



## Rhodium-catalyzed modification of phthalocyanines

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### ABSTRACT

Rhodium-catalyzed carbon–carbon bond forming reactions using phthalocyanine–boronate ester were investigated. The reaction of Pc–boronate ester with substituted aldehydes gave 1,2-addition products (secondary alcohols), while  $\alpha,\beta$ -unsaturated carbonyl compounds (aldehydes, ketones, esters, and amides) furnished 1,4-addition products. The reaction of Pc-substituted alkynes with *o*-formyl and acetyl phenylboronic acid gave 1*H*- and 1-methyl inden-1-ol annulation derivatives. All reactions were performed in mixtures of organic–aqueous solvents.

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Phthalocyanines (Pc) and structurally related tetrapyrrolic macrocycles have many interesting properties with applications in numerous important technological fields.<sup>1</sup> Pc possess outstanding electronic properties including strong absorption in the red region of the visible spectrum and, dependent on the nature of the central metal ion, strong fluorescence. They have been extensively studied for applications in diverse fields such as catalysis, biomimetic model systems for primary processes of natural photosynthesis, dyads for use in optic–electric devices, super molecular assemblies, active components in semiconductors, electrochromic devices, information storage systems, and liquid crystal displays.<sup>2</sup>

Pc and related molecules offer unique properties as photosensitizers for photodynamic therapy (PDT) while their strong fluorescence permits diagnosis of disease.<sup>3</sup> Thus they have been used to image and treat different types of cancers,<sup>4</sup> skin lesions as well as macular degeneration (AMD).<sup>5</sup> Nonsubstituted Pc are extremely insoluble molecules. Their solubility and tissue specificity can be modulated by attaching various groups to the macrocycle rendering them suitable for a wide spectrum of applications. Therefore a substantial amount of work has been focused on modifying and functionalizing Pc. There are two main methods to achieve such goals. In the first method, a straightforward, one step procedure has been developed involving the *cyclo*-tetramerization of substituted *ortho*-dicarboxylic acids or their derivatives.<sup>6</sup> This method cannot be applied to all metallo-Pc derivatives due to sensitivity of the substituents under the selected reaction conditions. A second, more flexible approach involves direct substitution onto a

pre-fabricated Pc and thus a great deal of attention has been focused on developing this procedure.

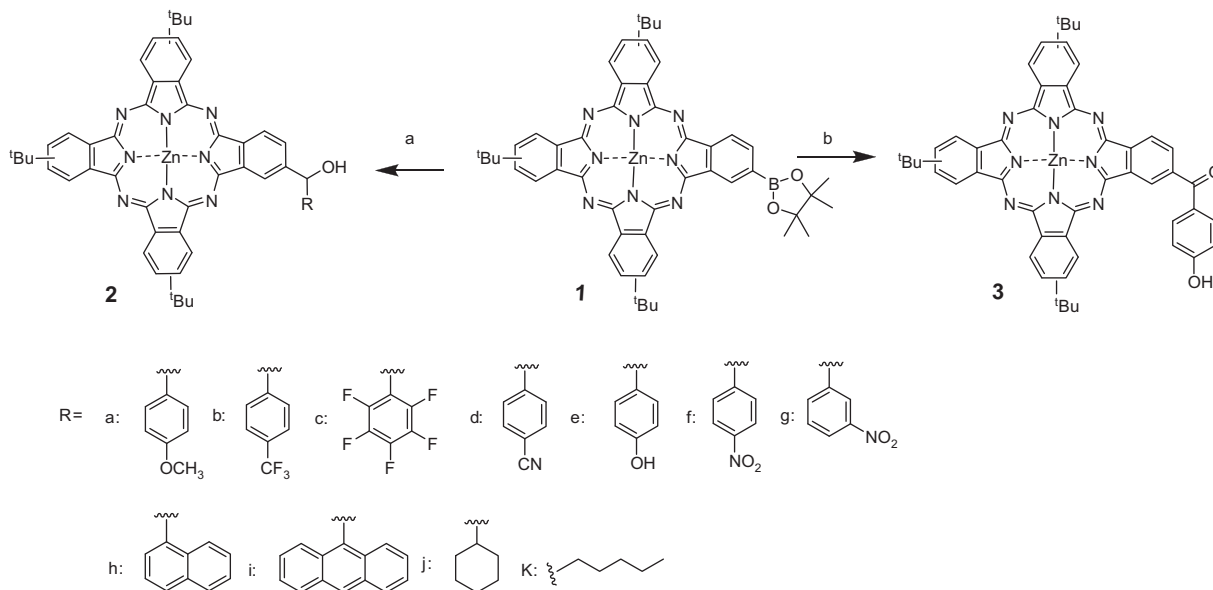
There has been a dramatic growth in the use of transition metal catalysts in important organic synthetic transformations. Due to the tremendous versatility and utility of Pd in C–C bond formation, much effort has been devoted to the development of new reactions, and novel applications are reported continuously. The Pd-catalyzed coupling reaction is a powerful tool for further derivatization of Pc and porphyrins.<sup>7</sup> Using halogenated Pc as template, Pd-catalyzed coupling reactions provide an interesting route to synthesize new families of unusually elaborated Pc macrocycles.

