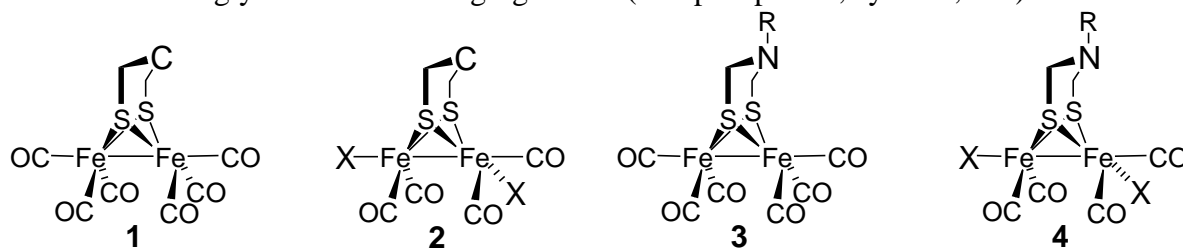


Mechanisms for Electrocatalytic Proton Reduction by Biomimetic Models of the Iron Hydrogenase Active Site

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Biomimetic models of the iron hydrogenase active site are promising candidates for the development of homogenous proton reduction catalysts. Over the last five years, numerous models have been synthesized and many of them have proven to be catalysts for electrochemical hydrogen production. The complexes can mainly be divided into four classes, dependant on the nature of the central atom of the dithiolate bridge (carbon or nitrogen) and on the presence or absence of strongly electron donating ligands X (X = phosphines, cyanide, etc.).



Inclusion of a nitrogen heteroatom in the dithiolate bridge offers a basic site in close proximity to the diiron centers, whereas the Fe-Fe bond itself can be protonated in the structures of type **2** and **4** due to the fact that the electron density is increased by electron donating ligands. The different model complexes **1-4**, all of which are electrochemical proton reduction catalysts, can thus enter their respective catalytic cycle in different protonation states.

In this contribution, we wish to present the latest results we have obtained for complexes of type **3** and **4**. In contrast to our previous report, we have discovered that complex **3** is capable to generate hydrogen at milder potential than originally believed. Complex **4**, which can enter the catalytic cycle in a double-protonated state, generates hydrogen at an even milder potential. Based on our latest findings, we are able to present new mechanistic proposals for the different catalysts.