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Active Pd species in the formation of polysubstituted olefins and naphthalenes in the reaction between arylboronic acid and diphenylacetylene

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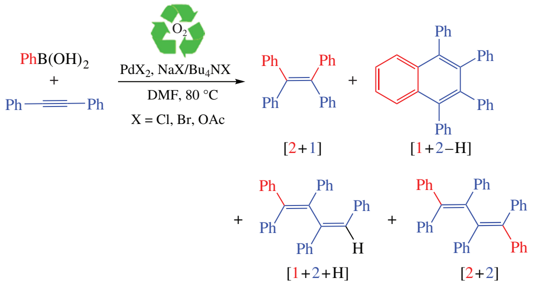
'Ligand-free' Pd-catalyzed reaction between arylboronic acid and diphenylacetylene affords a set of polyphenylated olefins and 1,2,3,4-tetraphenylnaphthalene whose yields are dependent on counteranion of Pd^{II} salt and additive nature. Tetraphenylethylene and hexaphenylbuta-1,3-diene are likely formed in tandem arylation/cross-coupling reaction with the participation of hydroxo/alkoxo alkenyl Pd species, whereas 1,2,3,4-tetraphenylnaphthalene formation probably proceeds through tandem arylation/C–H activation by halide-containing alkenyl Pd complexes.



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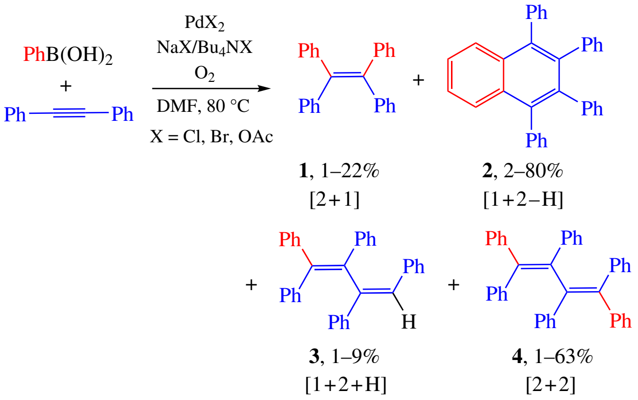
π-Conjugated molecules are highly desired compounds in the synthesis of semiconductors, light emitters, pharmaceuticals, *etc*.[1–4] The reaction between arylboronic acid (frequently used as arylating agent in oxidative cross-coupling processes)[5,6] and diarylacetylene can be considered as one of the ways for obtaining such molecules. Depending on particular reaction conditions, this coupling can afford three- and four-substituted alkenes,[7–9] polysubstituted butadienes[9,10] or polyarylnaphthalenes.[11] However, in order to achieve satisfactory yields of these products, in most cases it was necessary to use strong organic ligands for transition metal catalyst, or stoichiometric amounts of toxic copper or silver salts as oxidants.

In this study we have found that the reaction between phenylboronic acid and diphenylacetylene[†] under so-called 'ligand-free' conditions (*i.e*., when no additives of strong organic ligands to stabilize Pd were used) under oxygen atmosphere (as an oxidant) gave four types of polysubstituted products **1–4** (Scheme 1, for details see Online Supplementary Materials, Section S1).

