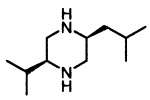
Abstract

Organometallic alkylating reagents can be used in carbon-carbon bond forming reactions. Using chiral ligands, these reactions can be made enantioselective. Detailed structural knowledge is of great importance for the development of new and more efficient reagents. We have studied the structures of some organometallic reagents containing lithium, magnesium, copper and zinc. We have also successfully performed absolute asymmetric synthesis.

By using multinuclear and multidimensional NMR-techniques we have investigated the structure of a chiral catalyst **1** for the enantioselective addition of an ethyl group to benzaldehyde. The reacting complex was found to adopt a boat conformation with diethylzinc coordinating the two nitrogen atoms in the ligand.



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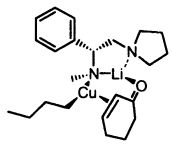
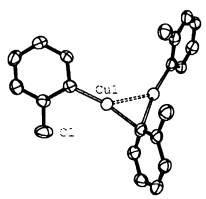
We have also performed NMR-investigations on a chiral lithium amidocuprate reagent. When the lithium amidocuprate was reacted with cyclohexenone, complex **9** was formed. It was found that the butyl group in **9** was not transferred to cyclohexenone until the reaction was quenched.



9

We have synthesized new organolithium (**11**), organocopper (**12**), and organocuprate (**6**) complexes. Complex **11** shows a very unusual twisted ladder structure resembling a double helix. The structure of **6** provides insight into the formation of the generally accepted organocopper tetramer. Complex **12** represent a surprisingly oxygen and moisture insensitive organocopper reagent. Due to its stability and ease of handling, **12** can find application in organic and inorganic synthesis.



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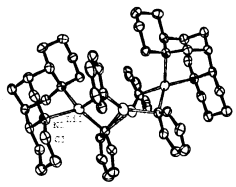

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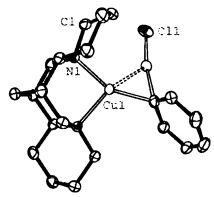

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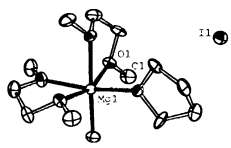
Preparation of an enantiopure six-coordinate octahedral Grignard reagent (**14**) from achiral starting materials provides a route for absolute asymmetric synthesis. Alkylation of butyraldehyde with **14** resulted in formation of (*R*)-2-pentanol in 5-22% enantiomeric excess. When benzaldehyde was used as substrate (*S*)-1-phenyl ethanol was formed in 4-10% enantiomeric excess.



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Keywords: chiral organozinc reagents, chiral lithium organocuprates, chiral organocopper reagents, six-coordinate Grignard reagents, absolute asymmetric synthesis, asymmetric synthesis, X-ray crystallography, NMR spectroscopy.

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