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Efficient hydroarylation of terminal alkynes with sodium tetraphenylborate performed in water under mild conditions

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ABSTRACT

The hydroarylation of terminal alkynes with sodium tetraphenylborate was performed in high yield within 3 h at room temperature in water, using palladium(II) complexes with imidazole ligands as catalysts. Under these conditions, differently substituted phenylacetylene substrates were converted to arylalkenes and aryl-substituted dienes. High conversion and excellent selectivity were achieved in the hydroarylation of alkynols with sodium tetraphenylborate. Only one product, arylalkene with an OH group, was formed in these reactions with the yield dependent on the kind of alkynol used. A plausible hydroarylation reaction mechanism was proposed on the basis of the palladium species identified in the reaction mixture and H/D exchange studies. The contribution of water as the hydride source was evidenced.

1. Introduction

The functionalization of alkynes *via* the addition of an aryl group, namely the arylation of alkynes, presents a very attractive pathway to organic compounds such as arylalkenes [1–4]. These compounds are intermediates in the synthesis of biologically active species, pharmaceutical and agrochemical agents (Fig. 1) [5–8]. The medical properties of stilbene derivatives, the products of hydroarylation, have been extensively studied [9,10]. For example, *trans*-resveratrol and its derivatives exhibit significant antioxidant activities [11–15].

Arylalkenes are usually produced by the Heck coupling of aryl halide and olefin [16–18]. This method is highly efficient in applying to a wide range of substrates. However its main drawback is the formation of halide-containing wastes, harmful for the environment. Therefore, other methods, avoiding the application of aryl halides as substrates to obtain products in a greener way, are needed. An interesting alternative is offered by catalytic hydroarylation, which involves the activation of the triple bond of alkyne, used instead of alkene.

The hydroarylation of alkynes can be performed according to different protocols, the Fujiwara reaction being the most explored one [19,20]. In the Fujiwara hydroarylation, benzene derivatives bearing alkyl, OR, or OH groups [21,22] or N-heteroarenes [23–25] react with electron-deficient alkynes in an acidic medium. Advantageously, the products of *Z* conformation are preferably formed. Another method used for the production of arylalkenes from alkynes employs arylboron compounds, as the donors of the aryl group, instead of benzene derivatives. In this method, the C–H activation step is omitted, making the procedure more universal. The hydroarylation of alkynes with arylboronic acid has been attained with Pd [26–29], Rh [30,31], Ni [32–35], Cu [36–38], Mn [39] and Co [40].

Till now, most of the hydroarylation reactions of alkynes with arylboronic acid have referred to internal alkynes, and only in a few cases has the successful hydroarylation of terminal alkynes been reported [19,20,41]. Typical palladium catalysts used in these reactions have been $PdCl_2(PPh_3)_2$ and $Pd(OAc)_2$. In contrast, the application of sodium tetraphenylborate as the phenylating agent has been reported only scarcely [41–43].

We have focused our efforts on the hydroarylation of terminal alkynes and alkynols. In this paper, we present the results obtained in the hydroarylation with sodium tetraphenylborate using Pd(II) complexes with imidazole ligands as catalysts. Complexes of this type can be prepared in high yield with different imidazoles, and they are stable in the presence of air and water. Their ability to activate arylboronic compounds has been confirmed in the Suzuki–Miyaura cross-coupling and carbonylative coupling under mild conditions [44–47]. Therefore it was expected that Pd(II) imidazole complexes would also be good catalysts for the hydroarylation of terminal alkynes in the water medium.

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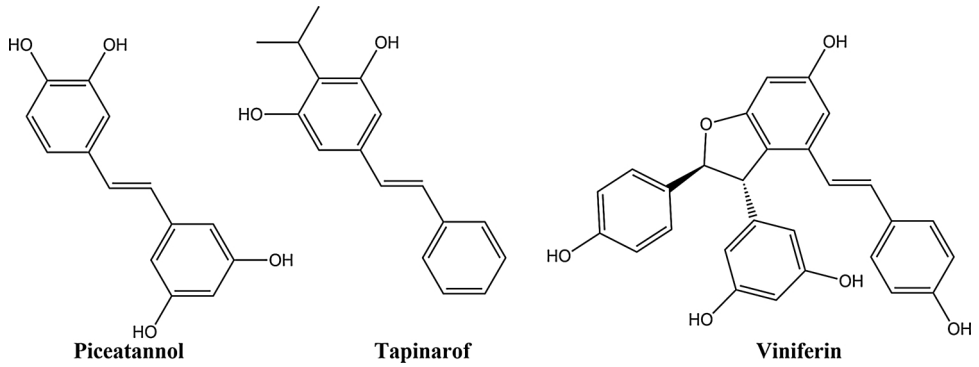


Fig. 1. Stilbenes present in pharmaceutical agents and in natural products.

2. Experimental

2.1. Synthesis of $PdCl_2(imidazole)_2$ complexes

$PdCl_2(imidazole)_2$ complexes (**I–V**) were obtained according to the reported procedure [47].

