

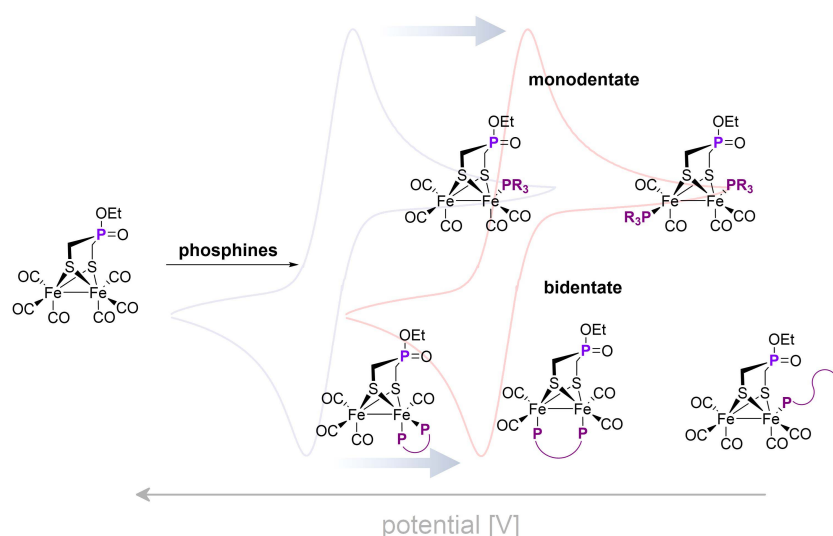
PHOSPHINE-SUBSTITUTED DIIRON PHOSPHADITHIOLATE COMPLEXES

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The H-cluster of the redox enzymes known as [FeFe] hydrogenases plays a crucial role in the H₂ production. It contains a secondary amine group, serving as proton-transferring shuttle between the active site and the protein's proton channel.^[1] Despite the intensive research regarding the function of [FeFe] hydrogenases, the exact states of the subsite and the course of the actual catalytic cycle are still controversial. To elucidate the catalytic processes of the H-cluster such as proton-coupled electron transfer or pure electron transfer and the states that are formed under these conditions, various mimics were synthesized and analyzed using numerous spectroscopic techniques.^[1] A recently synthesized model of the active side comprises a higher homologue of nitrogen, i.e. phosphorus, in the dithiolate linker, which opens up new paths for investigation of the H₂ production.^[2] We further investigated the influence on the electronic properties of the iron centers by introducing phosphines as ligands, which can lead to different reactions compared to these of the native H-cluster. The obtained complexes were characterized by IR spectroscopy and X-ray diffractometry as well as electrochemical investigation, showing differences depending on the phosphines introduced and their number.



Scheme 1. Schematic overview of the different phosphine bond modes obtained and the influence on the electrochemical behavior.

[1] Kleinhaus, J. T.; Wittkamp, F.; Yadav, S.; Siegmund, D.; Apfel, U.-P.; *Chem. Soc. Rev.*, **2021**, *50*, 1668.

[2] Wittkamp, F.; Boydas, E. B.; Roemelt, M.; Apfel, U.-P.; *Catalysts*, **2020**, *10*, 522.