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

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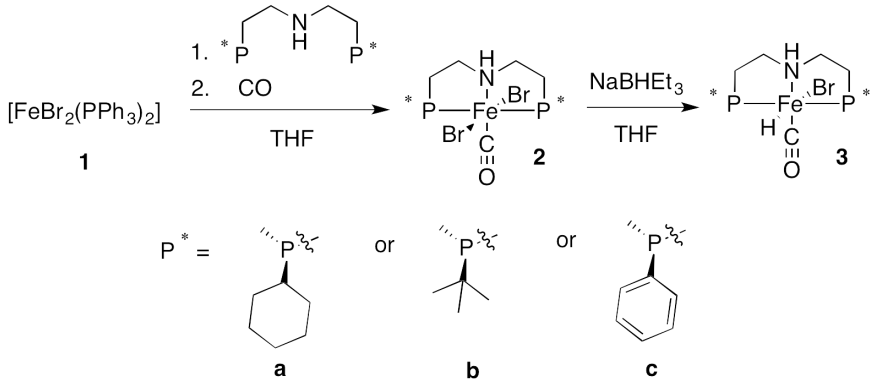
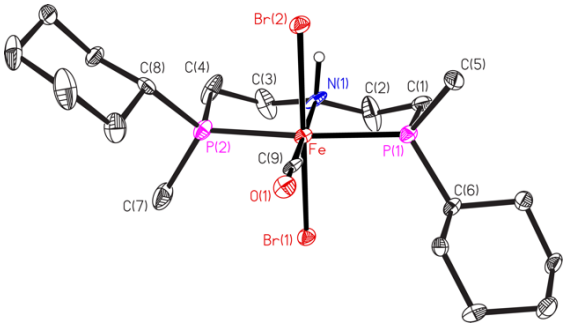
Iron(II) complexes of PN(H)P pincer ligands are active catalysts in the direct hydrogenation of ketones,[1] and also enantioselective versions appeared.[2,3] Based on our long-term experience in the synthesis of chiral phosphine ligands, we prepared enantiopure, *P*-stereogenic, C_2-symmetric PN(H)P 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 PCl_3. Starting from the iron(III)-free iron precursor **1** and ligand **a**, the blue precatalyst [$FeBr_2$(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.



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