2.2. General procedure for the hydroarylation of terminal alkynes with $NaBPh_4$

The reactions were carried out in an air atmosphere in Schlenk tubes equipped with a magnetic stir bar. In a typical run, $PdCl_2(imidazole)_2$ (**I–V**) was loaded into the tube, and 2 mL of the solvent was added. Next, glacial acetic acid (1.0 mmol, 0.12 mL), $NaBPh_4$ (1.0 mmol, 0.34 g), and the corresponding alkyne (1.0 mmol) were introduced to the tube. The reaction mixture was stirred at room temperature or in a silicon oil bath at 60 °C for 1 h or 3 h. After this time, the reactor was cooled down, and the organic products were extracted with 10 mL of *n*-hexane. 0.26 mL of dodecane was added as internal standard. The extracts were analysed by using a GC-flame ionization detector.

3. Results and discussion

For the first catalytic tests, we selected Pd(II) complexes with different imidazole ligands, such as 1-benzylimidazole (**I**), 1-methylbenzimidazole (**II**), 1,2-dimethylimidazole (**III**), 1-benz-2-methylimidazole (**IV**), and 1-butyl-2-methylimidazole (**V**) (Fig. 2).

The reaction of phenylacetylene with sodium tetraphenylborate ($NaBPh_4$) was carried out at room temperature in water (Fig. 3, Table 1). It was found that addition of AcOH is necessary to obtain hydroarylation products, similarly as it was described for other systems [41]. It should be noted, that the catalytic system is multiphasic because the alkynes are insoluble in water. In addition, the palladium complexes are poorly water-soluble although they dissolve partly in the reaction medium.

In each reaction, the conversion of phenylacetylene was 100%, and two products were identified. One, stilbene (**2a**), was formed by the addition of the aryl group of tetraphenylborate to phenylacetylene. The other product, (**3a**), containing three aryl groups, was formed by two molecules of phenylacetylene and one phenyl group originating from tetraphenylborate. Both products formed as single isomers (Fig. 3). The compound **3** had previously been found in a small amount as a side product in the hydroarylation of the internal alkyne with boronic acids in the presence of Rh/NiZn catalyst [48]. In addition, an analogous product had been obtained in the Fujiwara hydroarylation of ethyl propiolate with benzene catalysed by the chelating dicarbene palladium (II) complex in the presence of $AgBF_4/HBF_4$ [21]. However, in most of hydroarylation reactions, exclusively stilbene derivatives (**2**) were formed [49]. Considering the literature data, the formation of product **3a** can be considered as an original feature of our system.

In all reactions investigated in these studies, product **3a** was created with higher yield than product **2a**. The biggest difference between the yield of **2a** and that of **3a** was observed for complex **I** (Table 1, entry 1). In contrast, an excess of **3a** over **2a** was smaller for complexes **II** and **IV**, which formed *ca.* 40% of **2a** and *ca.* 60% of **3a** (Table 1, entries 2 and 4). Thus, the kind of imidazole ligand influenced reaction selectivity. In particular, the introduction of a methyl group at the C2 carbon of the imidazole ring in the benzimidazole ligand (complex **IV**) resulted in a decrease in **3a** yield from 71% (catalyst **I**) to 57% (catalyst **IV**) (Table 1).

The optimization of the reaction conditions was performed for a palladium complex with a 1-benzylimidazole ligand (**I**) (Table 2). Interestingly, almost the same yield of the products was obtained at room temperature and at 60 °C (Table 2, entries 1 and 2). Advantageously, hydroarylation experiments can be carried out under mild conditions. The lowering of catalyst loading from 1.0 to 0.5 mol% did not affect the results significantly (Table 2, entries 2 and 4), but, at 0.1 mol% of catalyst, the conversion of phenylacetylene decreased from 98% to 50% (Table 2, entry 5). The shortening of the reaction time from 3 to 1 h had a negative effect on the conversion of phenylacetylene, which decreased to 66%. In order to check whether an amount of $NaBPh_4$ lower than 1 mmol was sufficient to convert phenylacetylene to the desired products, 0.5 mmol was used. However, only 75% of phenylacetylene reacted in these conditions, indicating the participation of less than four

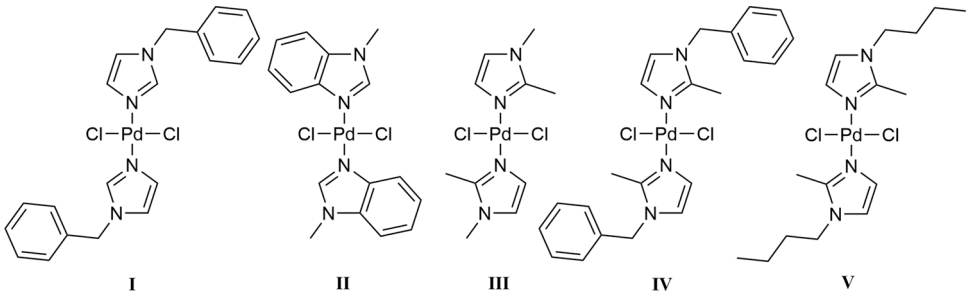


Fig. 2. The palladium-imidazole complexes **I–V** used in these studies.