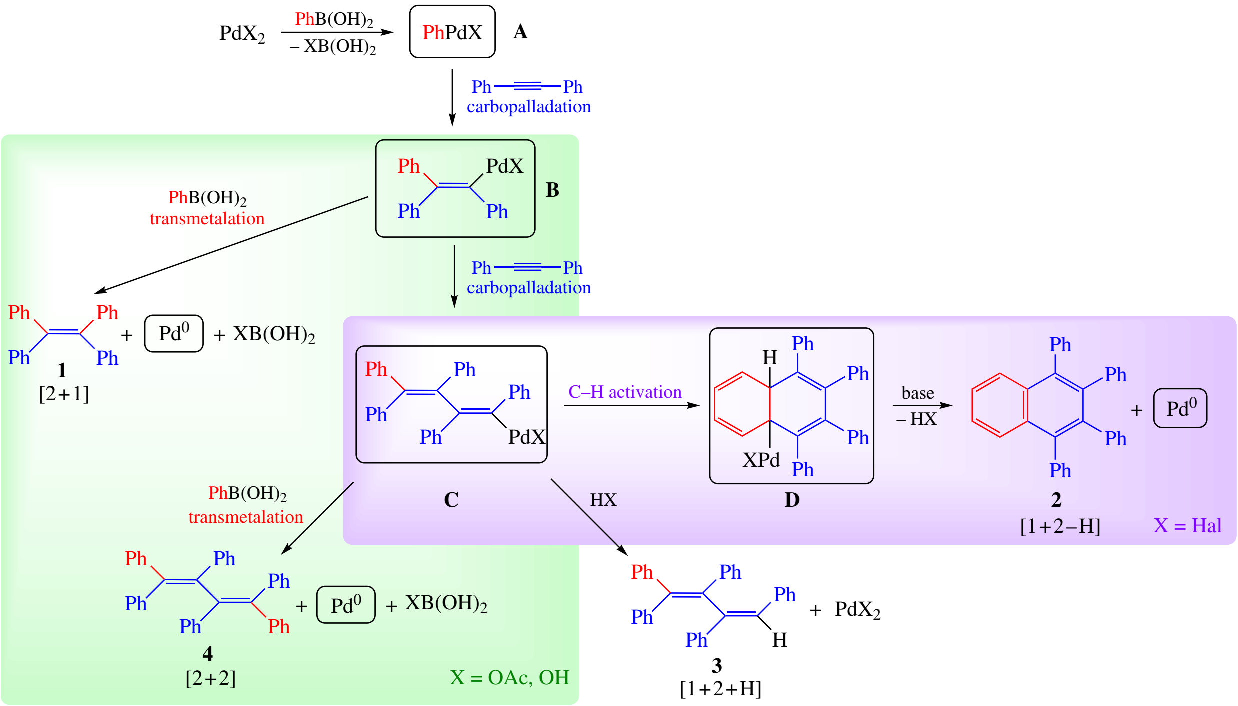
Considering the general viewpoints about possible Pd catalyst transformations in the reaction systems containing arylboronic acid and diarylacetylenes,[1,8,10,12–14] probable pathways for the products **1–4** formation can be proposed (Scheme 2). Tetraphenylethylene **1** (the product of the assembly of two arylboronic acid molecules and one diphenylacetylene molecule, designated correspondingly as [2+1]) and hexaphenylbuta-1,3-diene **4** ([2+2], using the same terms) can form as a result of tandem arylation (through carbopalladation **A**→**B** or **A**→**B**→**C**)/Suzuki–Miyaura cross-coupling (through transmetalation of **B** or **C**). 1,2,3,4-Tetraphenylnaphthalene **2** was likely the product of tandem carbopalladation (**A**→**B**→**C**)/C–H activation (**C**→**D**) [1+2−H] (*i.e*., deprotonation occurs in the intermediate product of [1+2] assembly). If the terminal step of the alkenyl Pd complex **C** is the protonation, 1,2,3,4,5-pentaphenylbuta-1,3-diene **3** [1+2+H] was formed.

Yields of products **1–4** and, therefore, the integral selectivity of the reaction were substantially dependent on the counterion of Pd^{II} salt used as the catalyst precursor. In the absence of additive, the main reaction product was diene **4**, and its yield was more than two times higher when Pd(OAc)$_2$ was used instead of PdCl$_2$



Scheme 1

[†] All catalytic reactions were carried out by mixing phenylboronic acid (2.5 mmol), diphenylacetylene (2.5 mmol), and naphthalene (GC internal standard, 0.5 mmol) in DMF (5 ml). The resulted solution was placed in a 25 ml two-necked round bottom flask equipped with a magnetic stir bar and a septum inlet containing Pd precursor (0.04 mmol), NaOAc (0.8 mmol, if used) as the base, and Bu$_4$NBr (0.8 or 1.6 mmol, if used) under oxygen (balloon). The reaction was initiated by placing the reactor in a pre-heated oil bath (80 °C) with stirring (480 rpm). The reaction was continued for 30 h. Samples for GC/GC-MS analysis were collected using a syringe with a steel needle at different reaction time points. Mass-spectra of the reaction products are presented in Online Supplementary Materials.



Scheme 2

(Table 1, entries 1 and 2). In our opinion, it resulted from higher reactivity of alkenyl Pd complexes **C** (see Scheme 2) containing acetate ions (or hydroxide ones possibly formed from acetate ions by the action of trace water), if comparing with halide-containing complexes in the Suzuki–Miyaura-type transmetalation step leading to product **4**. It is well-known that the Suzuki–Miyaura reaction is extremely sensitive to the concentration and nature of base, because of the formation of active oxopalladium intermediates, in accordance with several comprehensive studies.[15–18]

However, when NaOAc being typical base used for cross-coupling processes was added to the reaction catalyzed by PdCl$_2$, yield of **4** dramatically dropped, while yields of tetraphenylethylene **1** (that was also the product of tandem carbopalladation/transmetalation, see Scheme 2) and 1,2,3,4-tetraphenylnaphthalene **2** grew significantly (see Table 1, entry 3). Note that the formation of **2** in analogous documented[11] reaction involved pre-synthesized organometallic compound as catalyst and stoichiometric amounts of silver or copper salt as oxidants. An increase in the yield of **2** in the presence of the base may be accounted for that the necessary C–H activation proceeds through β-hydride elimination in **D** accelerated with the assistance of base. Conversely, if base is absent, the reverse protonation would suppress the product formation.[19,20]

