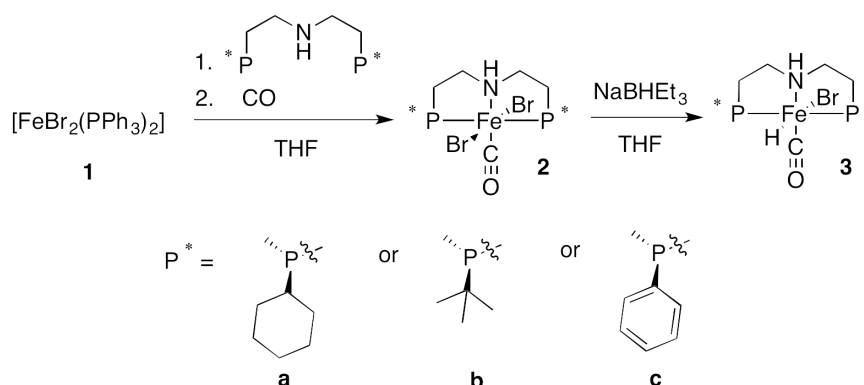


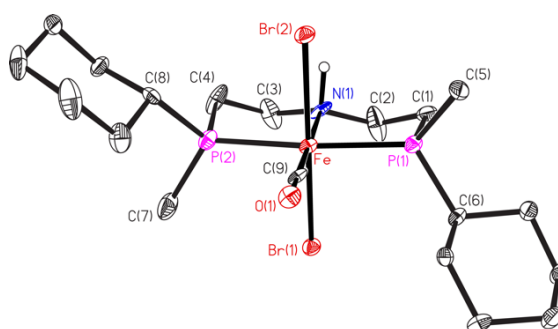
## Chiral Iron(II) PN(H)P Pincer Complexes for the Asymmetric Hydrogenation of Ketones

E. Gubler<sup>1</sup>, A. Mezzetti<sup>1\*</sup><sup>1</sup>ETH Zürich

Iron(II) complexes of PN(H)P pincer ligands are active catalysts in the direct hydrogenation of ketones,<sup>1</sup> and also enantioselective versions appeared.<sup>2,3</sup> Based on our long-term experience in the synthesis of chiral phosphine ligands, we prepared enantiopure, *P*-stereogenic, *C*<sub>2</sub>-symmetric PN(H)P pincer ligands and their iron(II) complexes, which will be tested in the asymmetric hydrogenation of ketones.



The enantiopure pincer ligand **a** bearing cyclohexyl and methyl substituents on each P atom was obtained in a 7-step synthesis from PC<sub>3</sub>. Starting from the iron(III)-free iron precursor **1** and ligand **a**, the blue precatalyst [FeBr<sub>2</sub>(CO)(**a**)] (**2a**) formed immediately upon setting the reaction mixture under CO atmosphere (1.1 bar). Complex **2a** (see X-ray structure below) was converted into the hydride **3a**, which showed good activity but low selectivity (22% ee) in the hydrogenation of acetophenone at room temperature in toluene. We are currently preparing ligands with sterically more demanding dialkylphosphine donors (such as **b**) and arylalkylphosphine donors (such as **c**) to improve the enantioselectivity.



[1] E. Alberico, P. Sponholz, C. Cordes, M. Nielsen, H. Drexler, W. Baumann, H. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2013**, *52*, 14162.

[2] S. A. M. Smith, P. O. Lagatidis, A. Lüpke, A. J. Lough, R. H. Morris, *Chem. Eur. J.* **2017**, *23*, 1.

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