Catalytic H₂ Evolution/Oxidation in [FeFe]-hydrogenase biomimetics: account from DFT on the interplay of related issues and proposed solutions.

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S1. Effect of the nature and number of P ligands installed on the Fe₂ core on ΔE° gap.

Upon 1e reduction, repulsions originated by Et's groups are removed and strain is alleviated, but only in μ-H isomers, in which the breaking of one Fe-H and Fe-Fe bonds occurs, allowing the Fe moieties to move apart. The bulky PEt_3's have thus more space to be accommodated, a situation described as "US" (shorthand form for "unstrained").

In contrast, the reduction of 4-PEt_3 t-H does not alleviate the steric strain, that still affects $Fe^{II}Fe^{I}$ products: the origin of this difference resides in the *μ-CO* that is present *exclusively* in t-H. Conceivably, four P ligands provide each Fe with large amount of electron density to back-donate to the strong π-acceptor CO. Moreover, μ-CO in the 4-PEt_3 t-H is trans oriented to a strong σ donor per Fe, which better funnels electron density into Fe-μC(O)-Fe bonds. These strong interactions hold together the two Fe subunits, impeding to release repulsions, in sharp contrast to what occurring in μ-H isomers.

The non-obvious opposite reductive behavior (ΔE°gap >0) in similar 4-PMe_3 has been justified by a lower crowding experienced by PMe_3 vs PEt_3, once the two ligands have been installed in metal coordination.

S2. Effect of a strong σ-donor apically bound at Fe on ΔE° gap.

As an example, replacing CH_3S^- at Fe_p by a CO leads to ΔE°gap >0, regardless of the presence of four PEt_3 in the other coordination positions. It can be noted that the most stable isomer in such case features the CO in Fe basal position. As mentioned before, L_{ap} is crucial to convey further electron density into Fe orbitals, that in turn π-back donate it to the bridging CO. This makes one Fe-CO bond stronger in t-H.

Notably, models with a neutrally charged σ-donor (e.g., NHC) replacing CH_3S^- still feature ΔE°gap < 0, despite being starting t-H not subject to steric destabilization (US). Structural parameters (Fe-H, Fe-Fe and Fe-P distances) clearly show that t-H's with neutral L_{ap} have the two Fe subunits quite separated already at the $Fe^{II}Fe^{II}$ state, thus resulting *stable before and after reduction.* This is compatible with the less electron density pushed by neutral ligands into the Fe-μCO bond in trans to bis-carbene (L_{ap}).

The σ-donating power of L_{ap} and the Fe-μCO-Fe bond strength are directly related and this explains why diferrous L_{ap} = CH_3S^- instance features compact and strained structure, whereas L_{ap} = (neutral donors) do not. Unexpectedly, species with L_{ap}=CO (weak σ-donor; strong π-acceptor) feature the same US t-H structure as L_{ap} = NHC, but opposite reductive behavior.

Unexpectedly (see the body text of the main discussion), species with L_{ap}=CO (weak σ-donor; strong π-acceptor) feature the same US t-H structure as Lap=NHC, but opposite reductive behavior, i.e., ΔE°gap >0. The apparent contradiction requires considering the electronic properties that coordinated L's have on the Fe-Fe, rather than the Fe-μCO-Fe bond strength (see Scheme S1). Although in ferrous species the 18-electron rule would formally require a genuine Fe-Fe bond formation, one may argue that in very electron rich metal cores (as in the case of L_{ap}=donors) such requisite is less strictly necessary, due to some compensation brought by strong donors. In contrast, with CO, Fe is clearly electron poorer, so that the electron counting entails Fe-Fe bond formation. In such case, therefore, the steric strain in t-H is essentially due to a relatively strong Fe-Fe bond. The subsequent reduction alleviates the strain, because the Fe-Fe bond is relatively weaker than the Fe-CO bond of the more electron rich derivatives.
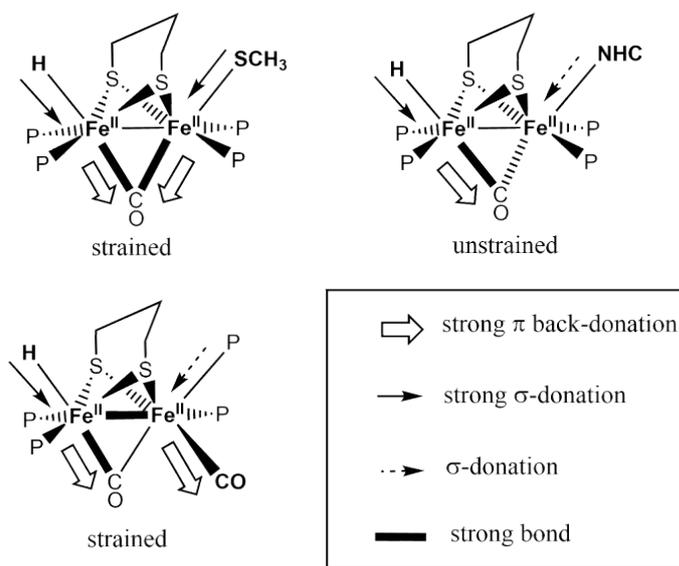
Scheme S1. Electron donating/accepting influence on key bonds that govern the repulsive strain presence (absence) in oxidized diiron structures.

A generalized picture of the "strain release/retention" model is: $\Delta E°$ gap $</>$ 0 ultimately depends on change/retention that the initial strain state (S/US) of t-H and μ-H of a given species manifests upon reduction. As an example, $\Delta E°$ gap < 0 can be obtained both by [(S→US)$_{\mu H}$/(S→S)$_{tH}$] and "[(S→US)$_{\mu H}$/(US→US)$_{tH}$]".