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Chiral Ruthenium Aminophosphine and Phosphine Iminopyridine Complexes: Synthesis and Application to Asymmetric Hydrogenation and Transfer Hydrogenation

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Abstract : Aminophosphines are a privileged class of ancillary ligands with emerging importance in homogeneous catalysis. The unique combination of soft phosphorus (P) and hard nitrogen (N) centres affords a variety of transition metal complexes as potential pre-catalysts for synthetically useful reactions. Herein three ligand systems will be reported; two bidentate ligands - (S)-8-(diphenyl-phosphino)-1,2,3,4-tetrahydronaphthalen-1-amine, (S)THNANH2, and (Rc)-1-((Sp)-2-diphenylphosphino) ferrocenylethylamine, (RcSp)PPFNH2 - and a tridentate (Rc)-1-((Sp)-2-diphenylphosphino) ferrocenylimino-pyridine, (RcSp)PPFNNH2 ligand; the latter prepared from the condensation of selected ferrocene aminophosphines with pyridine-2-carboxaldehyde. Suitable combinations of these aminophosphine ligands with ruthenium precursors have afforded highly efficient systems for the asymmetric hydrogenation and transfer hydrogenation of selected ketones in 2-propanol. The Ru-(S)THNANH2 precatalyst was the most efficient in the asymmetric hydrogenation of selected ketones with 100% conversions within 4 hours at a catalyst loading of 0.1 mol%. The Ru-(RcSp)PPFNNH2 precatalyst was the most efficient in the asymmetric transfer hydrogenation of the ketones with conversions as high as 98% with 0.1 mol% catalyst. However, the enantioselectivities were generally low.

Keywords: aminophosphine, asymmetric hydrogenation, homogeneous catalysis, ruthenium (II), transfer hydrogenation

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