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Efficient Suzuki coupling of aryl chlorides catalyzed by tricyclohexylphosphine adducts of cyclopalladated ferrocenylimines

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Abstract

The air and moisture stable tricyclohexylphosphine (PCy_3) adducts of dimeric cyclopalladated ferrocenylimines **5** and **6** have been easily synthesized and successfully used in palladium-catalyzed Suzuki cross-coupling of aryl chlorides. Using 0.1 mol% of **6** in the presence of 2 equivalent of Cs_2CO_3 as base in dioxane at 100 °C provided coupled products in excellent yields in the reaction of non-activated and deactivated aryl chlorides with phenylboronic acid. For activated chlorides such as 4-chloronitrobenzene and 4-chloroacetophenone, the catalyst loadings could be lowered to 0.01 mol% without loss of activity.

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Keywords: Suzuki coupling; Cyclopalladated ferrocenylimines; Tricyclohexylphosphine adducts; Aryl chlorides; Phenylboronic acid

1. Introduction

Palladium-catalyzed reactions are widely used in organic synthesis for formation of carbon–carbon and carbon–heteroatom bonds [1]. The Suzuki reaction of aryl halides/triflates with boronic acids has been one of the most widely studied owing to its applicability and the low toxicity of the reagents [2]. There is currently much interest in development of catalysts that can activate aryl chlorides since these substrates are cheaper and more readily available than the corresponding bromides and iodides [3]. Substantial progress has been made by using catalysts with bulky, electron-rich phosphines [2–7] and *N*-heterocyclic carbenes [2,3,8]. Moreover, palladacyclic catalysts are amongst the most active catalysts for forming carbon–carbon and carbon–heteroatom bonds [2b,3b,7c,8c–9]. A large number of phosphorus, nitrogen or sulfur based palladacycles derived from phosphines, phosphites, phosphinites, amines, imines, oximes or thioethers have been synthesized and used in the Suzuki reaction. The advantages of such palladacyclic catalysts include their ease of synthesis, facile modification and convenience of handling (insensitivity to air or moisture). Most of the palladacycles show considerable activity with activated aryl chlorides but only limited activity with deactivated substrates [3b]. It was recently reported, however, that isolated or in situ formed secondary [10] or tertiary phosphine [11] adducts (L = $HP(tBu)_2$, $HPCy_2$ or PCy_3, $PtBu_3$, e.g.) of dimeric phosphorus- or nitrogen-containing palladacycles (Fig. 1) efficiently promote the Suzuki coupling of both activated and deactivated aryl chlorides.

Our work had focused on cyclometallation of ferrocenylimines and applications of these systems [12]. We have found that cyclopalladated ferrocenylimines **4** are effective for the Heck reaction [13] and the dimerization of arylmercurials [14]. They also showed good activity in the Suzuki coupling reaction of aryl iodides and bromides. In contrast, only activated aryl chlorides gave good results [15]. We thought it interesting to study whether the activity of palladacycles **4** with aryl

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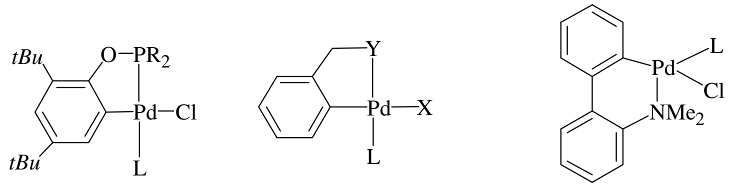
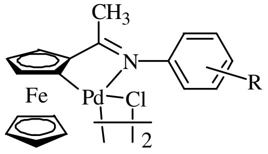


1 L = PR_3 **2** Y = NR_2, =NR L = PR_3
X = TFA, OTf, Cl, etc. **3** L = HPR_2 or PCy_3

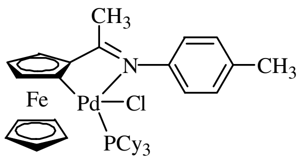
Fig. 1. Examples of adducts resulting from the corresponding dimeric palladacycles with phosphines.

chlorides could be enhanced with the corresponding tricyclohexylphosphine adduct **5**. Novel palladacycle **6** was also prepared for comparison. The results of this study are presented below.