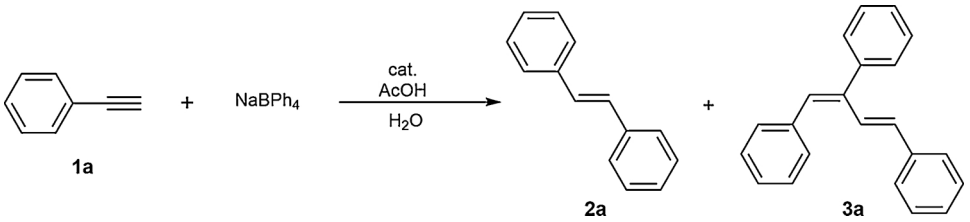


Fig. 3. Palladium catalysed hydroarylation of phenylacetylene with $NaBPh_4$.

Table 1
Hydroarylation of phenylacetylene in the presence palladium(II) complexes (**I–V**).[a]

Entry	Complex	Conv. (%)[b]	Yield (%)[b]	
			2a	**3a**
1.	**I**	100	29	71
2.	**II**	100	39	61
3.	**III**	100	31	69
4.	**IV**	100	43	57
5.	**V**	100	32	68

[a] *Reaction conditions:* catalyst (1.0 mol%), phenylacetylene (1.0 mmol) $NaBPh_4$ (1.0 mmol), AcOH (2.0 mmol), 2 ml water, rt, 3 h.
[b] Determined by GC.

Table 2
Optimization of hydroarylation conditions with catalyst I.[a].

Entry	Catalyst [mol%]	Solvent	Conv **1a**[b]	Yield[b]	
				2a	**3a**
1.[c]	1.0	water	100	29	71
2.	1.0	water	100	31	69
3.[d]	1.0	water	66	28	38
4.	0.5	water	98	35	63
5.	0.1	water	50	17	33
6.[e]	0.5	water	75	24	51
7.[f]	0.5	water	61	11	47
8.[g]	0.5	water	76	12	56
9 [h]	0.5	water	92	21	71
10.[i]	0.5	water	93	17	76
11.[j]	0.5	water	93	31	62
12.[k]	0.5	water	5	–	5
13.[l]	0.5	water	14	–	14
14.	1.0	2-propanol	0	–	–
15.[m]	1.0	2-propanol/water	33	19	14
16.	1.0	THF	0	–	–
17.[n]	1.0	water	72	31[o]	39

[a] *Reaction conditions:* catalyst **I** (1.0 mol%), phenylacetylene **1a** (1.0 mmol, 0.11 mL) $NaBPh_4$ (1.0 mmol), AcOH (2.0 mmol), in 2 mL water, rt, 3 h.
[b] Determined by GC.
[c] 60 °C.
[d] 1 h.
[e] $NaBPh_4$ (0.50 mmol, 0.17 g).
[f] phenylacetylene **1a** (1.0 mmol, 0.11 mL) was added after 1 h.
[g] phenylacetylene **1a** (2.0 mmol, 0.22 mL).
[h] 1-benzylimidazole (0.25 mmol, 0.079 g) was added.
[i] 1-benzylimidazole (0.5 mmol, 0.079 g) was added.
[j] 1-benzylimidazole (0.5 mmol, 0.079 g) was added, 60 °C.
[k] 1-benzylimidazole (1.0 mmol, 0.16 g) was added.
[l] 1-benzylimidazole (1.0 mmol, 0.16 g) was added, 60 °C.
[m] addition (2.0 mmol, 0.036 g) H_2O.
[n] $PdCl_2(PPh_3)_2$ as catalyst.
[o] *Z* (25%) and *E* (6%) isomers.

phenyl groups in the reaction. Considering the solvent, the reaction can be carried out efficiently in water, while the products were not formed in organic solvents (2-propanol, THF). However, the addition of water to 2-propanol made it possible to obtain 33% conversion (Table 2, entry 15).

In is worth to note that hydroarylation with $PhB(OH)_2$ used instead of $NaBPh_4$ was not successful. The test reactions, performed with phenylacetylene and phenylboronic acid in water, THF and water/THF mixture did not lead to any products. This is in line with previous observations that $PhB(OH)_2$ gave good results in hydroarylation of internal alkynes, but not with terminal ones [20,29]. For example, only traces of the product were obtained from phenylacetylene [29].

Attempts to increase the reaction selectivity and influence the ratio of products **2a/3a** by changing the substrate amounts failed. Similarly, the introduction of an excess of phenylacetylene during the reaction changed the composition of the products only slightly, although selectivity to product **3a** increased. Interestingly, the addition of an excess of free 1-benzylimidazole resulted in an increase in selectivity to product **3a** (decrease in the **2a/3a** ratio) with only a small decrease in conversion (Table 2, entries 4 and 9). On the other hand, the application of a bigger amount of 1-benzylimidazole (1 mmol) caused the inhibition of the reaction and a decrease in the conversion of phenylacetylene at room temperature and at 60 °C (Table 2, entries 12 and 13). The highest yield of **3a** (76%) was obtained at 0.5 mmol of 1-benzimidazole (Table 2, entry 10).

