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Synthesis and reactivity of new functionalized Pd(II) cyclometallated complexes with boronic esters

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Treatment of the functionalized Schiff base ligands with boronic esters **1a**, **1b**, **1c** and **1d** with palladium (II) acetate in toluene gave the polynuclear cyclometallated complexes **2a**, **2b**, **2c** and **2d**, respectively, as air-stable solids, with the ligand as a terdentate [C,N,O] moiety after deprotonation of the –OH group. Reaction of **1j** with palladium (II) acetate in toluene gave the dinuclear cyclometallated complex **5j**. Reaction of the cyclometallated complexes with triphenylphosphine gave the mononuclear species **3a**, **3b**, **3c**, **3d** and **6j** with cleavage of the polynuclear structure. Treatment of **2c** with the diphosphine $Ph_2PC_5H_4FeC_5H_4PPh_2$ (dppf) in 1:2 molar ratio gave the dinuclear cyclometallated complex **4c** as an air-stable solid.

Deprotection of the boronic ester can be easily achieved; thus, by stirring the cyclometallated complex **3a** in a mixture of acetone/water, **3e** is obtained in good yield. Reaction of the tetrameric complex **2a** with *cis*-1,2-cyclopentanediol in chloroform gave complex **2c** after a transesterification reaction. Under similar conditions complexes **3a** and **3d** behaved similarly: with *cis*-1,2-cyclopentanediol, pinacol or diethanolamine complexes **3c**, **3b**, **3g** and **3f**, were obtained. The pinacol derivatives **3b** and **3g** experiment the Petasis reaction with glyoxylic acid and morpholine in dichloromethane to give complexes **3h**, and **3i**, respectively.

1. Introduction

In past decades the chemistry of cyclometallated transition metal complexes has attracted much attention, being the five-membered palladacycles the most widely studied [1]. Cyclometallated complexes present applications in catalytic and synthetic processes [2], as chiral auxiliaries [3] or as building blocks for molecular architectures of higher complexity [4]. They also show interesting mesogenic [5] and luminescent and electronic properties [6] and potential applications in medicine and biology [7].

On the other hand, boronic acids and boronic esters have found numerous applications in organic and medicinal chemistry [8]. In particular, boronic esters have proven to be of great importance in asymmetric synthesis [9]; the facile introduction and recovery of chiral auxiliaries is the key step, and transesterification is the one of the simplest procedures by which chiral auxiliaries may be introduced to, and recovered from, an ester. Another important application of boronic acids is the Petasis multicomponent reaction of aryl- and vinylboronic acids with aldehydes and amines, sometimes referred to as the boronic acid Mannich reaction, which is a powerful and convenient method for the one-pot formation of unnatural amino acid derivatives [10,11].

Although the synthesis and reactivity of boronic acids and esters is well studied, few complexes in which this group is part of a coordinated ligand are known [12–14].

With this in mind we reasoned that combining the properties of cyclometallated complexes and of boronic acids could be of great interest and we therefore decided to examine functionalized Schiff bases with boronic esters as ligands in the cyclometallation reaction with palladium(II). As a result herein we present the synthesis of, to the best of our knowledge, the first functionalized cyclometallated complexes with boronic acids and boronic esters. Their reactivity towards the transesterification and the Petasis reaction is also described.

2. Results and discussion

For the convenience of the reader the compounds and reactions are shown in Schemes 1–3. The compounds described in this paper were characterized by elemental analysis (C, H, N) and by IR

