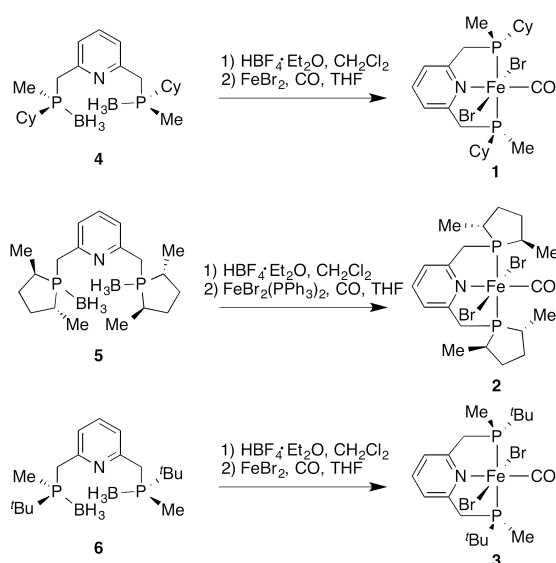


Iron(II) Complexes of Chiral, C₂-Symmetric, P- or C-Stereogenic PNP Pincer Ligands and their Application in the H₂ Hydrogenation of Ketones

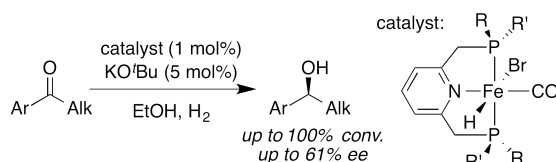
R. Huber¹, A. Passera¹, A. Mezzetti^{1*}

¹ETH Zürich

Chiral pincer ligands for iron(II) have been recently developed and applied in the direct H₂ hydrogenation of ketones.^{1,2} We report here the preparation and characterization of iron(II) dibromocarbonyl complexes **1**, **2**, and **3** of the type [FeBr₂(CO)(L)], where L is one of the tridentate, P- or C-stereogenic, C₂-symmetric PNP pincer ligands (*S_p,S_p*)-2,6-bis((cyclohexyl(methyl)phosphanyl)methyl)pyridine (**4**), 2,6-bis(((2*R*,5*R*)-2,5-dimethylphospholan-1-yl)methyl)pyridine (**5**), or (*S_p,S_p*)-2,6-bis(*tert*-butyl(methyl)phosphanyl)methyl)pyridine (**6**).



The corresponding bromocarbonylhydride complexes were prepared by addition of NaBHET₃ (1 equiv.) and either isolated or directly used in catalysis. They were active in the direct H₂ hydrogenation of a variety of arylalkyl ketones under 50 bar of H₂ pressure and in the presence of KO^tBu as base. The enantioselectivity reached 61% ee with (*S*)-1-(2-naphthyl)ethanol. The origin of enantioselectivity was investigated using DFT calculations.



[1] A. Zirakzadeh, K. Kirchner, A. Roller, B. Stöger, M. Widhalm, R. H. Morris *Organometallics* **2016**, 35, 3781.

[2] S. A. M. Smith, P. O. Lagaditis, A. Lüpke, A. J. Lough, R. H. Morris *Chem. Eur. J.* **2017**, DOI: 10.1002/chem.201701254.