In order to get deeper understanding of the observed selectivity, changes of conversion and yield were analyzed for the reaction of **1a** with $NaBPh_4$ (Fig. S2). It was found that already at the beginning of the reaction two products were formed with a predominance of **3a**. After *ca.* 60 min. the amount of **2a** stabilized while product **3a** was still formed. Thus, products **2a** and **3a** were formed separately and **2a** was not converted to **3a**.

Under the same reaction conditions $PdCl_2(PPh_3)_2$ was tested for comparison (Table 2, entry 17). The conversion of **1a** was lower (72%) than that with catalyst **I** (100%) and he selectivity was also worse. Two isomers of hydroarylation product **2**a were created: isomer *Z* (25%) and isomer *E* (6%). The product **3a** was formed in 39% yield and small amount of the phenylacetylene dimer was observed (1%).

Promising results obtained in the reaction of phenylacetylene (**1a)** with $NaBPh_4$ in the presence of **I** provided motivation to test the scope of that reaction using a variety of terminal alkynes (Fig. 4). For this purpose, the optimized conditions indicated as entry 4 in Table 2 were employed.

The obtained results shown an influence of the alkyne structure on the hydroarylation selectivity.

The phenylacetylene substrate **1e,** bearing a methyl group in the 2-position, reacted similarly to unsubstituted **1a**, forming two products (Table 3, entry 5). The presence of a methyl group at the 4-position (**1b**) caused a lower conversion, 87% (Table 3, entry 2). In reactions of **1c** and **1d**, containing chlorine and fluorine substituents, two products were formed, although the conversion of **1d** was lower than that of **1c**. In most reactions leading to two products, the yield of **3** was higher than that of **2**. An exception was noted for **1n,** methyl-2-propynyl ether, which gave 56% of **2n** and 37% of **3n**.

The steric effect of the substituents was observed in reactions of alkynes with an electron-donating OMe group at the 4-position of the aryl ring, **1f** and **1k**. The former one, **1f** without other substituents, was converted in 88%, while conversion decreased to 18% when a methyl group was present at the 2-position (**1k**). Interestingly, only one product, namely **2f** or **2k**, was formed from both of the substrates. A similar selectivity was noted for the alkyne **1 h** containing an electron-

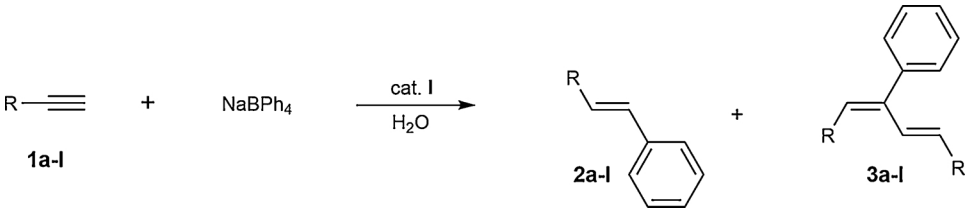
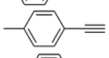
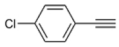
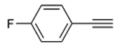
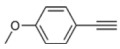
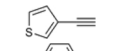
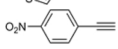
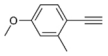
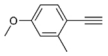
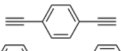
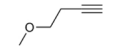


Fig. 4. Hydroarylation of various alkynes.

Table 3
Results of the hydroarylation of different alkynes (**1a–l**) with sodium tetraphenylborate catalysed by complex **I**.[a].

Entry	Alkyne		Conv **1**[%][b]	Yield[%][b]	
				2	**3**
1.		**1a**	98	35	63
2.		**1b**	87	31	56
3.		**1c**	100	53	47
4.		**1d**	68	15	53
5.		**1e**	100	30	70
6.		**1f**	88	88	–
7.		**1 g**	56	12	44
8.		**1 h**	54	54	–
9.		**1i**	20	20	–
10.		**1 j**	7	7	–
11.[c]		**1 j**	81	81	–
12.		**1k**	18	18	–
13.[c]		**1k**	51	51	–
14.		**1l**	17	17	–
15.		**1 m**	27	12 (8)[d]	–
16.		**1n**	93	56	37

[a] *Reaction conditions:* catalyst **I** (2.5×10^{-5} mol, 0,0125 g), alkyne **1** (1.0 mmol) $NaBPh_4$ (1.0 mmol, 0.34 g), AcOH (2.0 mmol, 0.12 mL), in 2 mL water, rt, 3 h.
[b] Determined by GC.
[c] 60 °C.
[d] Two products.

withdrawing NO_2 substituent at the 4-position. In this case, a relatively low conversion (58%) was achieved. However, only product **2 h** was formed selectively.

The internal alkyne **1 m** gave two products at a low substrate conversion. One product of the hydroarylation, **2 m**, was formed with 12% yield. The other compound was formed by the attachment of two phenyl rings to the triple bond of alkyne (8% yield).

