

Review

Performances of symmetrical achiral ferrocenylphosphine ligands in palladium-catalyzed cross-coupling reactions: A review of syntheses, catalytic applications and structural properties

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Abstract

Ferrocene derivatives bearing donor atoms led to the generation of several classes of metallo-ligands, which collectively show an impressive diversity of applications, especially in metal-catalyzed modern organic reactions. Based on the impetus provided by the use of the diphosphine

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1,1'-bis(diphenylphosphino)ferrocene (dppf) the investigations directed towards the synthesis of new ferrocenylphosphines remain of fundamental and industrial interest. The present review aims to describe the performances in palladium-catalyzed cross-coupling reactions of *symmetrical achiral ferrocenylphosphine* ligands, mainly diphosphines. We specifically choose to restrict our review efforts to these species due to their wide accessibility to all the chemist community. First, the synthetic routes that have been applied to the synthesis of these ferrocene derivatives are overviewed. Then, the recent advances in the chemistry of symmetric achiral di- and polyphosphine ferrocene-based ligands related to metal-catalyzed bond-forming reactions (C–C, C–N and C–O bonds) are discussed, with a special thrust to consolidate all the important work in this area. Finally, the structural properties of these ligands are discussed in relation with their reactivity, in the light of the mechanistic studies reported on parameters like coordination bite angle, electronic, steric and geometric features of ligands, conformation, and multidentarity. The many achievements and new challenges on this topic are summarized within the article. The literature cut-off date was beginning 2006. © 2007 Elsevier B.V. All rights reserved.

Keywords: Ferrocenylphosphine; Catalysis; Palladium; Cross-coupling (Heck, Suzuki, Kumada, Negishi, Sonogashira, cyanations, aminations, etherations); Structure; Mechanisms (bite angle, conformation, multidentarity)

1. Introduction

The discovery of ferrocene and the elucidation of its outstanding “sandwich”-structure, more than 50 years ago [1], initiated a new era of organometallic chemistry in the history of contemporary chemistry [2,3]. The selective functionalization of ferrocene derivatives with donor atom (P, S, N, etc.) led to a second generation of different classes of chiral and achiral molecular ligands. These ubiquitous species show important applications in metal-catalyzed modern organic reactions. Based on the impetus provided by the applications of the diphosphine 1,1'-bis(diphenylphosphino)ferrocene (dppf), the investigations directed towards the synthesis of new ferrocenylphosphines – sterically and/or electronically modified either at the ferrocenyl backbone or at the phosphorus atoms [4] – are still of fundamental and industrial interest.

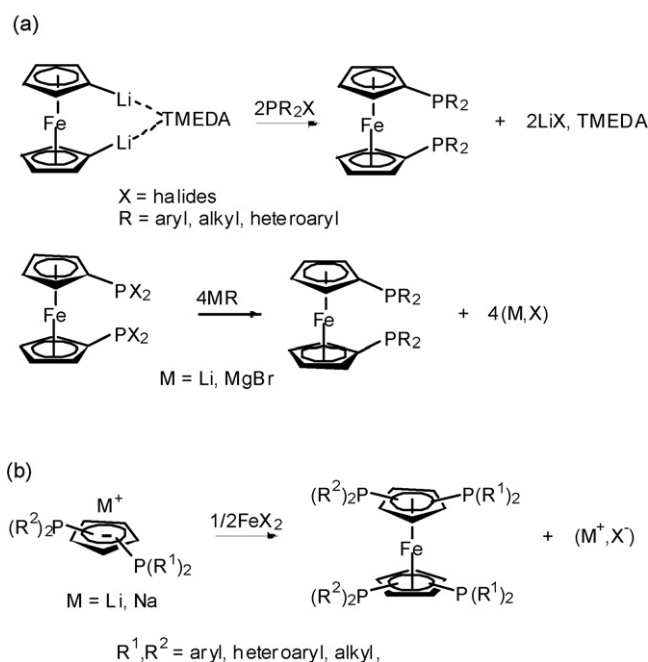
The chemistry of ferrocene-based ligands has been intensively investigated, and a number of excellent reviews have appeared in the recent years [5]. They generally cover some particular aspects of ferrocenylphosphine chemistry: for instance, Bandoli and Dolmella reviewed in 2000 the coordination ability exhibited by the dppf ligand to transition metals [6]. In 2001 a concise review presented the applications of group 10 ferrocenylphosphine complexes in achiral coupling reactions [7]. More recently, Colacot and Atkinson et al. have reviewed the applications of chiral ferrocenylphosphines in homogeneous catalysis, and the syntheses and application of *unsymmetrical* ligands with a ferrocene backbone in homogeneous catalysis, respectively [8,9]. Bianchini and co-workers reported as well a review covering stereoselective catalysis by metal complexes with chiral ferrocenylphosphines in 2004 [10].

The present review aims to describe the performances in palladium-catalyzed cross-coupling reactions of symmetrical achiral ferrocenylphosphine ligands, mostly diphosphines. We specifically choose to restrict our review efforts to these species due to their wide accessibility to the entire chemist community [11] (including non-specialist of metallo-ligands synthesis) and particularly to researchers involved in catalyzed carbon–carbon bond formation or in total synthesis. The well-known general robustness of the ferrocene derivatives both at the solid state and in solution is an additional advantage, which makes all the more appealing, the ferrocenylphosphine ligands of easy access. The first section gives an overview of the synthetic routes that were

applied to the synthesis of these ferrocene derivatives. In the following sections are presented the important applications of the ligands which were reported over the past decades in palladium (or nickel)-catalyzed cross-coupling reactions. The chemistry of the di- and polyphosphine ferrocene-based ligands in catalytic cross-coupling is detailed in carbon–carbon, carbon–nitrogen and carbon–oxygen bond-forming reactions. The last part is devoted to structural and mechanistic discussions with the view to highlight some critical properties of ferrocenyl ligands such as coordination bite angle, conformation, electronic and steric features and multidentarity effect.

2. Synthesis of symmetrical ferrocenylphosphine ligands

The synthesis of ferrocene-based phosphine ligands with identical substitutions on the two cyclopentadienyl rings (Cp) has been conducted following two general routes (Scheme 1a and b). The first one – which is also the most often employed –



Scheme 1.

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