Iron(II) Complexes of Chiral, C_2-Symmetric, P- or C-Stereogenic PNP Pincer Ligands and their Application in the H_2 Hydrogenation of Ketones

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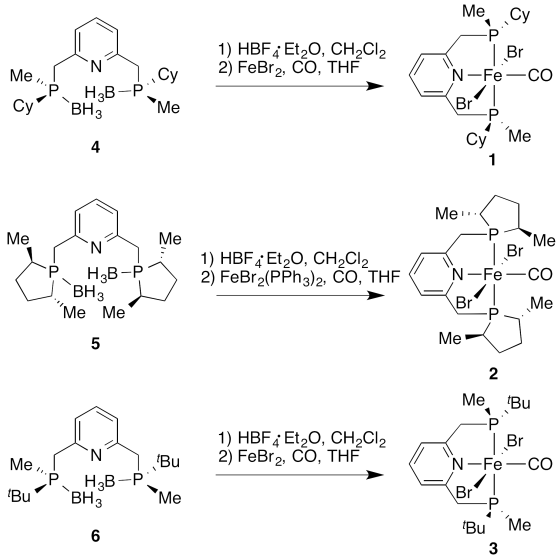
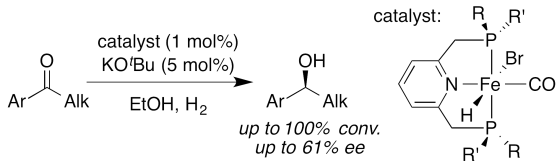
Chiral pincer ligands for iron(II) have been recently developed and applied in the direct H_2 hydrogenation of ketones.[1,2] We report here the preparation and characterization of iron(II) dibromocarbonyl complexes **1**, **2**, and **3** of the type $[FeBr_2(CO)(L)]$, where L is one of the tridentate, P- or C-stereogenic, C_2-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 $NaBHEt_3$ (1 equiv.) and either isolated or directly used in catalysis. They were active in the direct H_2 hydrogenation of a variety of arylalkyl ketones under 50 bar of H_2 pressure and in the presence of KO^{t}Bu 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.