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Organometallic Diiron Complex Chemistry Related to the $[2Fe]_H$ Subsite of $[FeFe]H_2ase$

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Keywords: Dihydrogen / Hydrogenase / Diiron complexes / Diphosphane / Dithiolate / Hydride / Proton

During the last decade, the structure of the subsite of $[FeFe]H_2$ases (or Fe-only hydrogenases) has inspired organometallic chemists to find out whether it was possible to build synthetic molecules, based on sulfur, iron, carbon monoxide and cyanide or surrogates, having the same efficiency for hydrogen production/uptake as that of the enzyme. A short nonexhaustive overview of recent advances in this chemistry is presented.

Introduction

$[FeFe]H_2$ases (or Fe-only hydrogenases) belong to the family of metalloenzymes called hydrogenases, which have the ability to catalyze, with a high efficiency, both hydrogen uptake and production ($2H^+ + 2e = H_2$).[1] Crystal structure determinations of the active site of iron-only hydrogenases,[2] the H-cluster, revealed a unique organometallic assembly (Scheme 1A) reminiscent of long-known (carbonyl)(dithiolato)diiron molecules (Scheme 1B), whose chemistry has been widely developed in the 1980s–1990s.[3] The H-cluster encloses a dimetallic core, the $[2Fe]_H$ subsite, which is connected to a Fe_4S_4 cluster by a cysteinyl bridge coordinated to the proximal iron atom (Fe_p) (the other iron atom is called distal and denoted Fe_d). Different functional states related to the $[Fe^{II}–Fe^{I}]$ (H_{ox}) or $[Fe^{I}–Fe^{I}]$ (H_{red}) systems have been characterized. In both of these systems, the presence of bridging (H_{ox}) or semi-bridging (H_{red}) carbonyl groups is proposed. The axial site (Y) is either vacant or occupied by a light atom ($H^–$) or a small molecule or ion (H_2O or $OH^–$). The nature of the $S–CH_2–X–CH_2–S$ link, where X might be CH_2, NH or O, has not been firmly established to date.

Philippe Schollhammer (left), Professor of Chemistry, obtained his Ph.D. in 1994 at UBO (Université de Bretagne Occidentale, Brest-France) under the supervision of Prof. F. Y. Pétillon. In 2001, during a sabbatical leave, he joined the group of Prof. R. H. Henderson at the University of Newcastle upon Tyne, UK. His current research interests include activation of small molecules by organometallic dinuclear complexes.

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Jean Talarmin (3rd from left), Directeur de Recherche au CNRS, obtained his Ph.D. in 1982 at UBO under the supervision of Prof. J. Courtot-Coupez, and he then spent one year in the group of Prof. Chris Pickett at the Unit of Nitrogen Fixation (University of Sussex, Brighton UK). His research interests mainly involve the electrochemically induced reactivity of transition-metal centres towards the activation of substrates of biological significance.

Frédéric Gloaguen received his undergraduate degree in Brest in 1990 and his Ph.D. in Grenoble in 1994. He worked at the University of Poitiers and was hired by CNRS in 1996. After a sabbatical leave in 2001 spent at the University of Illinois, he joined UBO in 2002. He is interested in all aspects of the catalysis of electrochemical reactions involved in energy storage and utilization.

Jean-François Capon (right), born in 1968, studied chemistry at UBO. He received his Ph.D. in 1995 for work on the reactivity of dimolybdenum allenylidene complexes and carbenium ions species stabilized by adjacent organometallic moieties, performed in the group of Prof. René Kergoat, where he became an assistant professor. His research interests include bioinorganic chemistry and carbene chemistry at the UMR CNRS 6521.

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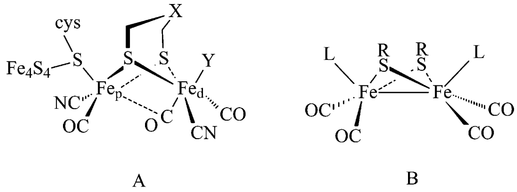
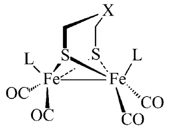


Scheme 1.

Evidently, such a structure has inspired organometallic chemists to find out whether it was possible to build synthetic molecules, based on sulfur, iron, carbon monoxide and cyanide or surrogates, having the same efficiency as that of the enzyme. Some satisfactory, rudimentary or sophisticated structural models involving combinations of propanedithiolato (pdt),[4] azadithiolato (adt),[5] oxadithiolato (odt)[6] or thiadithiolato (tdt)[7] and various sets of terminal ligands[8] (CO, CN^-, RNC, NHC or PR_3) have been synthesized (Scheme 2). These models were proposed in view of getting a better understanding of the chemistry of the active diiron subsite and the minimal structural requirements for hydrogenase activity to provide alternative electrocatalysts for efficient hydrogen production.

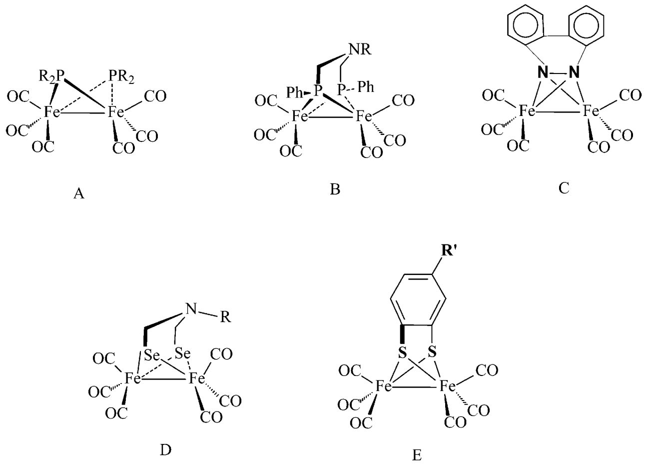


X = CH_2, NR, O, S
L = CO, RNC, CN^-, PR_3, NHC

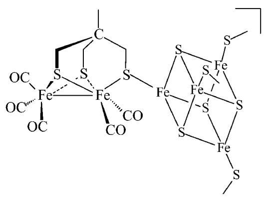
Scheme 2.