Table 1 Yields of products **1**–**4** in the reaction between PhB(OH)$_2$ and PhC≡CPh (see Scheme 1).[a]

Entry	Catalyst precursor	Base	Additive	Product yields (%)			
				1	**2**	**3**	**4**
1	PdCl$_2$	–	–	1	2	3	27
2	Pd(OAc)$_2$	–	–	3	1	1	63
3	PdCl$_2$	NaOAc	–	15	28	8	4
4	PdCl$_2$	–	Bu$_4$NBr	2	6	5	1
5	PdCl$_2$	NaOAc	Bu$_4$NBr	22 (16)[b]	57 (80)[b]	5 (1)[b]	3 (2)[b]
6	PdCl$_2$	NaOAc	NaBr	21	62	3	2
7	PdCl$_2$	NaOAc	Bu$_4$NCl	20	35	9	3
8	Pd(OAc)$_2$	NaOAc	–	7	8	trace	23
9	Pd(OAc)$_2$	–	Bu$_4$NBr	2	10	6	3
10	Pd(OAc)$_2$	NaOAc	Bu$_4$NBr	14 (8)[b]	72 (38)[b]	7 (2)[b]	2 (trace)[b]

[a] Reaction conditions: catalyst precursor ($C = 0.008$ mol dm^{-3}), base ($C = 0.16$ mol dm^{-3}), additive ($C = 0.16$ mol dm^{-3}), DMF, 80 °C, 30 h.
[b] With the additive $C = 0.32$ mol dm^{-3}.

If the proposals were fair about higher reactivity of hydroxo- or acetate Pd alkenyl complexes **B** and **C** in comparison with halide complexes in the transmetalation steps with formation of products **1** and **4**, additives of halide salts favoring halide complexes formation should suppress the accumulation of **1** and **4**. Indeed, in the presence of Bu$_4$NBr and in the absence of base the yields of all products **1**–**4** were essentially low (see Table 1, entries 4 and 9). At the same time, simultaneous application of NaOAc and Bu$_4$NBr resulted in considerable increase in the yield of **2** with a slight increase in the yield of **1** and suppressing of **3** and **4** formations (entry 5). Apparently, acetate ions would favor competition of the transmetalation step against carbopalladation by one more diphenylacetylene molecule involving intermediate **B** containing AcO$^-$ or HO$^-$ counterions. This should lead to an increase in the yield of **1** and a decrease in the yield of **4** (see Scheme 2). On the other hand, NaOAc as base should promote C–H activation. The contribution of the latter process is also higher in the presence of Bu$_4$NBr. Note that using NaBr instead of Bu$_4$NBr had a slight effect on the yields of **1**–**4** while the nature of halide counterion was more essential: in case of Bu$_4$NCl yield of **2** significantly drops (see Table 1, entries 5–7). The positive role of bromide salt was more pronounced with its higher concentration (entry 5), which can be explained by probable catalytic activity of bromide-containing Pd alkenyl complexes **C**–**D** in the formation of 1,2,3,4-tetraphenylnaphthalene **2** (see Scheme 2). At the same time, an increase in the yield of **2** with an increase in Bu$_4$NBr concentration can be explained by the rise of the Pd fraction in solution potentially responsible for the catalysis. Multiple experimental evidence for an increase in the portion of dissolved Pd species over heterogeneous (often inactive) phase under the action of halide salts was published earlier.[21–23] However, the issue of the distinguishing between homogeneous and heterogeneous catalysis mechanisms is beyond the scope of this work.

The patterns of the influence of additives on the yields of products **1**–**4** observed in the reactions with PdCl$_2$ were confirmed by the results of the reaction using $Pd(OAc)_2$. Maximum yield of 1,2,3,4-tetraphenylnapthalene **2** was obtained when NaOAc and Bu_4NBr were used simultaneously (see Table 1, entry 10); however, increasing concentration of Bu_4NBr in this case led to significant drop in the yields of **1–4** due to decrease in the stability of the active catalyst (as follows from integral kinetic curves for the reactants). At the same time, the additives of bromide or acetate salts substantially suppressed the formation of hexaphenylbuta-1,3-diene **4** (entries 9, 10).

To conclude, hexaphenylbuta-1,3-diene **4** can be obtained with satisfactory yield (*ca*. 60%) using simple $Pd(OAc)_2$ without any additives under 'ligand-free' conditions with oxygen as oxidant. If 'ligand-free' catalytic system $PdCl_2$/NaOAc/Bu_4NBr is employed, 1,2,3,4-tetraphenylnaphthalene **2** can be prepared in 80% yield (see Table 1, entries 2, 5).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.02.018.

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