Involves the asymmetric reduction of Z-N-acylated dehydroamino acids (48) with a cationic rhodium catalyst complexed to a chiral biphosphine ligand. The high %ee's have been generally restricted to the Z-isomers; elucidation of the underlying mechanistic factors for this have been the subject of a series of papers by Halpern, et. al.10. An extensive number of chiral biphosphines have been examined for efficacy in this process; the most commonly employed and successful systems are listed below Scheme 12. The chemical yields for these hydrogenations are often quantitative, and the turnover rates are often high. The reaction tends to be fairly insensitive to the nature of the R groups in the general structure 48 (see Tables) and various esters, free acids and amides have all been found to give excellent results. The mechanism of the reaction has been primarily worked out by Halpern 10 and is schematically detailed in Scheme 13. The first irreversible step in each of the diastereomeric manifolds is the oxidative addition of hydrogen to the coordinated olefin species (52 to 53 and 56 to 57, respectively); it is thus the relative rates of these competing parallel pathways that ultimately determines the enantioselectivity. E-Substituted and β,β-disubstituted dehydroamino acids generally give lower %ee's and lower yields of hydrogenation products (Table, Scheme 14).