This approach has been extended to other carbonyldiiron molecules in which the dithiolato ligand has been replaced by other bridging groups with the hope to obtain new insights into mechanistic features of hydrogenogenesis or to benefit from the favourable electronic effects of these bridges (Scheme 3).[9]

A remarkable mimic of the H-cluster has been elaborated,[10] (Scheme 4) but until now no efficient proton-reduction catalyst based on the [2Fe2S] or [2Fe3S] cores has been obtained. This has raised the question of the differences between the pathways of proton activation at the biological site and those at synthetic mimics.



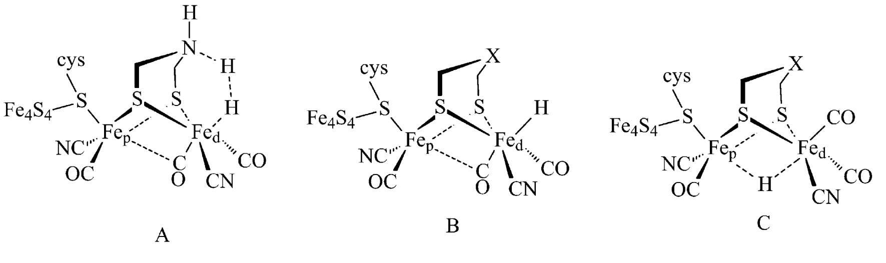
Scheme 3.



Scheme 4.

Numerous theoretical studies have been performed in order to have a better knowledge of the uptake/production of hydrogen by [FeFe]H_2ase.[11] They afforded important insights into the mechanisms of electrocatalytic hydrogen evolution at the diiron subsite as well as the effects of the redox state and ligand characteristics on the structural/electronic behaviour and reactivity of the model compounds. Among the proposed mechanisms, the most attractive involve, depending on the nature of the dithiolato bridge, the formation of key intermediates featuring hydrido–proton interaction (Scheme 5A) or terminal (Scheme 5B) or bridging hydrido ligands (Scheme 5C).

An exhaustive survey of the diiron chemistry related to the active site of the [FeFe]H_2ases is beyond the scope of this microreview that intends only to report some of the results obtained by us and others as well as the strategies developed during the last three years in this very challenging and exciting field of research. Since 2000, several re-

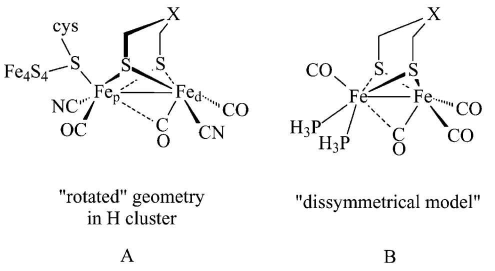


Scheme 5.

views have been published,[3e,3f,3i,3j,4a,12] but most of them have become outdated because of the impressive increase in chemical studies devoted to structural, functional and theoretical modelling of the enzyme H-cluster during the past few years. Electrocatalytic aspects will not be addressed in this microreview. The reader is directed to related articles that have been published previously and to a recent short review by Talarmin et al. focusing on some aspects of the electrochemistry of dithiolatodiiron models.[13]

1. Rotated Geometry of the Active Site and the Use of Chelating Ligands with Diiron Frameworks [2Fe2S]

A promising challenge is to mimic the rotated conformation of the natural site (Scheme 6A) in order to obtain efficient synthetic electrocatalysts for proton reduction. Indeed, this inversion feature would be one of the major structural keys to get a terminal hydrido instead of a less reactive bridging hydrido ligand.[11a,12j] Theoretical studies have proposed recently that the replacement of two carbonyl groups by more electron-donating ligands at one metal centre in (hexacarbonyl)(dithiolato)diiron systems could favour a transition state with an inverted pyramid at one metal centre (Scheme 6B).[14] Such molecules, even though they are far from having the structural features of the natural site, would provide better mimics of the mechanistic functioning of the active site.



Scheme 6.

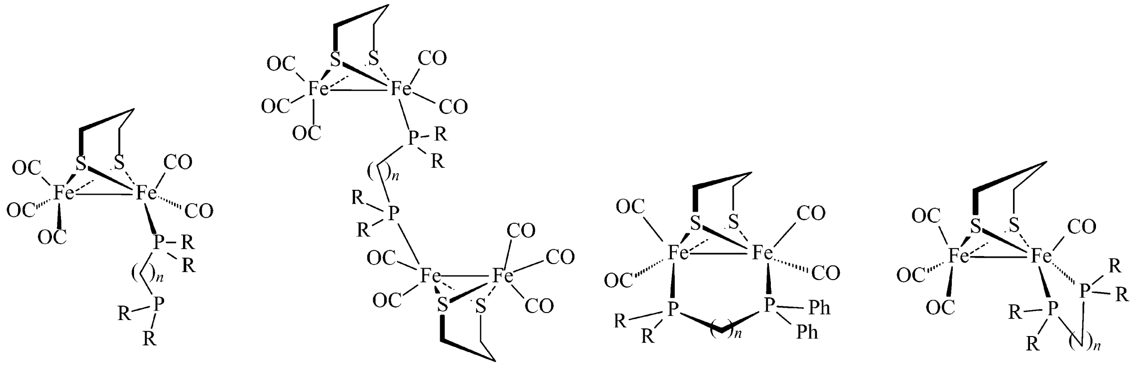
It is worth noting that no dissymmetrically disubstituted species $[Fe_2(CO)_4L_2(\mu\text{-}S_2R)]$ with monodentate ligands has been reported to date. Indeed, typical substitution reactions with hexacarbonyl precursors afford systematically monosubstituted and symmetrically disubstituted species.[3a,3e,3f,8] For this reason, the synthesis of unsymmetrical models requires the use of chelating ligands, such as diphosphane, bis(N-heterocyclic carbene) and phenanthroline, that are able to coordinate to one metal centre in polymetallic systems.[15]