The effect of the kind of alkyne substrate on product composition can be illustrated by the ratio of products **2/3**. Alkynes **1a**, **1b**, and **1e** reacted with $NaBPh_4$ providing products **2** and **3** in the molar ratio of about 1:2; for alkyne **1d,** the ratio was about 1:3, and for alkyne **1 g,** about 1:4. A different trend and a lower yield of **3** were found for **1c** and **1n**. The 4-chlorophenylacetylene, **1c,** was transformed to the corresponding products **2/3** in a molar ratio of about 1:1, and the methyl-2-propynyl ether, **1n**, in a ratio of about 1.5:1. In seven cases (**1f**, **1 h–1 m**), product **3** was not created. It is worth noting that the conversion of **1 j** and **1k** significantly increased at a higher temperature, 60 °C. Fortunately, selectivity remained unchanged, and only products **2 j** and **2k** were formed.

It can be concluded that product **3** was formed with application of alkynes having only one small substituent on the phenyl group. The amount of product **2** increased with increase of the number and bulkiness of substituents. On the other hand, the electron properties of substituents probably didn't affect significantly the reaction selectivity. For example, alkynes containing a donating group (*e.g.* $-CH_3$) or a withdrawing group (*e.g.* –Cl) formed both products.

Alkynols presented the next group of substrates tested in hydroarylation with catalyst **I** (Table 4). Nickel [50] and rhodium [51] complexes were reported as catalyst of hydroarylation reactions of alkynes bearing hydroxyl group. In both cases, boronic acid was used as phenylating agent. Two reactions of terminal alkynols with $NaBPh_4$ were carried out in the presence $PdCl_2(PPh_3)_2$ [41].

Under the applied mild conditions, the selected alkynols reacted with moderate to excellent yield forming exclusively one product of the **2** type. The highest yield of the arylation product, 94–95%, was obtained for **1 u** and **1 t** containing secondary and tertiary alcohols, respectively (Table 4, entries 5 and 7). The secondary alcohol **1 w**, an analogue of **1 t**, gave slightly lower yield, 89%. Interestingly, with $PdCl_2(PPh_3)_2$ two products were obtained from **1 t** with the total yield of only 28% [41].

The primary alkynol, prop-2-yn-1-ol (**1o**), reacted with $NaBPh_4$ to give the expected hydroarylation product **2** with a 70% yield (Table 4, entry 1). The presence of two methyl substituents at the α-carbon of alkynol (**1 s)** increased the yield to 86% indicating the positive influence of steric hindrance. In contrast, the prolongation of the distance between the triple bond and the OH group (**1p** and **1 r**) resulted in a significant decrease in the yield of the product compared to **1o**.

Table 4
Results of the hydroarylation of different alkynols (**1o–u**) with sodium tetraphenylborate catalysed by complex **I**.

Entry	Alkynol		Conv. **1** [%][b]	Yield **2** [%][b]
1.		**1o**	72	70
2.		**1p**	10	10
3.		**1 r**	12	12
4.		**1 s**	93	86
5.		**1 t**	95	95
6.		**1 w**	89	89
7.		**1 u**	98	94

[a] *Reaction conditions:* catalyst **I** (2.5×10^{-5} mol, 0,0125 g), alkynol **1** (1.0 mmol) $NaBPh_4$ (1.0 mmol, 0.34 g), AcOH (2.0 mmol, 0.12 mL), in 2 mL water, 60 °C, 3 h.
[b] Determined by GC.

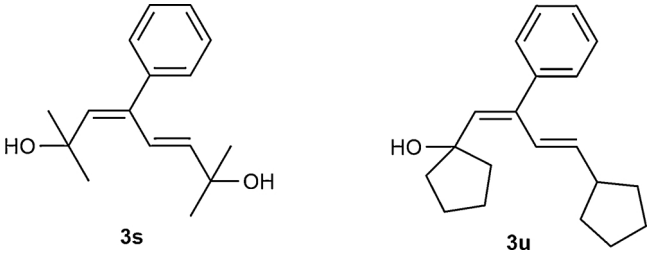


Fig. 5. Side products **3 s** and **3 u** obtained in the hydroarylation of: 2-methyl-3-butyn-2-ol (**1 s**) and 1-ethynylcyclopentanol (**1 u**).

In two cases, **1 s** and **1 u**, apart from the main products, small amounts of side products were also created. In reaction of the alkynol **1 s**, the product of m/z = 246, **3 s**, was identified by GC–MS. It was formed by two molecules of alkynol and one phenyl group (Fig. 5a). It is worth noting that our system selectively transformed **1 s** to the arylated alcohol **2 s**, while an arylated diene was obtained with the catalyst $PdCl_2(PPh_3)_2$. [41] **1 u** showed similar reactivity to **1 s** and formed the product **3 u** comprising three-molecules, but not having one OH group (m/z = 281) (Fig. 5b).

4. Mechanistic studies

In order to get knowledge about the nature of the active catalyst, the Hg(0) poisoning test was performed [52]. For this purpose, two reactions were carried out with a 500-fold excess of Hg(0) to catalyst **I**. In the first reaction, Hg(0) was added together with other substrates at the beginning, while in the second reaction, Hg(0) was introduced after 20 min (Fig. 6). The conversion of phenylacetylene in these reaction was monitored for 3 h and compared to the mercury-free system. In the presence of Hg(0), the efficiency of the catalytic system decreased slightly, but conversion still remained high, 85% or 75%, when Hg(0) was added after 20 min or at the beginning, respectively. These results indicated the domination of the soluble palladium species as the catalytically active form.

