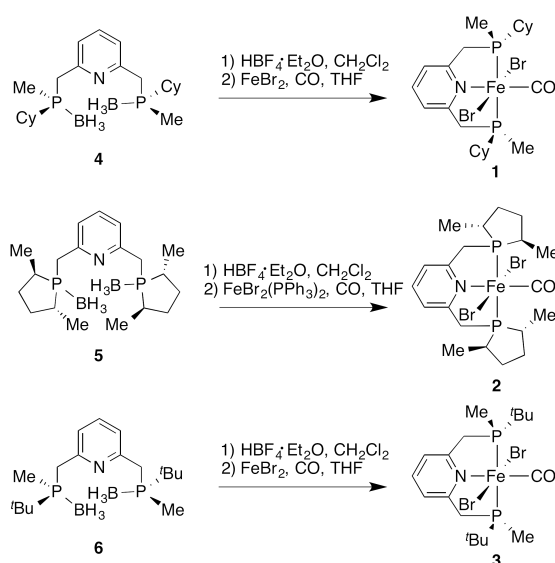


## Iron(II) Complexes of Chiral, C<sub>2</sub>-Symmetric, P- or C-Stereogenic PNP Pincer Ligands and their Application in the H<sub>2</sub> Hydrogenation of Ketones

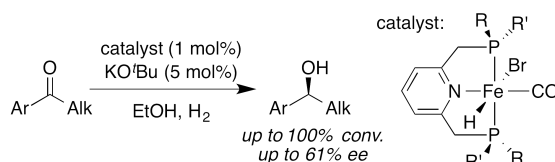
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Chiral pincer ligands for iron(II) have been recently developed and applied in the direct H<sub>2</sub> hydrogenation of ketones.<sup>1,2</sup> We report here the preparation and characterization of iron(II) dibromocarbonyl complexes **1**, **2**, and **3** of the type [FeBr<sub>2</sub>(CO)(L)], where L is one of the tridentate, P- or C-stereogenic, C<sub>2</sub>-symmetric PNP pincer ligands (*S<sub>p</sub>,S<sub>p</sub>*)-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<sub>p</sub>,S<sub>p</sub>*)-2,6-bis(*tert*-butyl(methyl)phosphanyl)methyl)pyridine (**6**).



The corresponding bromocarbonylhydride complexes were prepared by addition of NaBHET<sub>3</sub> (1 equiv.) and either isolated or directly used in catalysis. They were active in the direct H<sub>2</sub> hydrogenation of a variety of arylalkyl ketones under 50 bar of H<sub>2</sub> pressure and in the presence of KO<sup>t</sup>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.