Among the wide family of chelating ligands, diphosphanes $R_2P–R'–PR_2$ appear to be the ideal tool for developing a new generation of dissymmetrically disubstituted diiron systems with, in particular, the possibility to control the electronic and steric behaviour of metal centres as well as their coordination spheres. We and others started a few years ago to investigate the reactivity of hexacarbonyldiiron complexes with propanedithiolato and azadithiolato systems towards diphosphanes.[6a,6b,16]

2. $[Fe_2(CO)_4(\kappa^2\text{-diphos})(\mu\text{-pdt})]$ Compounds and Their Protonation

Depending on both the reaction conditions (solvent, temperature, duration, stoichiometry, use of Me_3NO) and the nature of the diphosphane, the formation of several products can be observed in various yields from mixtures of diphosphane with the hexacarbonyl precursor $[Fe_2(CO)_6(\mu\text{-pdt})]$ (pdt = propanedithiolato). Four main products have been observed (Scheme 7): $[Fe_2(CO)_5(\kappa^1\text{-diphos})(\mu\text{-pdt})]$ (**1**), $[\{Fe_2(CO)_5(\mu\text{-pdt})\}_2(\mu\text{-diphos})]$ (**2**), $[Fe_2(CO)_4(\mu\text{-diphos})(\mu\text{-pdt})]$ (**3**) and $[Fe_2(CO)_4(\kappa^2\text{-diphos})(\mu\text{-pdt})]$ (**4**).

Chelated compounds $[Fe_2(CO)_4(\kappa^2\text{-diphos})(\mu\text{-pdt})]$ (**4**) exist as mixtures of basal–basal (ba–ba) and basal–apical (ba–ap) isomers (Figure 1), which are in slow equilibrium at room temperature. Their ratio depends on the solvent and on the nature of the diphosphane.[16] The typical geometry around each iron atom can be described as a square pyramid supplemented by a metal–metal bond whose length is in the narrow range of 2.5–2.6 Å. The two geometries around each metal are eclipsed.



Scheme 7.

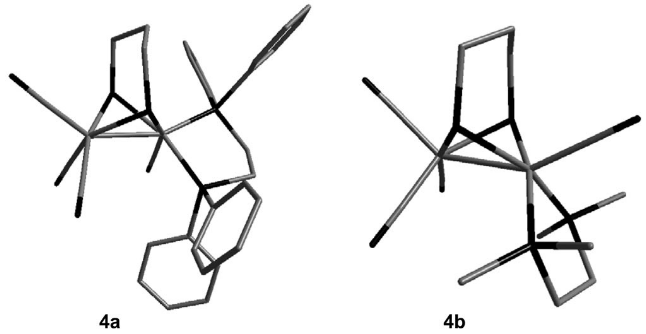


Figure 1. Stick drawing of the molecular structures of the basal–apical isomer of $[Fe_2(CO)_4(\kappa^2\text{-dppe})(\mu\text{-pdt})]$ (**4a**)[16g] and of the basal–basal form of $[Fe_2(CO)_4(\kappa^2\text{-dmpe})(\mu\text{-pdt})]$ (**4b**) [16n] (dppe = $Ph_2P(CH_2)_2PPh_2$, dmpe = $Me_2P(CH_2)_2PMe_2$).

Variable-temperature NMR spectroscopic experiments reveal two well-known fluxional processes in such molecules: (i) the windshield wiper motion of the dithiolato bridge, which can be described as an exchange between the boat- and chair-like conformations of the dithiametallacyclohexane $\{FeS_2C_3\}$ and (ii) the exchange between the basal and apical positions of the two phosphorus atoms of the diphosphane (Scheme 8). At low temperature, four isomers can be detected.

This work has been extended to other chelating groups such as bis(N-heterocyclic carbene),[17] phenanthroline [18] and carbene–pyridine[19] (Scheme 9).

Protonation of chelated diphosphane derivatives $[Fe_2(CO)_4(\kappa^2\text{-diphos})(\mu\text{-pdt})]$ with $HBF_4\cdot Et_2O$ in CH_2Cl_2 at 298 K affords typical,[3j] expected μ-hydrido complexes $[Fe_2(CO)_4(\kappa^2\text{-diphos})(\mu\text{-pdt})(\mu\text{-H})](BF_4)$ (**5**). An X-ray analysis of the chelated bis(diphenylphosphanylethane) (dppe) derivative indicated that protonation induces the reorientation of the chelating dppe to a basal–basal coordination in the protonated form (Figure 2).

