Substituent Effects of Ligands on Asymmetric Induction in a Prototypical Palladium-Catalyzed Allylation Reaction: Making Both Enantiomers of a Product in High Optical Purity Using the Same Source of Chirality

Dean S. Clyne, Yvan C. Mermet-Bouvier, Nobuyoshi Nomura, and T. V. RajanBabu*

Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210

Received July 16, 1999

The substituent effects of the ligands 1 through 8 play a crucial role in determining the enantioselectivity in the palladium-catalyzed asymmetric allylation reaction between 1,3-diphenylprop-2-en-1-yl acetate and the sodium salt of diethyl malonate. For a given chirality of the backbone, electron-deficient and electron-rich ligands generally gave opposite enantiomers, while sterically hindered ligands had the same enantioselectivity as electron-rich ligands. In the case of flexible backbones with ligands of comparable size, a variation of the enantioselectivity with the electronic properties of the ligand is predictable. In ligands with rigid backbones, the steric effects of the substituents appear to play a more decisive role, and caution should be exercised in interpreting the role of electronic effects in such cases. Examples are provided for maximizing both the chemical yield and the enantioselectivity of the allylation reaction through the tuning of the electronic properties of the ligands. In selected cases, the major sense of the asymmetric induction could be reversed solely by changing the electronic properties of the ligands. Bisphosphinites from (R)-(+)·1,1'-bi-2-naphthol (BINOL) can be tuned to produce both (R)- and (S)-products in 80 and 87% ee, respectively. Stoichiometric reaction of complexes 10e* and 10j* with the sodium salt of diethyl malonate gave malonate adducts with enantiomeric excesses in agreement with those obtained under the catalytic conditions. Also reported are the details of an NMR study of the Pd·(η^3-1,3-diphenylallyl)bis-diphenylphosphinite and the corresponding bis-dicyclohexylphosphinite complexes 10e* and 10j*.