Highly Enantioselective Rhodium-Catalyzed Hydrogenation with Monodentate Ligands

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The homogeneous enantioselective hydrogenation of functionalized prochiral olefins is one of the most frequently studied and most efficient transition metal-catalyzed reactions. In the first reports using chiral Wilkinson type catalysts, low enantiomeric excesses (ee’s) were obtained using monodentate phosphines as ligands. All attempts to develop monodentate ligands which would afford high ee’s in this reaction met with limited success, the best result being reached with CAMP, already published in 1972, giving ee’s up to 90% in the hydrogenation of dehydroamino acid.1

Although new monodentate phosphorus ligands play a significant role in other transition metal-catalyzed reactions, highly enantioselective hydrogenations are exclusively based on bidentate phosphorus ligands. Starting with Kagan’s diop ligands,1 a large number of bidentate ligands with excellent selectivities was reported.2 Using chiral Wilkinson type catalysts, low enantiomeric excesses (ee’s) were obtained using monodentate phosphines as ligands. All attempts to develop monodentate ligands which would preclude the possibility that rhodium catalysts based on monodentate ligands could show the same high selectivity, especially when the two ligands on rhodium strongly restrict each other’s conformational freedom. Encouraging is a recent report by Pringle and co-workers on a monodentate phosphonite ligand which leads to 92% ee at 73% conversion in the rhodium-catalyzed hydrogenation of methyl 2-acetamido acrylate.3

We here report monodentate phosphoramidites as new ligands for the enantioselective rhodium-catalyzed hydrogenation of olefins with unprecedented high ee’s up to 99.8%. Phosphoramidite ligands have not been used in asymmetric hydrogenation4 but showed excellent enantioselectivities in copper-catalyzed dialkylzinc additions to enones.5 With Rh(COD)2-BF4 as the catalyst precursor and monodentate ligand (S)-14 (2 equiv with respect to rhodium)6,7 we obtained quantitative conversion under ambient conditions (rt, 1 bar H2, 20 h) and a

(24) Easily prepared in one step from (-)-1,1’-bi-2-naphthol and hexamethylenephosphoramidite triacide, see: Hulst, R.; De Vries, N. K.; Feringa, B. L. Tetrahedron. Asymmetry 1994, 5, 699. We labeled this ligand MonoPhos (monodentate Phosphoramidite).
(25) The optimal ligand-to-rhodium ratio in the reactions appears to be 2:1. With less than two equiv of ligand, no reaction occurs.
The hydrogenation of dehydroamino acid and itaconic acid derivatives was examined in CH$_2$Cl$_2$ and EtOAc under ambient pressure at room temperature or 0 °C (Table 2). Optimum ee’s were obtained in EtOAc as solvent at 0 °C without prehydro-