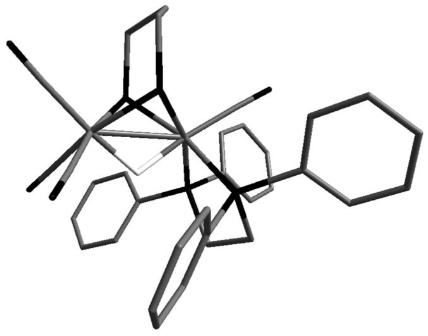
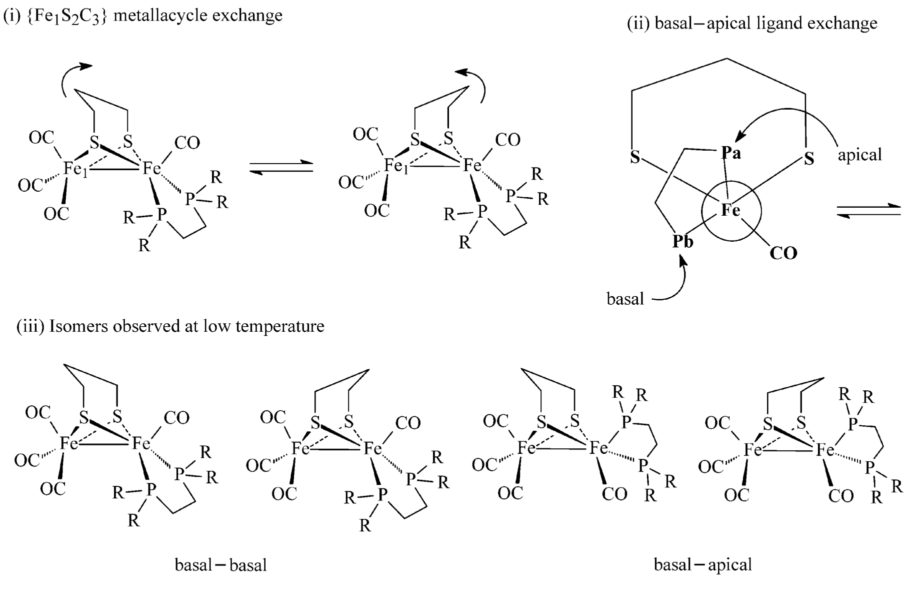
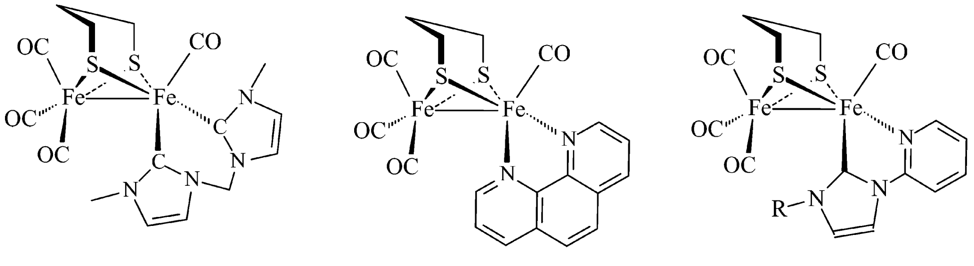


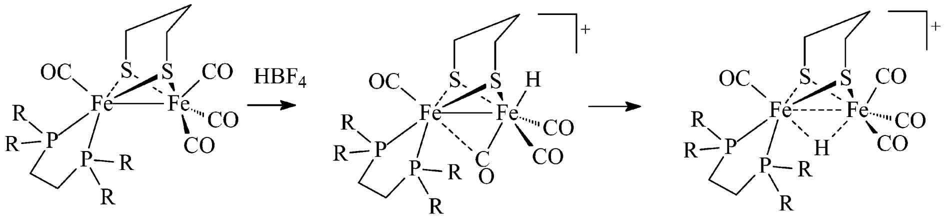
Figure 2. Stick drawing of the molecular structure of $[Fe_2(CO)_4(\kappa^2\text{-dppe})(\mu\text{-pdt})(\mu\text{-H})](BF_4)$ (**5a**).[16g]



Scheme 8.



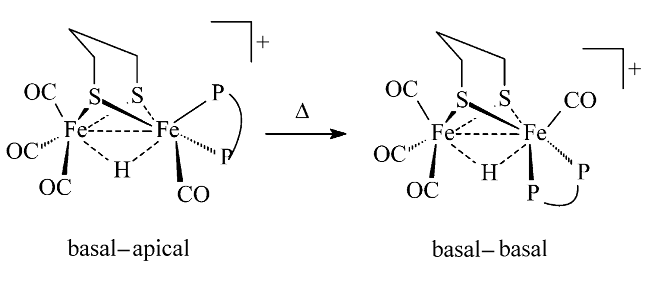
Scheme 9.



Scheme 10.

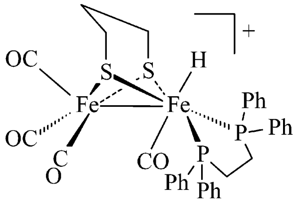
Monitoring these reactions at low temperature by NMR spectroscopy provided evidence for the formation of terminal hydrido intermediates during the process, which led to the μ-hydrido derivative $[Fe_2(CO)_4(\kappa^2\text{-diphos})(\mu\text{-pdt})(\mu\text{-H})](BF_4)$ (Scheme 10). This was the first chemical precedent of a terminal hydrido species resulting from protonation at a single metal atom in dithiolatodiiron models. It is worth noting that the treatment of $[Fe_2(CO)_4L_2(\mu\text{-pdt})]$ (L = PMe_3,[20] $P(OMe)_3$[21]) under the same conditions did not result in any signal that would be typical of a terminal hydrido. This strongly suggests that unsymmetrical disubstitution, combined with sufficiently high basicity of atomic centres in disubstituted tetracarbonyl dithiolato dimetallic complexes $[Fe_2(CO)_4L_2(\mu\text{-pdt})]$, favours an adequate geometrical arrangement at the diiron centre that affords a terminal hydrido species upon protonation. These results were generalized by studies of protonation of species with chelated bis(N-heterocyclic carbene) and phenanthroline ligands.[17,18] In addition, DFT analysis of the substitution of PMe_3 for CO in complexes $[Fe_2(CO)_4(\kappa^2\text{-dppv})(\mu\text{-dithiolato})]$ (dppv = *cis*-$Ph_2PCH{=}CHPPh_2$) pointed out that the electron-richness of the $\{Fe(CO)(dppv)\}$ fragment assists the rotation of the $Fe(CO)_3$ group and the formation of a bridging CO in the transition state.[16c]

The slippage of the diphosphane ligand was also evidenced in these experiments by the observation of the transformation, upon warming of the bridging hydrido complex of the basal–apical form into the basal–basal one (Scheme 11).



