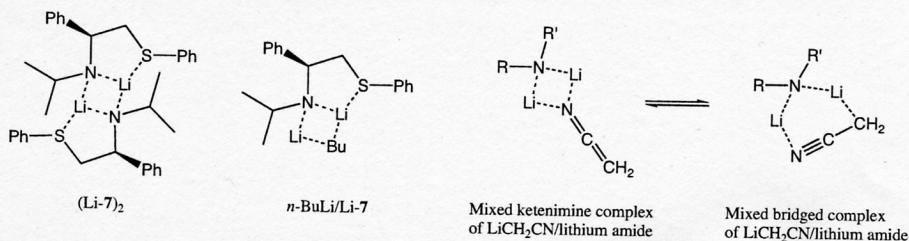
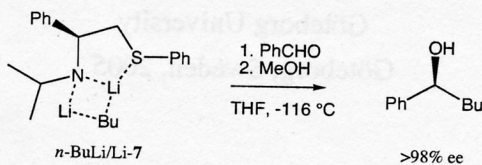


Abstract

Addition of organolithium reagents such as *n*-BuLi to chiral lithium amides results in the formation of mixed complexes. These complexes have been studied by NMR spectroscopy, showing dimeric complexes in Et₂O-*d*₁₀ and THF-*d*₈, and trimers in toluene-*d*₈. Detailed information of these complexes was obtained from ⁶Li,¹H-HOESY experiments, and from ¹⁵N labeled lithium amido ethers and sulfides. The mixed complexes of LiCH₂CN and lithium amides exist as bridged and ketenimine structures in equilibrium in Et₂O, as indicated by information gained from the ⁶Li,¹H-HOESY spectra and the small observed ⁶Li,¹⁵N and ⁶Li,¹³C couplings. Mixed ketenimine complexes of LiCH₂CN are observed in THF.



The chiral lithium amides have been utilized as reagents for asymmetric additions of organolithium reagents to benzaldehyde. The lithium amido sulfide (*S*)-Li-7 mediates the addition of *n*-BuLi to benzaldehyde, yielding phenylpentanol with >98.5% enantiomeric excess (ee). The selectivity of the LiCH₂CN addition to benzaldehyde is modest in comparison to that of *n*-BuLi, however the stereoselectivity is strongly solvent dependent. In Et₂O, (*S*)-Li-7 produces (*S*)-β-hydroxynitrile in 29% ee while in THF the (*R*)-β-hydroxynitrile is formed in 75% ee. Among all the addition reaction studied, the lithium amido sulfides produce much higher selectivities than the lithium amido ethers.



The lithium amides and the mixed lithium/sodium amides formed by chiral γ -amino ethers were studied by NMR spectroscopy. These mixed alkali metal amides have been used for kinetic studies of the asymmetric deprotonation of cyclohexene oxide.