Available online at www.sciencedirect.com

ScienceDirect

Journal of Organometallic Chemistry 692 (2007) 5279–5284

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Study on the electronic effects on stereoconservativity of Suzuki coupling in chiral groove of binaphthyl

Michal Juríček, Henrich Brath, Peter Kasák [1], Martin Putala *

Department of Organic Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina, 842 15 Bratislava, Slovak Republic

Received 28 May 2007; received in revised form 6 August 2007; accepted 9 August 2007
Available online 15 August 2007

Abstract

Suzuki diarylation of enantiopure 2,2′-diiodo-1,1′-binaphthyl catalyzed by triphenylphosphane palladium complex is accompanied by almost complete racemization of binaphthyl moiety (7% e.e.). Based on formerly proposed mechanism, secondary oxidative addition of Pd(II) to Pd(IV)-complex, competitive to transmetallation, is expected to be responsible for racemization. In accordance with it, racemization pathway can be suppressed in the favour of stereoconservative route by electronic factors, which control the rate of oxidative addition. Among the electronic factors, decreasing donating ability of the tested phosphane ligands resulted in increase of e.e. of the diarylated product up to 65%, using triindol-1-ylphosphane. However, this factor slows down also the rate of the primary oxidative addition that lowers the yield of the diarylated product. Further decrease in donating ability of the ligand makes palladium complex almost inactive in this cross-coupling reaction. Effect of the leaving group of binaphthyl 2,2′-dielectrophile (as a matter of the reactivity of C–X bond towards oxidative addition) was found to be even more dramatic: almost stereoconservative route in case of 2,2′-dibromo-1,1′-binaphthyl (95% e.e.), but no reaction in case of corresponding ditriflate.

Keywords: Binaphthyl; Mechanism; P ligands; Palladium complexes; Stereoconservative; Suzuki cross-coupling

1. Introduction

Configurationally stable, enantiopure 2,2′-substituted 1,1′-binaphthyl derivatives [1,2] represent important group of chiral compounds with applications reported either in asymmetric catalysis as ligands [3], in supramolecular chemistry as building blocks [4] or in materials science as compounds with interesting optical or/and electronic properties [5]. Preparation of binaphthyl derivatives bearing carbon groups at positions 2 and 2′ requires use of stereoconservative Negishi [6,7] or Kumada [6] cross-couplings from enantiopure ditriflate **1** (just in the case of methylation [6]) or more reactive diiodide **2** [6,7]. We showed that Suzuki diarylation of the diiodide **2** proceeds with almost complete racemization of binaphthyl moiety [8,9]. However, stereoconservativity of Suzuki diarylation at positions 2 and 2′ can be achieved by umpolung, using 1,1′-binaphthyl-2,2′-diboronic acid as binaphthyl precursor [9].

As an explanation of racemization during Suzuki arylation of diiodide **2** we proposed following mechanism based on configurationally unstable pallada(IV) cycle **3** (Scheme 1) [8]:

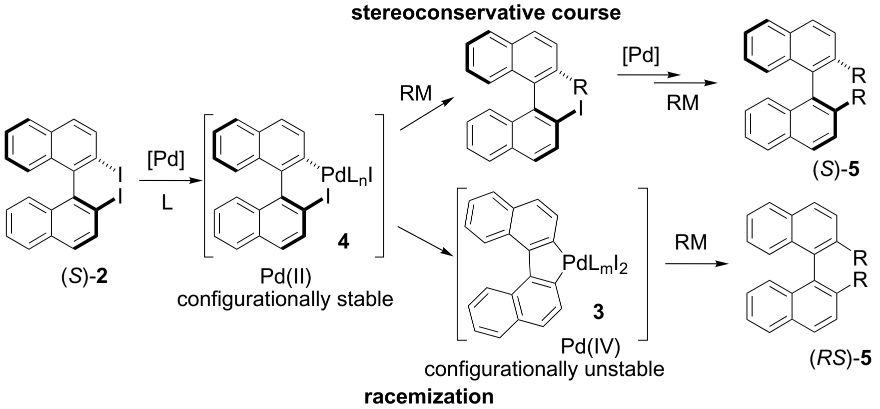
1. The first step – an oxidative addition of **2** to the palladium complex (insertion of palladium to C–I bond of a **2** in position 2) gives palladium(II) complex **4**, analogous to usual intermediates in cross-coupling reaction from aryl halides [10].
2. If the organometallic reagent (organozinc or organomagnesium halide) is sufficiently reactive, transmetallation can take place and the first C–C bond is formed. A C–C bond at position 2′ is formed analogously. In such a mechanism there is no reason for

---

* Corresponding author. Tel.: +421 2 60696 323; fax: +421 2 60696 690.
E-mail address: putala@fns.uniba.sk (M. Putala).