Scheme 11.

The basal–apical or basal–basal position of the diphosphane in neutral compounds may have an influence on the stereoselectivity of the protonation. Indeed, a species protonated at the iron atom bearing the diphosphane ligand was detected when the diphosphane was dppe and not dmpe [bis(dimethylphosphanylethane)] (Scheme 12).

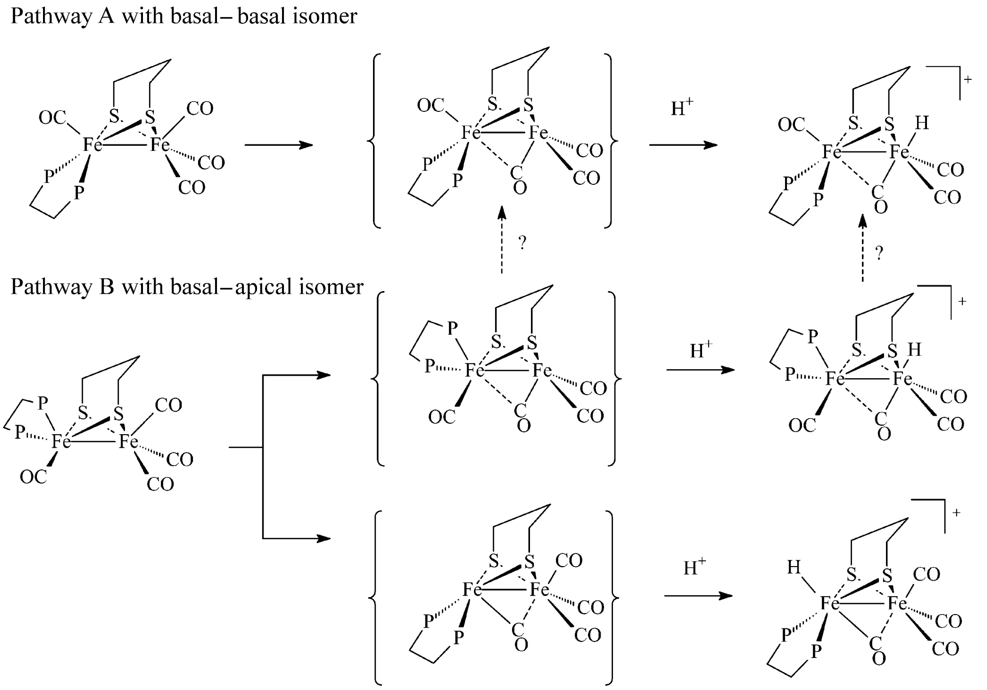


Scheme 12.

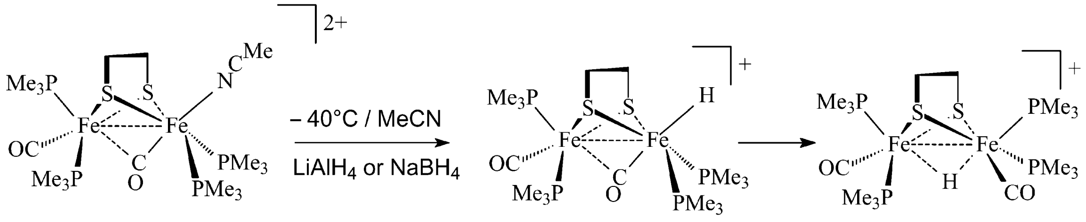
A significant difference between the two neutral chelated complexes lies in the ratio of the basal–apical and basal–basal isomers: in CD_2Cl_2 the (ba–ap/ba–ba) ratio is 5:1 for **4a** and 1:6 for **4b**. A basal–basal conformation of the diphosphane ligand may induce protonation at the $\{Fe(CO)_3\}$ moiety because of the presence of a carbonyl ligand at the basal position on this metal centre, making the inversion of this moiety (pathway A in Scheme 13) easier. In the case of the basal–apical isomer, the presence of a CO ligand at a basal position on the $\{Fe(CO)P_2\}$ moiety may allow its inversion too, making possible two pathways for protonation of the two iron centres (pathway B in Scheme 13).

It is worth noting that the sole example of a structurally characterized dithiolatodiiron species featuring a terminal hydrido ligand has been obtained by treatment of a dimetallic iron(II) precursor with $LiAlH_4$ or $NaBH_4$.[22] Indeed, complex $[Fe_2(PMe_3)_4(NCMe)(CO)(\mu\text{-CO})(\mu\text{-edt})]^{2+}$ (edt = ethanedithiolato) possess a labile acetonitrile group that can be replaced at low temperature by a hydrido ligand to give $[Fe_2H(PMe_3)_4(CO)(\mu\text{-CO})(\mu\text{-edt})]^+$ (Scheme 14). This species is sufficiently stable to be structurally characterized. However, upon warming, it isomerizes into its μ-hydrido form, $[Fe_2(PMe_3)_4(CO)(\mu\text{-H})(\mu\text{-edt})]^+$, which is stable toward protonolysis. The terminal hydrido complex reacts with a proton in the presence of MeCN to regenerate its precursor with formation of H_2.