In an attempt to identify the palladium species involved in the catalytic cycle, ESI-MS analyses were performed for the reaction mixtures containing phenylacetylene, $NaBPh_4$, and various imidazole complexes.

The ESI-MS spectra of the reaction mixtures showed that the chloride dissociated from palladium to form $Pd(im)_2$ (Fig. 7). Such chlorine-free fragments were found for three different imidazoles. The coordination of AcO to palladium was evidenced by the signal at m/z = 509 assigned to Pd(1-benz-2-methylimidazole)$_2$(AcO). The two next analogues containing other imidazoles were also found. Moreover, the ions of composition $PdCl(im)_3$ were identified, indicating the easy exchange of imidazole ligands [47].

The ESI-MS data evidenced the presence of Pd-imidazole intermediates in the reaction mixture. It can be assumed that imidazole coordinated to palladium-stabilized catalysts and influenced its reactivity.

After the identification of palladium-imidazole complexes in the reaction mixture, attempts were undertaken to explain the formation pathway of products **2** and **3**. To that end, deuterated substrates were employed, and first D_2O was used in the reaction of phenylacetylene (**1a**) with $NaBPh_4$ in the presence of catalyst **I.** Under these conditions, two products, **2a**-*d* (m/z = 181) and **3a**-*d* (m/z = 283), containing one D-atom each, were formed. Additionally, NMR studies of the reaction mixture revealed the presence of D-atoms at the C=C bond. By comparing the ^{1}H NMR spectra of the non-deuterated and deuterated compounds **2**, changes resulting from deuterium substitution were defined (Fig. 8). The signal (**b**), detected at 7.1 ppm (Fig. 8a) and assigned to two protons at the double bond in product **2a,** was not observed for the product **2a**-*d* obtained in D_2O. Instead, the broad triplet (**a**) from one proton coupled with D was observed.

Two signals appeared in the 6.50–6.65 ppm range of the ^{1}H NMR spectrum of product **3a**: a singlet (***c***) and a doublet (***d***) (Fig. 9a). The correlation COSY spectrum showed that another doublet expected for the other proton at the double bond should be present at *ca.* 7.4 ppm; however, it overlaps with the aromatic signals. In the spectrum of **3a**-*d*, a doublet at 6.5 ppm was not observed. This is in agreement with the presence of a C=CD fragment in the molecule (Fig. 9b). Thus, the experiment with D_2O confirmed that water acted as a hydride donor in the reaction of phenylacetylene with $NaBPh_4$.

Hydroarylation of **1a** with sodium tetraphenylborate was also carried out in deuterated acetic, used as a solvent instead of water. Unfortunately, only 2% conversion was achieved in this reaction. This is clear evidence that water is essential to create products of hydroarylation.

On the basis of the obtained results, the mechanism of alkyne hydroarylation with $NaBPh_4$ was proposed (Fig. 10). In the first step, $NaBPh_4$ reacted with AcOH, in the presence of palladium, forming BPh_3 and biphenyl [42,43,53]. The presence of both the products was evidenced by GC–MS. An alternative pathway has been proposed in the literature, based on the formation of BPh_3 without the contribution of palladium [42,54]. However, the formation of benzene, rather than biphenyl, was expected in this case. Simultaneously with the formation of BPh_3, palladium was reduced and a Pd(0) species (**B**) was created. Imidazole ligands play a key role in stabilizing the active forms of Pd (0), preventing their degradation to inactive palladium black. Next, the oxidative addition of BPh_3 led to a Pd(II) intermediate with Ph and BPh_2 ligands (**C**) [41,55]. Oxidative addition of BPh_3 to Pd(0) was proposed in other systems employing $NaBPh_4$ as phenylating agent [41–43,55]. In contrast, oxidative addition of C–B bond to Pd(0) was ruled out in hydroarylation with 4-acetylphenylboronic acid [28]. After the coordination of phenylacetylene to palladium, migratory insertion

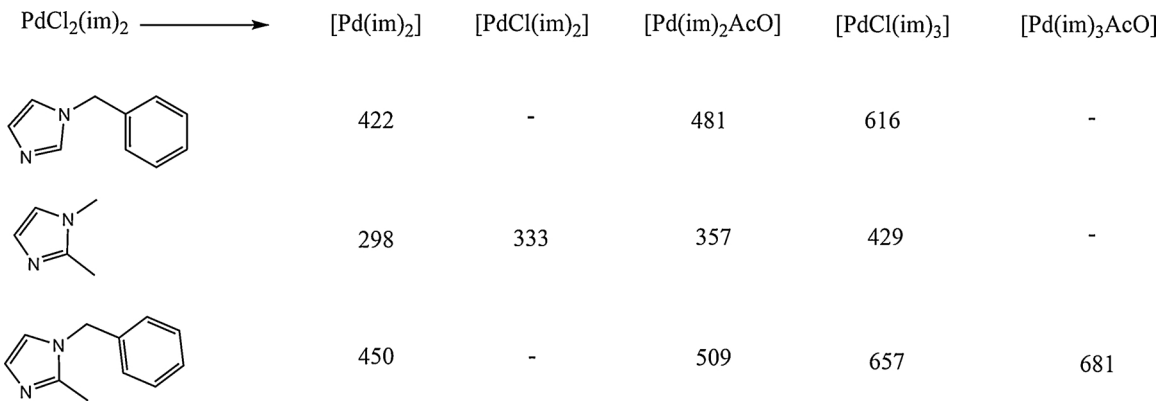


Fig. 6. Effect of mercury on the reaction of phenylacetylene with $NaBPh_4$ catalysed by complex **I.**

