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Review

Synthesis of axially chiral biaryl compounds by asymmetric catalytic reactions with transition metals

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Dedicated to the memory of our colleague and friend Guy Lavigne (1947–2015).

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ABSTRACT

Axially chiral biaryl structures are unique systems encountered in various synthetic compounds such as BINAP and BINOL, polymers, but also in natural products presenting a pharmaceutical interest such as Vancomycin, Steganacin or Korupensamine. The axial chirality of these products, so-called atropisomerism, is induced by the restricted rotation around the aryl–aryl bond. This review will summarize the different strategies imagined by chemists to control such chirality, focusing on asymmetric catalytic processes with transition metals. Only transition metal complexes bearing chiral ligands will be considered and the core of this review will consist of the enantioselective coupling of two achiral substrates.

1. Introduction

In the world of chemical synthesis, asymmetric catalysis is probably one of the most challenging synthetic tool, one of the most demanding in terms of ligand and catalyst design, understanding of mechanism, and optimization of reaction conditions. Mainly boosted by the growing demand of pharmaceutical, agrochemical and perfume industries, asymmetric catalysis has attracted increasing interest during the last decades.

As reported in chemistry textbooks, a molecule is chiral if it is not superimposable with its mirror image. Such a property can be acquired by the presence of central chirality, planar chirality or axial chirality in molecules, the latter of which being encountered in substituted allenes, *ortho*-substituted biaryls or even rotationally hindered aryl amides.

The axial chirality of the biaryl products is induced by the restricted rotation around the aryl–aryl bond, so-called atropisomerism. To exhibit such chirality, there must be at least three ortho substituents about the biaryl axis. Atropisomerism is encountered in various synthetic compounds such as BINAP and BINOL, but also in natural products presenting a pharmaceutical interest such as Vancomycin, Steganacin or Korupensamine A (Fig. 1.1), underlining the need to develop efficient strategies toward their synthesis in optically pure form.

The atroposelective synthesis of axially chiral biaryl compounds has been highlighted in a few recent reviews [1–3], but in contrast to those, ours will focus exclusively on the generation of axially chiral biaryl structures by means of asymmetric catalytic reactions with transition metals. The present review is meant to give a comprehensive contribution to the field as it includes, to our knowledge, all the references that appeared in the relevant areas from the first report up to the end of 2014. Only transition metal complexes bearing chiral ligands will be considered, therefore the core of this review will consist of the enantioselective coupling of two achiral substrates. Less numerous examples of diastereoselective coupling will also be reported.

This review will be divided into seven parts, each focusing on a different type of coupling reaction with its characteristic features and limitations, and with an emphasis on the different types of chiral ligands described in the literature.

2. Kumada–Tamao–Corriu cross-coupling reaction

The availability and ease of synthesis of organomagnesium halides made them attractive reagents for cross-coupling reactions with organohalides and the first transition metal-catalyzed C—C coupling reaction involving a Grignard reagent was described in 1971 by Kochi and Tamura with iron(III) salts [4], followed independently in 1972 by Kumada and Tamao and by Corriu and Masse for nickel [5,6]. Since then, both nickel and palladium catalysts have been used, however the greater reactivity and lower cost of nickel made it the metal of choice for this reaction [7]. In 1975, Tamao and Kumada used a chiral phosphine ligand with nickel to couple ortho-substituted aryl Grignard reagents with aryl halides and thus reported the first synthesis of axially chiral binaphthyls by a TM-catalyzed asymmetric cross-coupling reaction between 1-bromo-2-methylnaphthalene and 2-methyl-1-naphthylmagnesium bromide (Scheme 2.1) [8]. In the achiral version of the reaction, they already noted that chlorobenzene reacted very sluggishly compared to its bromide analog and that yields were much better when the bulky substituents were borne by the Grignard reagent rather than the aryl halide. Finally, a triphenylphosphine ligand appeared more efficient than bidentate diphosphines. In the first asymmetric version of the reaction, 1 mol% of a nickel complex bearing the optically pure bidentate diphosphine (R,R)-(−)-diop (**1**) (Fig. 2.1) was used. The reaction proceeded at room temperature and allowed the synthesis of enantioenriched 2,2′-dimethyl-1,1′-binaphthyl in 32% yield, however with very low enantioselectivity (1.9% ee reported). The use of ferrocenyl bidentate ligand (*S*)-(p*R*)-BPPFA (**3**), described by Hayashi and Kumada the previous year [9], allowed getting the product with a slightly improved enantioselectivity (4.6% ee) [8]. In 1977, the use of axially chiral diphosphine (*S*)-(−)-NAPHOS-(1,1) (**5**) under similar conditions furnished 2,2′-dimethyl-1,1′-binaphthyl with 12.5% ee [10].

The first efficient catalytic system, however, was only reported in 1988 by Hayashi and Ito with the use of optically pure ferrocenyl ligand (*S*)-(p*R*)-PPFOMe (**4a**) (Scheme 2.2) [11]. Thus several binaphthyls were obtained with up to 95% ee and 69% yield (for 2,2′-dimethyl-1,1′-binaphthyl) using 5 mol% of chiral nickel catalyst. Again, nickel complexes bearing monodentate phosphines revealed themselves more active than those with bidentate diphosphines (BINAP, **6**) or phosphine-amines ((*S*)-(p*R*)-PPFA, **2**) and more than palladium complexes. The substitution pattern on both substrates proved important since the coupling product was obtained in 84% yield and 80% ee, in 16 h at −10 °C and 2 mol% catalyst, when the methyl group was situated on the Grignard reagent, whereas only 25% yield and 16% ee were reached in 98 h with the methyl group placed on the naphthyl bromide, under otherwise identical conditions. The authors put forward the coordination of the oxygen atom of the ferrocenyl ligand to the magnesium in the Grignard reagent at the transmetalation step to explain the high enantioselectivity levels. The production of racemic 2-methyl-1,1-binaphthyl with the use of ligand **4c**, that