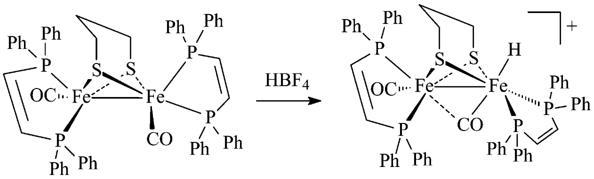
Finally, Rauchfuss et al. reported very recently that protonation of symmetrical dithiolatodiiron(I) bis-chelated complexes $[Fe_2(CO)_2(\kappa^2\text{-}L_2)_2(\mu\text{-dithiolato})]$ (dithiolato = pdt, adt, L = dppv) can occur at a single iron atom and that the isomerization of the terminal hydrido ligand is inhibited both by the basicity of the diiron centre and the steric control of the ancillary ligands in the coordination sphere of the metals (Scheme 15).[16i]



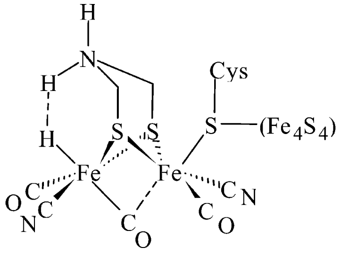
Scheme 13.



Scheme 14.



Scheme 15.



Scheme 16.

3. Introduction of a Pendant Nitrogen Base as Proton Relay in the Second Coordination Sphere

After the study of propanedithiolato compounds, the obvious follow-up to this work was an extension to dissymmetrically disubstituted azadithiolato derivatives. It has been shown that a pendant amine could facilitate the activation of hydrogen,[12k] and a process involving a proton–hydrido interaction in the H-cluster is one of the most attractive in the chemistry of all-iron hydrogenase (Scheme 16).[2d,11j,23]

Two strategies have been developed to check whether it was possible to induce the formation of a specific proton–hydrido interaction in dithiolatodiiron species. First, we have synthesized chelated diphosphaneazadithiolato molecules $[\mathrm{Fe_2(CO)_4(\kappa^2\text{-}dppe)\{\mu\text{-}SCH_2N(R)CH_2S\}}]$ (**6**) (Figure 3A) from their hexacarbonyl precursor in order to investigate the influence of the dissymmetrical disubstitution on the protonation process in the presence of a base in the dithiolato bridge.[16h] We have also introduced a functionalized diphosphane having a pendant amino group, $(PR_2CH_2)_2NMe$, in a propanedithiolato bridging complex (Figure 3B). Such a pendant base, lying in the second coordination sphere of the metal, could play the role of a proton relay, as reported by DuBois et al. in their recent studies on mononuclear nickel and iron complexes.[24]

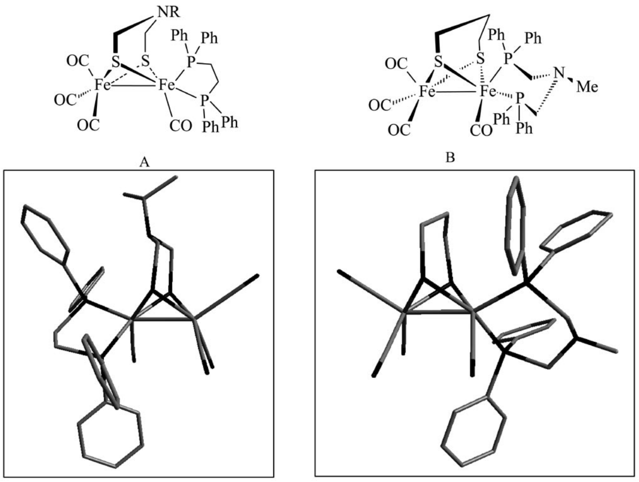
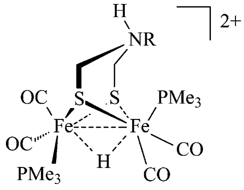


Figure 3. Schematic representations and stick drawing of the molecular structures of $[Fe_2(CO)_4(\kappa^2\text{-dppe})(\mu\text{-}SCH_2N(iPr)CH_2S)](BF_4)$ (**6a**)[16h] (A) and $[Fe_2(CO)_4\{\kappa^2\text{-}(Ph_2PCH_2)_2NCH_3\}(\mu\text{-pdt})]$ (**7**)[25] (B).

Although the formation of metal hydrides has previously indicated that the ligand set provides enough basicity for the Fe–Fe site of the pdt analogue, $[Fe_2(CO)_4(\kappa^2\text{-dppe})\{\mu\text{-}SCH_2N(R)CH_2S\}]$ (R = *i*Pr, CH_2CH_2OMe, CH_2Ph), to undergo protonation, these complexes get protonated exclusively at the N atom of the bridge.[16o] Neither subsequent proton transfer from the azadithiolato bridge to the metal site nor a second protonation occurring at the metal centre were observed. This contrasts with the related reactions reported for symmetrically PMe_3-disubstituted azadithiolato species. Indeed, recent studies have shown that symmetrically disubstituted azadithiolato derivatives $[Fe_2(CO)_4(PMe_3)_2\{\mu\text{-}SCH_2N(R)CH_2S\}]$ could undergo double protonation to afford a species with a bridging hydrido ligand and a protonated N atom (Scheme 17).[26] Nevertheless, even though the chelating ligation of dppe (or 1,10-phenanthroline[16o]) does induce neither a proton–hydrido interaction nor protonation at the metal site at the Fe^IFe^I level, this might arise upon reduction of the N-protonated cation in the presence of excess acid.