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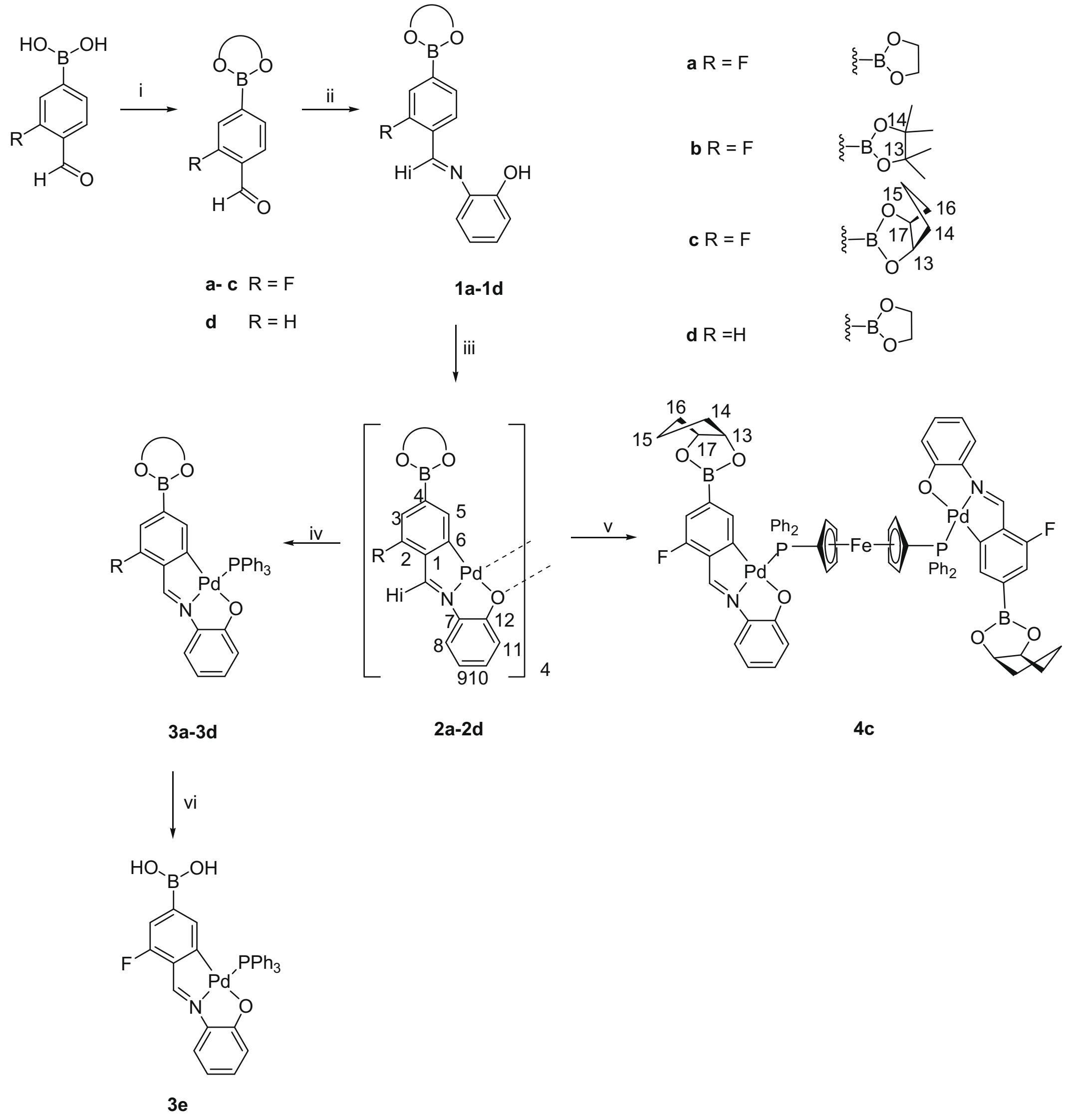
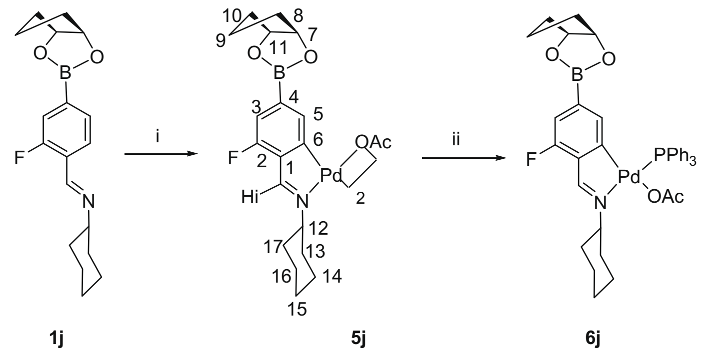


Scheme 1. (i) 1,2-Diol, toluene, reflux; (ii) aminophenol, chloroform, reflux; (iii) Pd(OAc)$_2$, toluene, 60 °C; (iv) PPh$_3$, chloroform; (v) dppf, chloroform; (vi) acetone/water.



Scheme 2. (i) Pd(OAc)$_2$, toluene, 60 °C; (ii) PPh$_3$, acetone.

spectroscopy and by ^{1}H, ^{31}P–{^{1}H} and, in part, ^{13}C–{^{1}H} NMR spectroscopy and mass spectrometry (see Section 4).

Reaction of ligands **1a–1d** with palladium (II) acetate in toluene at 60 °C gave the cyclometallated complexes **2a–2d**, as air-stable solids which were fully characterized. The IR spectra showed the shift of the ν(C=N) stretch toward lower wavenumbers, from the free ligand value, due to nitrogen coordination of the imine [15,16], and the absence of the ν(O–H) stretch, in accordance with loss of the –OH proton. This observation was confirmed by absence of the O*H* signal in the ^{1}H NMR spectra. The *H*C=N and *H*5 resonances in the ^{1}H NMR spectra were highfield shifted, as compared to the uncoordinated ligands, by *ca.* 1.5 and 0.9 ppm, respectively;