Recently, renewed interest has been given to Rh-catalysts for carbon–carbon bond forming reactions.<sup>8</sup> From a synthetic perspective, this transition metal allows for coupling reactions that are not always accessible with other metal catalysts. Many of the new reactions that are catalyzed by Rh-complexes show also promise from an environmental perspective since water can be used as a co-solvent, or in many cases as the sole solvent. The Rh-catalyzed transformation has also been employed in porphyrin modifications.<sup>9</sup> However no such studies have been reported for Pc. Here we report for the first time the use of Rh-catalyzed transformations for the synthesis of Pc derivatives.

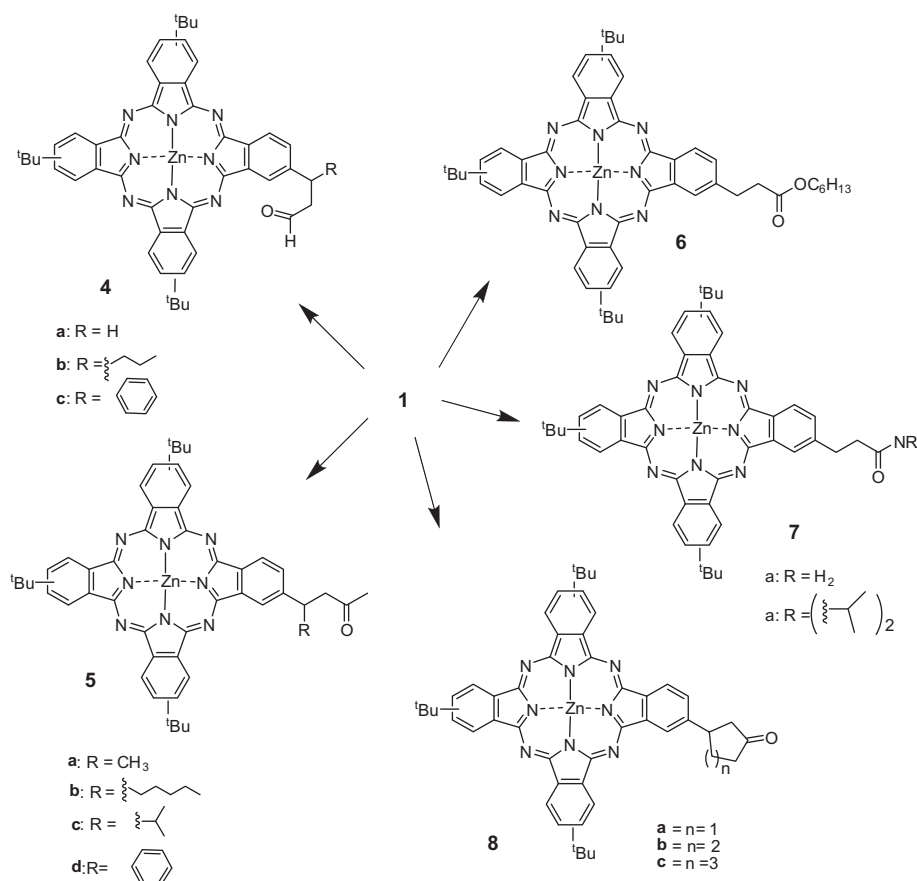
Several studies describing the formation of diarylcarbinol via the 1,2-addition of organometallic reagents to aldehydes have been reported. In 1998, Miyaura's group<sup>10</sup> made the first attempt to use Rh-catalyzed *trans*-metallation between aryl- or 1-alkenylboronic acids and aldehydes in aqueous solution. Subsequently a number of studies have been reported achieving high yield and enantio-selectivity. A variety of Rh-complexes were shown to exhibit excellent catalytic activity,<sup>11</sup> including cationic Rh-complexes with weak coordinating carborane counter ions,<sup>12</sup> using polar

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**Scheme 1.** [Rh(acac)-(CO)<sub>2</sub>], dppf, DME/water, 80 °C, (b) [Rh(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>Cl]<sub>2</sub>, P(tBu)<sub>3</sub>, toluene/acetone/water (20:3:2), 80 °C.



**Scheme 2.** [RhCl(cod)]<sub>2</sub>, NaHCO<sub>3</sub>, aqueous dioxane/H<sub>2</sub>O (10:1), 4–24 h, room temperature.

and nonpolar solvents, different ligands,<sup>13</sup> temperature, and base. Previously we reported the synthesis of the Suzuki Pc-boronate synthon and its successful use in the single step preparation of Pc–Pc heterodyads, Pc–Por dyads, and Pc–Por–Pc triads, directly connected through a C–C bond.<sup>14</sup> Using Miyauro's reaction protocol<sup>10</sup>, Pc boronate ester **1** with an excess of aldehyde and a catalyst, generated in situ from [Rh(acac)-(CO)<sub>2</sub>] and dppf, was heated at

80 °C in a mixture of DME/water (10:1) to yield the 1,2-addition products **2a** (30%), **2b** (35%), **2c** (60%), **2d** (65%), **2e** (35%), **2f** (50%), **2g** (450%), **2h** (60%), **2i** (60%), **2j** (50%), and **2k** (60%) in moderate yield<sup>15</sup> (Scheme 1). Hydrolytic deboration of the Pc-boronate ester gave a competing side product (structure not shown). A variety of aromatic aldehydes containing different functional groups (electron rich and electron deficient) were used. Pre-

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