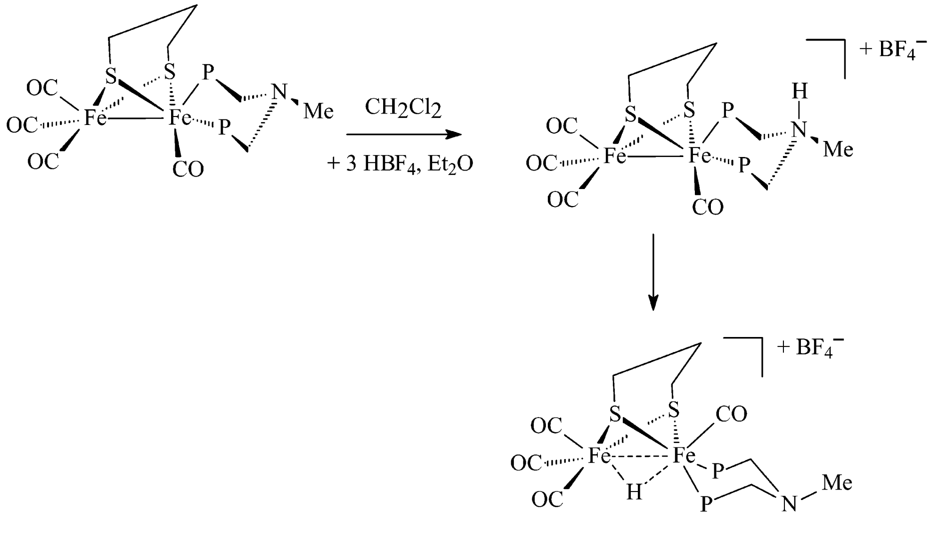


Scheme 17.

Preliminary results show that the first step in the reaction of complex $[Fe_2(CO)_4\{\kappa^2\text{-}(Ph_2PCH_2)_2NCH_3\}(\mu\text{-pdt})]$ (**7**) with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 consists of proton attack at the N atom of the diphosphane backbone. The added proton then moves from the N atom towards a bridging position at the Fe–Fe site when the solution is warmed (Scheme 18). This suggests that the amine group of the diphosphane in $[Fe_2(CO)_4\{\kappa^2\text{-}(Ph_2PCH_2)_2NCH_3\}(\mu\text{-pdt})]$ (**7**) acts as a proton relay and then directs the transfer of the proton.

4. Electron-Transfer-Catalyzed (ETC) Rearrangement of $[Fe_2(CO)_4(\kappa^2\text{-dppe})(\mu\text{-Dithiolato})]$ Where Dithiolato = Propane- or Azadithiolato

The electrochemical investigation of complexes $[Fe_2(CO)_4(\kappa^2\text{-dppe})(\mu\text{-dithiolato})]$ (dithiolato = $SCH_2CH_2CH_2S$, $SCH_2N(R)CH_2S$, R = *i*Pr, CH_2CH_2OMe, CH_2Ph) in MeCN– or thf–Bu_4NPF_6 demonstrated that their reduction



Scheme 18.

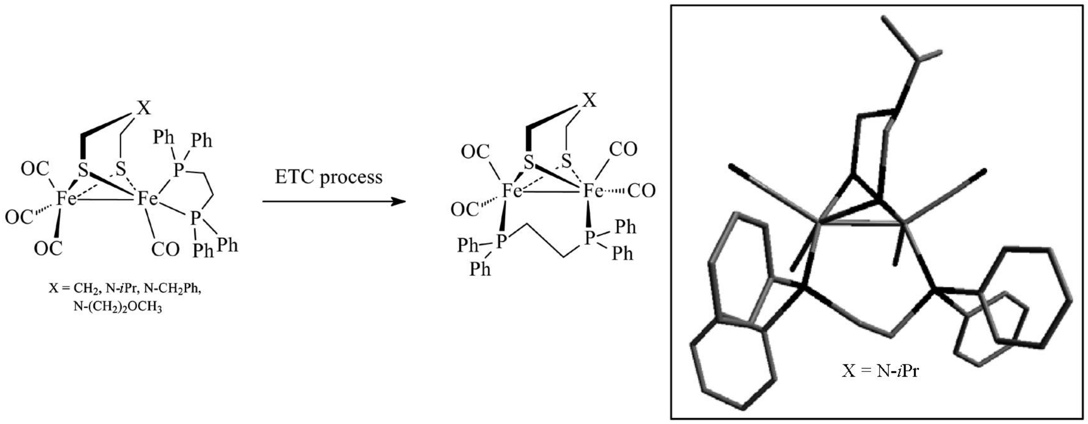
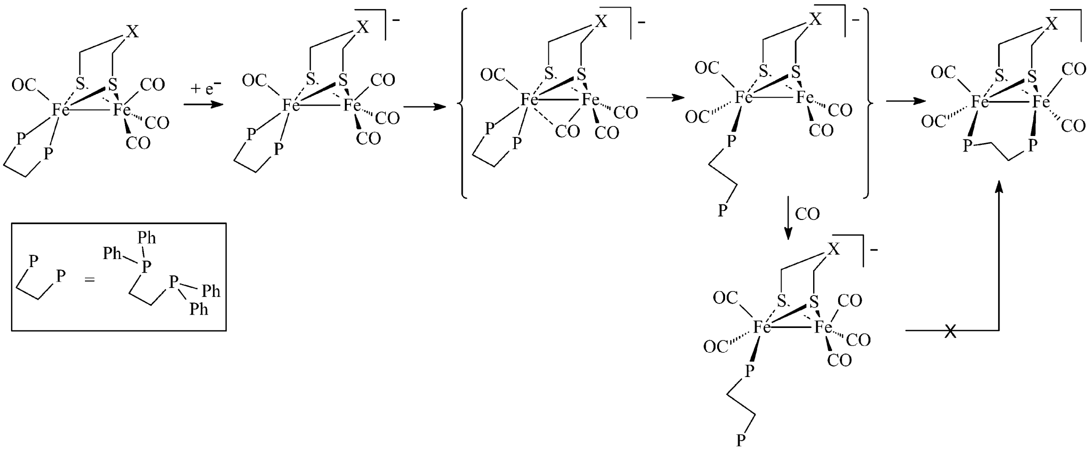


