Formation of Quaternary Stereogenic Centers by Wagner-Meerwein Rearrangement – Synthesis of Optically Active Cyclopentadienyl Complexes from Borneol and Fenchol

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Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

The development of optically active cyclopentadienyl complexes as enantioselective catalysts calls for simple synthetic procedures for cyclopentadienes with optically active alkyl substituents. While *exo*-bornyl chloride and *exo*-fenchyl bromide do not react or exclusively eliminate hydrogen halide with cyclopentadienylmetal compounds in ether solvents or ammonia, they undergo Wagner-Meerwein rearrangement and substitution with cyclopentadienylmagnesium chloride in toluene. The bornyl cation yields racemic *exo*-bornylcyclopentadiene and partially racemized isocamphylcyclopentadiene, but for the fenchyl cation no racemization pathway is available, and the main diastereomer among the lithium salts of the ensuing substituted cyclopentadienes can be isolated in 95 % diastereomeric purity by solvent extraction. This material with the IUPAC name lithium (2*R*)-2,5,5-trimethylbicyclo[2.2.1]hept-2-ylcyclopentadienide carries an alkyl substituent having no trivial name so far. *Exo*-norbornylcyclopentadiene could be synthesized in high yield with a similar procedure. The same protocol works with 1-bromoadamantane. The novel alkylcyclopentadienes have been converted to ferrocenes and molybdenum complexes of the type $[Cp^{R}Mo(CO)_3CH_3]$. (2*R*)-2,5,5-Trimethylbicyclo[2.2.1]hept-2-ylcyclopentadiene with an optical purity of 78 % *ee* (the optical purity of the starting material fenchol) was converted into an optically active titanocene dichloride and tested in the catalytic hydrogenation of 2-phenyl-1-butene. The hydrogenation product was obtained with 31 % *ee*, which compares favorably with results obtained with other group 4 metallocene dichlorides with one optically active alkyl substituent on each ring ligand. Facile procedures for the synthesis of the starting compounds *exo*-bornyl chloride and *exo*-fenchyl bromide based on the tosylate method have been developed with a tosylate melt or with toluene serving as solvents.

Key words: Bornyl Chloride, Fenchyl Bromide, Optical Activity, Enantioselective Hydrogenation, Titanocene Dichloride