R = *p*-CH_3(**a**), *p*-OCH_3(**b**),
p-Cl(**c**), *o*-Cl(**d**), *m*-Cl(**e**)

4



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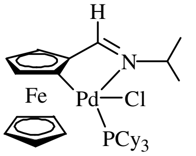


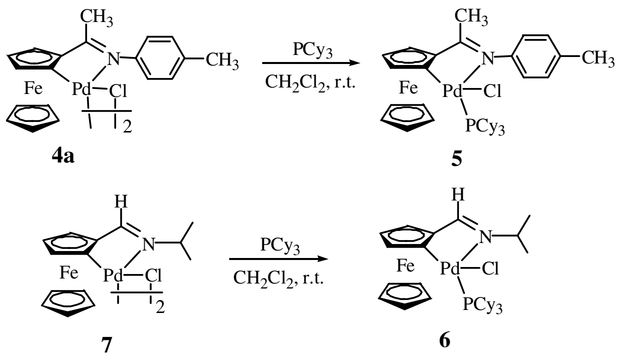
6

2. Results and discussion

2.1. Synthesis and characterization of complexes 5 and 6

The reaction of chloride-bridged palladacyclic dimers **4a** or **7** (Scheme 1) with 1.2 equivalent of PCy_3 per palladium in CH_2Cl_2 at room temperature produced the corresponding tricyclohexylphosphine adduct **5** or **6** as red crystals after recrystallization from CH_2Cl_2–petroleum ether in 53.4% and 57.0% yield, respectively. Both **5** and **6** are air and moisture stable both in the solid state and in solution.

The new compounds **5** and **6** were characterized by ^1H NMR, IR and high resolution mass spectrometry. The structure of **5** was determined by X-ray single crystal analysis. The molecule is shown in Fig. 2. Crystallographic and data collection parameters for **5** · CH_2Cl_2 are summarized in Table 1. Selected bond length (Å) and angles (°) are given in Table 2. As depicted in Fig. 2, the palladium adopts an approximately square planar configuration defined by the P, N, Cl(1) and C(6) atoms. The N–Pd–C(6) bond angle (80.5(2)°) is essentially identical to the corresponding values in PPh_3 adducts of cyclopalladated ferrocenylimines **4** [16,17]. The coor-



Scheme 1.

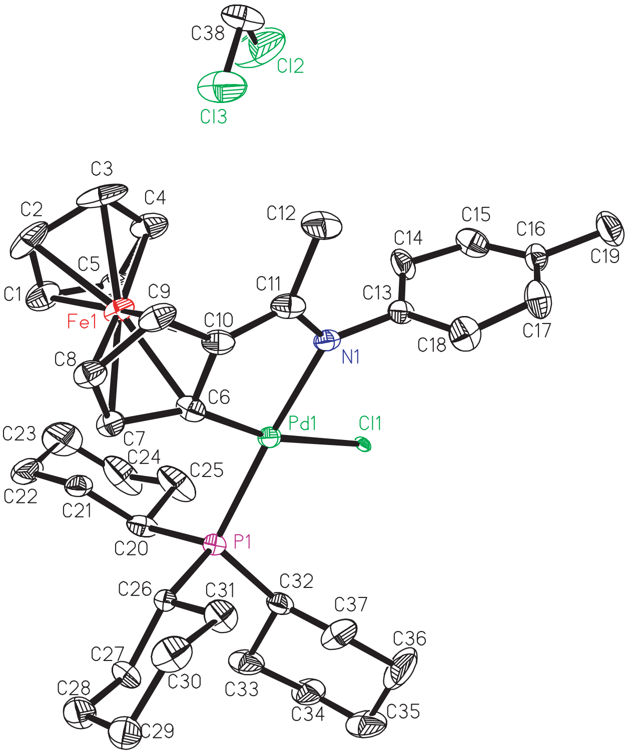


Fig. 2. Molecular structure of **5** · CH_2Cl_2.

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