Figure 4. ETC ($\kappa^2 \rightarrow \mu$) isomerization and stick drawing of the molecular structure of [$Fe_2(CO)_4(\mu$-dppe)(μ-SCH_2N(*i*Pr)CH_2S)] (**8**).[16h]



Scheme 19.

gives rise to an electron-transfer-catalyzed isomerization to the symmetrical isomer [$Fe_2(CO)_4(\mu$-dppe)(μ-dithiolato)] (**8**), where the dppe ligand bridges the iron centres (Figure 4).[16h]

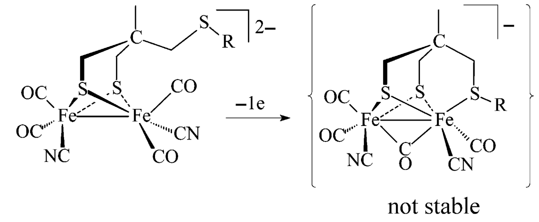
The mechanism of the isomerization may involve an anionic intermediate with a rotated geometry (Scheme 19). Indeed, it is conceivable that the rotation of the {$Fe(CO)_3$} fragment could be facilitated by the weakening of the Fe–Fe bond in the one-electron-reduced form of the complex.[14] The CO group in a bridging or semi-bridging position would contribute to relieve the electronic strain on the disubstituted iron centre. The complete migration of the bridging CO from one iron centre to the other concomitantly with the isomerization of the dppe ligand that could adopt an intermediate dangling coordination can be proposed to rationalize the process. In addition, this mechanism takes into account the deactivation pathway of the ETC isomerization under a CO atmosphere. However, a process involving a Fe–S bond cleavage could not be excluded.[11p]

Electronic properties of chelating ligands as well as their ability to isomerize upon reduction should be decisive for bringing about this catalytic rearrangement. It is worth noting that the complex [$Fe_2(CO)_4(\kappa^2$-I_{Me}–CH_2–$I_{Me})(\mu$-pdt)] (I_{Me}–CH_2–I_{Me} = 1,3-dimethylimidazol-2-ylidene) does not undergo such an ETC isomerization.

5. Mixed-Valent Fe^I–Fe^{II} Systems as Models of the H_{ox} State of H_2ase

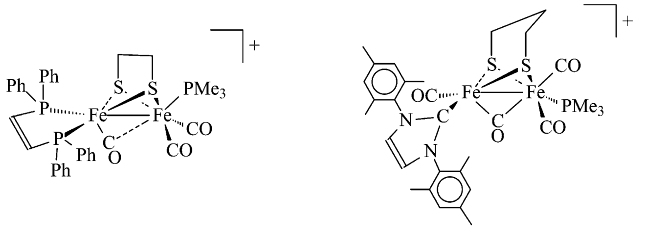
Few examples of Fe^I–Fe^{II} mimics of the H_{ox} state of the enzyme subsite have been described till now. A first evidence of such species was reported by Pickett et al.[27] IR monitoring of the one-electron oxidation of the iron(I) system featuring a [2Fe3S] core, [$Fe_2\{MeSCH_2C(Me)(CH_2S)_2\}(CN)_2(CO)_4]^{2-}$, revealed that this redox process induces the move of one carbonyl group to a bridging position (Scheme 20).

Very recently, Darensbourg, Rauchfuss and their respective groups described the first structural examples of [Fe^IFe^{II}] systems arising from the one-electron oxidation of [$Fe_2(CO)_3(PMe_3)(\kappa^2$-dppv)($\mu$-edt)] (dppv = $Ph_2PCH{=}CHPPh_2$)[16d] and [$Fe_2(CO)_2(PMe_3)$(IMes)(μ-pdt)] [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene][28] (Scheme 21). Their structural results confirmed that the oxidation of



Scheme 20.

$\{Fe^{I}Fe^{I}\}$ to $\{Fe^{I}Fe^{II}\}$ induces a pyramidal inversion of one iron atom that is stabilized by the bridging or semi-bridging carbonyl group. DFT investigation of mixed-valent $Fe^{II}Fe^{I}$ species and their reactivity towards carbon monoxide are now developed.[29]



Scheme 21.

Conclusions

A number of investigations have been devoted during the past decade to the synthesis and study of new molecules inspired by the active sites of the [FeFe] hydrogenases with the goal to achieve efficient electrocatalysts for an alternative production or oxidation of hydrogen. Attempts to model the diiron subsite of all-iron hydrogenases led to the revival of the chemistry of sulfur-rich carbonyldiiron complexes, but few efficient electrocatalysts have yet been obtained. A fine tuning of the structural and electronic features of the coordination sphere of synthetic diiron molecules is required to improve thermodynamically and kinetically their activity towards protons. New structural and chemical precedents are still necessary to gain a better understanding of the mechanisms implied at the molecular level and to achieve this goal. Recent advances since 2005 have involved the use of chelating reagents in order to exert a better control of the steric and electronic properties of artificial diiron frameworks. New generation of models of general formula $[Fe_2(CO)_4(\kappa^2\text{-}L_2)(\mu\text{-dithiolato})]$ and $[Fe_2(CO)_2(\kappa^2\text{-}L_2)_2(\mu\text{-dithiolato})]$ are now attempted.

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