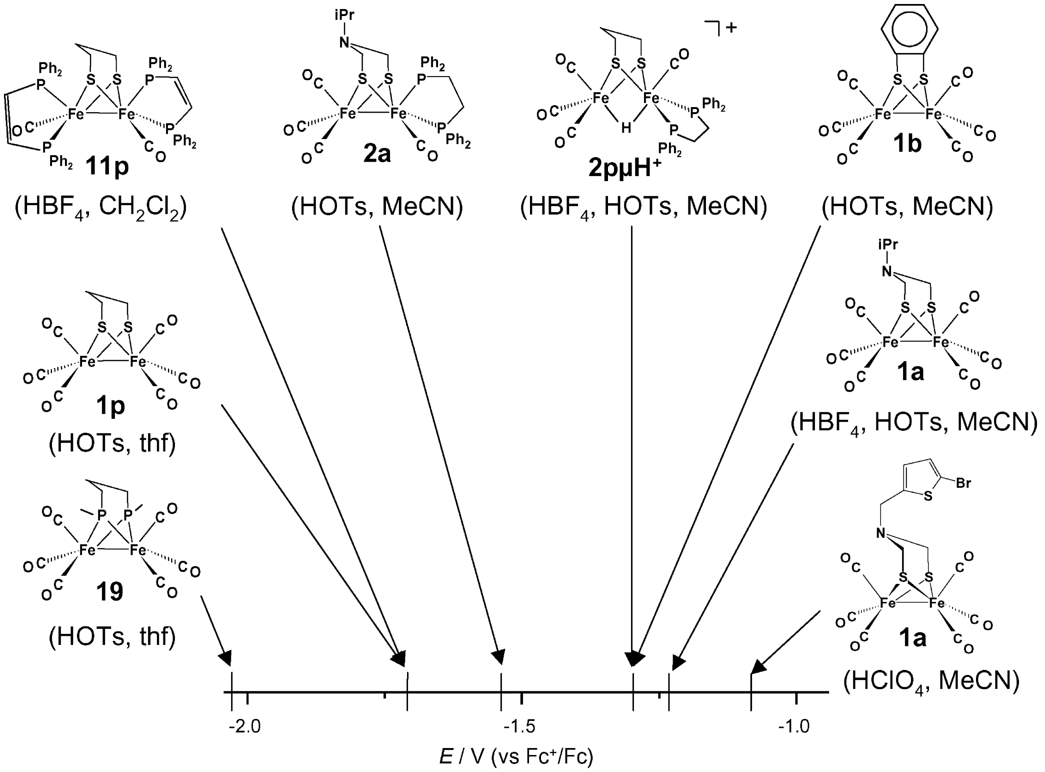


Fig. 1. Potentials of the reduction of HOTs, $HClO_4$ and $HBF_4{\cdot}Et_2O$ catalyzed by different $[Fe_2(CO)_{6-n}(L)_n(\mu\text{-dithiolate})]$ complexes; the conditions (acid, solvent) are indicated (from Refs. [31,68a,72,82d,86,87,106,109]).

thermodynamically a better catalyst than **11p** [31]. One may thus anticipate that the higher efficiency of **11a** as compared to **11p** arises from the fact that the former possesses an internal base in a suitable position to transfer a proton to the metal and to facilitate proton-hydride coupling at a later stage of the process.

5. Conclusion

The knowledge of the chemistry and electrochemistry of diiron dithiolate models of the $[2Fe]_H$ subsite has much improved in the past few years. Some aspects of the reactivity of the synthetic molecules in the presence of acid are in keeping with certain steps that DFT studies suggest as being part in the proton reduction processes catalyzed at the enzyme active site.

The electrochemical studies of hexacarbonyl complexes in the presence of acid have revealed a number of different proton reduction mechanisms and stressed the influence of the acid strength on these processes. Protonation of azadithiolate-bridged complexes at the amine function shifts the reduction of these complexes, and that of protons, positively compared to non-protonatable analogues. However, when the acid used is too weak to achieve N-protonation, this intrinsic property of the azadithiolate derivatives is lost. Most of the synthetic hexacarbonyl compounds present two catalytic proton reduction processes, and it is likely that the most negative one, that involves the transfer of a supplementary electron, is observed as a result of the limitation of the first (least negative) process by a slow chemical reaction. When a sufficiently strong acid is present in excess, the slow chemical step probably consists of the building and/or the release of the H_2 ligand.

Substitution of donor ligands for CO increased the basicity of the diiron centre and allowed its protonation. While treatment of symmetrically disubstituted complexes with an appropriate acid afforded bridging hydride species, terminal hydrides were detected as intermediates upon protonation of unsymmetrically disubstituted analogues, which suggested an easier access to the rotated geometry in the latter. In tetrasubstituted complexes possessing one chelating diphoshine at each metal centre, the stabilization of the terminal Fe–H bond towards isomerization permitted to establish that a terminal hydride reduces at a less negative potential than its bridging counterpart. Furthermore, terminal hydride were also shown to be more reactive towards hydrogenogenesis than the isomeric Fe(μ-H)Fe at the Fe(II)Fe(II) level. With the reasonable assumption that the reactivity order is still valid for a lower oxidation state of the diiron core, the transition from hexacarbonyl to tetrasubstituted derivatives might result in a substantial enhancement of the rate of H_2 release, which is thought to limit the least negative proton reduction process for the former category of compounds. Provided the reduction of HOTs occurs at the same potential as that of HBF_4 (as observed for other complexes), the kinetic gain would have no thermodynamic cost in this case (see **1p** and **11p** in Fig. 1).

In the particular case of symmetrically disubstituted azadithiolate derivatives that can protonate at the Fe–Fe site and at the amine function of the bridge, protonation at the N atom appeared to be faster than formation of the isomer with a bridging hydride. A slow migration of the proton from the N bridgehead atom (kinetic protonation site) towards the Fe–Fe bond (thermodynamic protonation site) was also evidenced. Since the bridging hydride reduces at a potential less negative than the N-protonated isomer, the tautomerization resulted in a positive shift of the reduction potential. Enhancement of the electron-richness of the metal site via further substitution considerably increased the rate of the proton migration while stabilizing the terminal ligation of the hydride ligand. Although no quantitative information is yet available concerning the relative rates of formation of a N–H bond and of a Fe–H bond in analogous $[Fe_2(CO)_{6-n}(L)_n(\mu\text{-xdt})]$ complexes with xdt = adt or pdt, one may infer from the reported studies that one role of the N bridgehead atom in the models, and in the enzyme in the hypothesis of an azadithiolate bridge at the $[2Fe]_H$ subsite, could be to maximize the protonation rate, while a subsequent fast N–H → Fe–H (terminal) migration would minimize the reduction potential of the protonated complex, and consequently, of the proton reduction catalysis.

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