Optically pure P-chiral diphosphine ligands (1,2-bis((o-alkylphenyl)phenylphosphino)ethanes, 1,2-bis(alkylmethylphosphino)ethanes (BisP*), bis(alkylmethylphosphino)methane (MiniPHOS), and related ligands) were prepared via phosphineboranes as the intermediates. The rhodium complexes of these ligands were used for the asymmetric hydrogenation of dehydroamino acid derivatives including beta-disubstituted derivative and beta-(acylamino)acrylates. Markedly high to almost perfect enantioselectivity was observed in these hydrogenations. The molecular structures of these complexes were determined by single crystal X-ray analysis. In the BisP* and MiniPHOS series, the bulky alkyl groups effectively shield the two diagonal quadrants and the methyl groups are placed at the other quadrants. The excellent enantioselection is responsible for this imposed asymmetric environment. Mechanistic study by multinuclear NMR indicates that the dihydride mechanism is operating in these hydrogenations and the enantioselection is determined at the migratory insertion step. The exact relationship between the sense of enantioselection and the molecular structure of the catalysts is presented.


Keywords: asymmetric catalysis, chiral recognition, rhodium compounds