[1] Present address: Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovak Republic.

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.08.010



Scheme 1. Proposed pathways for cross-coupling reaction of the diiodide **2**.

racemization, and product **5** is obtained enantiopure – with complete conservation of stereogenic information from substrate.

(3) However, in the case of less reactive organometallics (boronate or stannane), transmetallation is expected to be slower than insertion of palladium in **4** to C–I bond at the position 2′ to form a palladacyclic complex **3** containing palladium(IV). It is known that 1,1′-binapthalene derivatives having positions 2 and 2′ bridged with one-atom linker have a low racemization barrier (between 45 and 65 kJ mol^{-1} [11]). These derivatives lack non-bonding interactions at positions 2 and 2′ (ring flipping of fused unsaturated five-membered ring requires only low activation energy) and also non-bonding interactions at positions 8 and 8′ are decreased (the outer benzene rings of naphthalene units are pulled apart). Thus, the binaphthyl moiety is easily racemized in this step. The palladacyclic complex **3** is not necessary an intermediate, this can be also considered as an activated complex, through which either reversible migration of palladium from position 2 to 2′ accompanied by racemization can occur or the reactivity of binaphthyl-palladium species towards transmetallation can be increased. Then, after transmetallation and formation of C–C bonds at the both 2 and 2′ positions, racemic product **5** is formed.

Our mechanistic proposal was supported by the ^{31}P NMR spectra of intermediate Pd complexes prepared by the reaction of equimolar amount of the diiodide **2** and palladium(0) complex [8] (two signals from C_1-symmetric complex **4**, single signal from C_2-symmetric complex **3**). Although Pd(IV)-complexes are not accepted as general intermediates in cross-coupling reactions, we presume that the diiodide **2** is specific substrate offering to proximate C–I bonds.

Pd(IV)-complexes become more often to be considered as likely intermediates in some Heck and cross-coupling reactions [12]. For instance, 1,4-migration of Pd in Pd(II)-complex from the position 2 to the position 2′ on 1,1′-biphenyl derivatives via Pd(IV)-intermediate is expected to be more probable than to take place via concerted mechanism pathway [13]. Pt(IV)-complexes containing a biphenyl moiety similar to that in complex **3**, were characterized [14]. Also, structurally relative Pd,Pd-dibromopallada(IV)cyclopentadiene species stabilized with an *N*,*N*-ligand were observed as intermediates [15].

Here we report results of our effort to control the racemization of binaphthyl moiety during Suzuki reaction of binaphthyl 2,2′-dielectrophiles by control of the second oxidative addition either by use of less electron rich phosphane ligands or by use of less reactive binaphthyl 2,2′-dielectrophiles, which undergo oxidative addition less readily.

2. Experimental

2.1. Methods

Flash column chromatography was performed on Merck Silica Gel (60H). Merck Silica Gel F254 plates were used for thin layer chromatography and visualization was effected with UV-light (254 nm). Melting points were measured on a Electrothermal-IA9200 instrument and the values are uncorrected. Specific optical rotations were measured on a Perkin–Elmer 241 polarimeter and are given in deg $cm^2 g^{-1} dm^{-1}$. HPLC analysis was done on Chiralcel Daicel OD-H column using a UV–vis detector LCD 5000. UV–vis spectra were measured on a Hewlett–Packard Diode Array 8245 spectrophotometer. IR data were recorded on SPECORD M 80 spectrophotometer. ^{1}H, ^{13}C and ^{31}P NMR were recorded on VARIAN GEMINI 300 instrument at 298 K. Chemical shifts are reported in ppm downfield to internal standard TMS (0.00 ppm) and the solvent was used as a reference. Working frequency was 300 MHz for ^{1}H NMR, 75.5 MHz for ^{13}C NMR and 121.5 MHz for ^{31}P NMR. Coupling constants are given in Hz. GC–MS spectra (70 eV, 150 μA, EI) were recorded on Voyager GC/MS Finnigan instrument. Elemental analyses were determined with Erba Science 1106 instrument.