

ABSTRACT

Chiral alkali metal amides can be used in asymmetric synthesis. To more easily understand their reactivity, NMR spectroscopic studies of such complexes have been performed. The results show that the role of internal coordination and the coordination number largely affects the reactivity of the reagent. Mixed sodium amide/*n*-BuNa complex mixed and sodium/lithium amides have been characterised for the first time and a first example of comparison between the asymmetric induction by sodium and lithium amides have been performed. Mixed complexes consisting of two analogous lithium amides have been shown to give an increase asymmetric induction in the desymmetrisation of cyclohexene oxide. It has also been shown that commercially available chiral amines can be used as chiral lithium amide bases, giving a high enantiomeric excess of the product in deprotonation reactions, provided that they are attached to a solid support.

An unexpected structural similarity between the first structural characterised chlorocopper(I)/sparteine complexes and methyl- or phenyllithium/sparteine complexes is reported. Sparteine has also been used as a chiral ligand in an asymmetric solid-state reaction where the enantiomeric excess of the product increased from eight to ten percent, as compared to the same reaction performed in the presence of solvent. This is the first example of such comparison.

Several examples of absolute asymmetric synthesis *via* total spontaneous resolution are described, showing that it is possible to obtain enantiopure bulk products from achiral or racemic building blocks. Several chiral and stereochemically labile reagents as well as chiral stereochemically labile substrates, have been synthesised and the latter type has also been used in chirality transfer reactions. Factors that decide if a conglomerate or a racemic phase will form when stereochemically labile complexes in solution crystallise, are discussed. Chiral covalent networks have been synthesised from stereochemically labile metal complexes and in one particular case, a mixed valence compound crystallises as interpenetrating chiral nets of (10-3)-*a* topology.

Optically active trace impurities, present in concentrations well below the level of detection, are suggested to influence crystallisation processes and an example of non-stochastic distribution of handedness in helix crystallisation is reported. The origin of prebiotic homochirality and the possibility that all reactions take place in a cryptochiral environment, as a result of billion years of life, is discussed

KEYWORDS: Absolute asymmetric synthesis, Chirality, Coordination chemistry, Homochirality, NMR spectroscopy, Total spontaneous resolution, X-ray diffraction

