Synthesis of a DuBois-type Ph-PNP-Ligand by Metal Catalysis

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Biomimetic approaches are a common way to achieve highly active catalysts for sunlight induced water splitting. Structural investigations on natural hydrogenases revealed a motif called proton-relay which acts as a proton shuttle to the catalytic active metal center.[1] One of the first tries to mimic this motif was done by Yang et al., who synthesized various PNP-ligands.[2] However, in the last four years new ligands with this PNP-structure were synthesized and investigated by the working group of Peter Brüggeller.[3] During this period four different modifications on the amine (methyl, ethyl, *iso*-propyl and benzyl) could be synthesized, but the phenyl modification was not accessible by common synthetic approaches. The usual reaction pathway resulted only in the corresponding PN-ligand and it seems that the aniline has a too low nucleophilicity to react further to the PNP-ligand when using dianisylphosphine (figure 1). Nevertheless, the newly synthesized PN-ligand was coordinated to different transition metals (Pt, Pd, Ni, Co) and the crystal structure of these complexes revealed that two PN-ligands can react further to the PNP-ligand directly on the metal in case of Pd, Ni and Co (figure 2 left). On the contrary, to the Pt-complex still two PN-ligands are coordinated (figure 2 right).

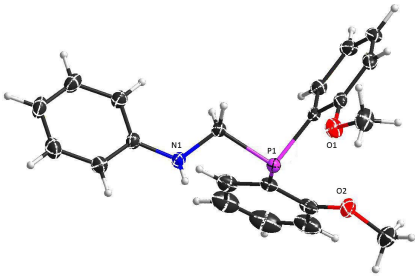

Figure 1: crystal structure of PN-ligand

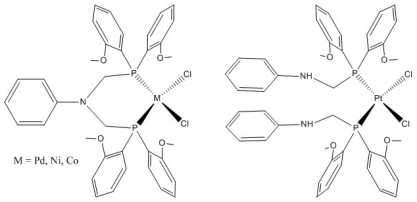

Figure 2: different structures depending on the metal centers

[1] A. Silakov, B. Wenk, E. Reijerse, W. Lubitz, *Phys. Chem. Phys. Chem., PCCP* **2009**, *11*, 6592

[2] J. Y. Yang, R. M. Bullock, M. R. DuBois, D. L. DuBois, *MRS Bull.* **2011**, *36*, 39

[3] W. Viertl, J. Pann, R. Pehn, H. Roithmeyer, M. Bendig, A. Rodríguez-Villalón, R. Bereiter, M. Heiderscheid, T. Müller, X. Zhao, T. S. Hofer, M. E. Thompson, S. Shi, P. Brüggeller, *Faraday discussions* **2019**, Advance Article DOI: 10.1039/c8fd00162f