A Study on Chiral Organocalcium Complexes: Attempts in Enantioselective Catalytic Hydrosilylation and Intramolecular Hydroamination of Alkenes

Frank Buch and Sjoerd Harder

Anorganische Chemie, Universität Duisburg-Essen, Universitätsstraße 5-7, 45117 Essen, Germany

Reprint requests to Prof. Dr. Sjoerd Harder. E-mail: sjoerd.harder@uni-due.de

Z. Naturforsch. **2008**, *63b,* 169 – 177; received August 29, 2007

The chiral β-diketimine ligand [(*S*)-Ph(Me)CH-N=C(Me)]$CH_2$was prepared by condensation of acetylacetone with the commercially available chiral building block (*S*)-Ph(Me)CH-NH_2. Reaction of *bis*(*o*-Me_2N-α-Me_3Si-benzyl)calcium with this β-diketimine led to double deprotonation. Reaction of *bis*(*o*-Me_2N-α-Me_3Si-benzyl)calcium with the commercially available chiral *bis*-oxazoline (*S*)-Ph-BOX gave diastereopure [(*S*)-Ph-BOX](*o*-Me_2N-α-Me_3Si-benzyl)calcium which in solution slowly decomposed with formation of *o*-Me_2N-α-Me_3Si-toluene. The corresponding amide complex [(*S*)-Ph-BOX]CaN$(SiMe_3)_2\cdot(THF)_2$ is stable and the crystal structure has been determined. In solution, this heteroleptic amide is in Schlenk equilibrium with the homoleptic species [(*S*)-Ph-BOX]$_2$Ca and Ca[N$(SiMe_3)_2]_2\cdot(THF)_2$. This Schlenk equilibrium can be steered to the heteroleptic side. Use of the enantiopure calcium amide catalyst for the hydrosilylation of styrene with $PhSiH_3$ or in the intramolecular hydroamination of aminoalkenes gave good product yields, but only small *ee*-values were observed (5 – 10 %). From stoichiometric reactions of the catalyst with the substrates it is concluded that the "true" catalytically active species is mainly present as a homoleptic calcium complex, which explains the poor enantioselectivities.

Key words: Alkaline Earth Metals, Calcium, Hydrosilylation, Hydroamination