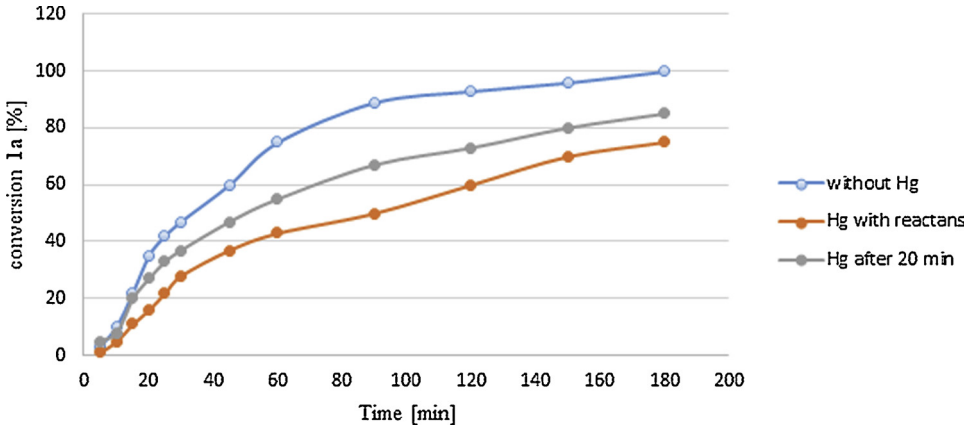


Fig. 7. The Pd-imidazole intermediates identified in the reaction mixtures.

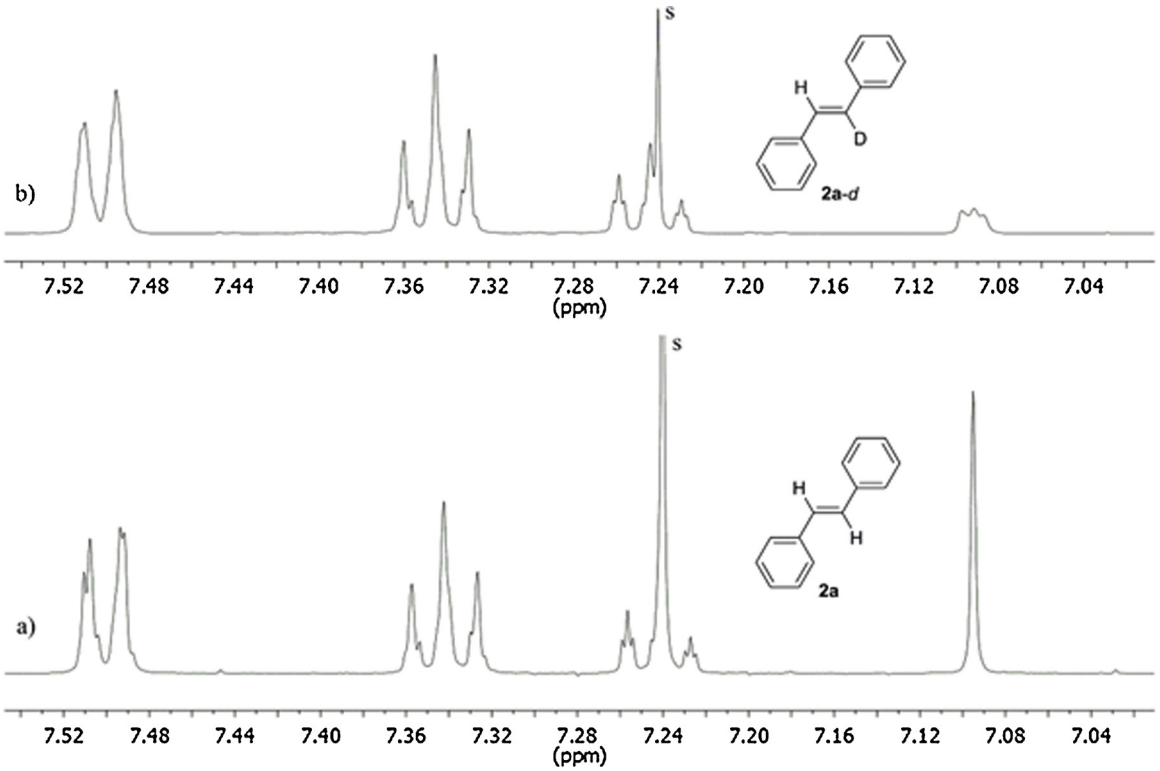


Fig. 8. ^{1}H NMR spectra in $CDCl_3$ of: (a) **2a**; (b) **2a**-*d*.

occurred giving the corresponding palladium intermediate (**E**) with the structure typical of an anti-Markovnikov-type product. Imidazole ligand facilitated this type of transformation, because it occupied less space around palladium than phosphine ligand (in $PdCl_2(PPh_3)_2$) [41].

