Abstract

Various ways of preparing enantiomerically pure 2-amino[6]helicene derivatives were explored. Ni(0) mediated cyclotrimerization of enantiopure triynes provided (*M*)- and (*P*)-7,8-bis(*p*-tolyl)hexahelicene-2-amine in >99% *ee* as well as its benzoderivative in >99% *ee*. The stereocontrol was found to be inefficient for a 2-aminobenzo[6]helicene congener with an embedded five-membered ring. Helically chiral imidazolium salts bearing one or two helicene moieties have been synthesized and applied in enantioselective [2+2+2] cyclotrimerization catalyzed by an *in situ* formed Ni(0)-NHC complex. The synthesis of the first helically chiral Pd- and Ru-NHC complexes and their application in enantioselective catalysis was demonstrated. The latter shows promising results in enantioselective olefin metathesis reactions. A mechanistic proposal for asymmetric ring closing metathesis is provided.