At this stage two alternative pathways can be considered. The reaction of (**E**) with water led to a palladium hydrido complex (**F**), which could next be transformed to product **2** or **3**. Product **2** (stilbene) was formed by a reductive elimination process. Alternatively, protonolysis of the Pd-vinyl intermediate **E** with AcOH may be considered as the route leading to product **2** *via* an intermediate **F,**. We were not able to identify a hydrido complex F, which is similar to that proposed in diboron mediated alkyne hydroarylation [28]. On the other hand, protonolysis of the Pd-vinyl complex **E** by AcOH present in excess in the catalytic mixture is very plausible.

Formation of product **3** can be also explained by two different schemes. In the first one, another molecule of phenylacetylene should coordinate to the palladium and two alternative pathways can be proposed. intermediate (**F**). Next, an intermediate (**G**) was formed as a result of migratory insertion. The diene product **3** was obtained after reductive elimination, and the catalytically active form (**B**) was recovered [56].

In the alternative pathway, second molecule of phenylacetylene coordinated to the intermediate **E** forming **G,** which was next transformed to the species **H,** by migratory insertion. The final step involved protonolysis of **H,** by AcOH to form product **3**. Only phenylacetylenes with one small substituent on phenyl group can create product **3**. The more expanded phenyl group made it difficult coordination of the second molecule of alkyne to palladium and blocked formation of product**3**.

It is important to underline that the reaction of commercially available stilbene with phenylacetylene under the corresponding catalytic conditions was unsuccessful. This result suggested that the first hydroarylation product (**2**) cannot be re-coordinated before the reaction with the second molecule of phenylacetylene. In fact, the selectivity of hydroarylation depended on the reactivity of palladium species (**F** and **E**) and competition between the reductive elimination of

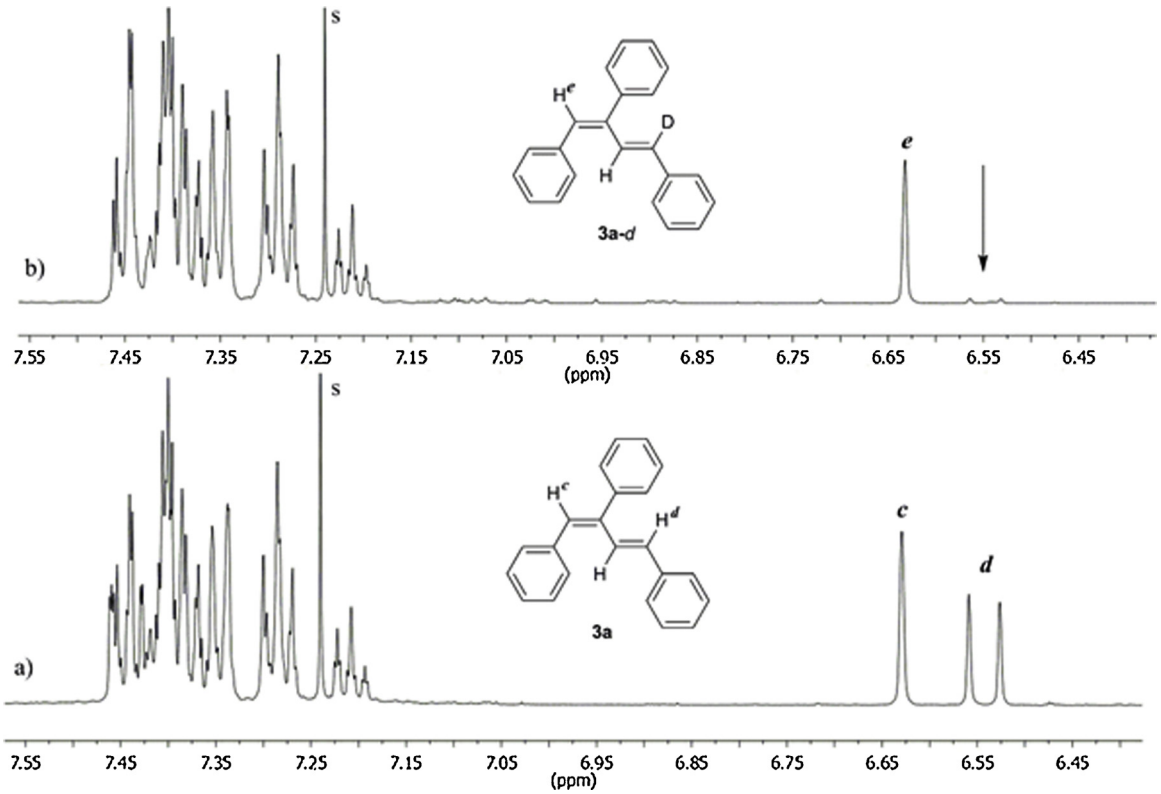


Fig. 9. ^{1}H NMR spectra in $CDCl_3$ of: (a) **3a**; (b) **3a**-d.

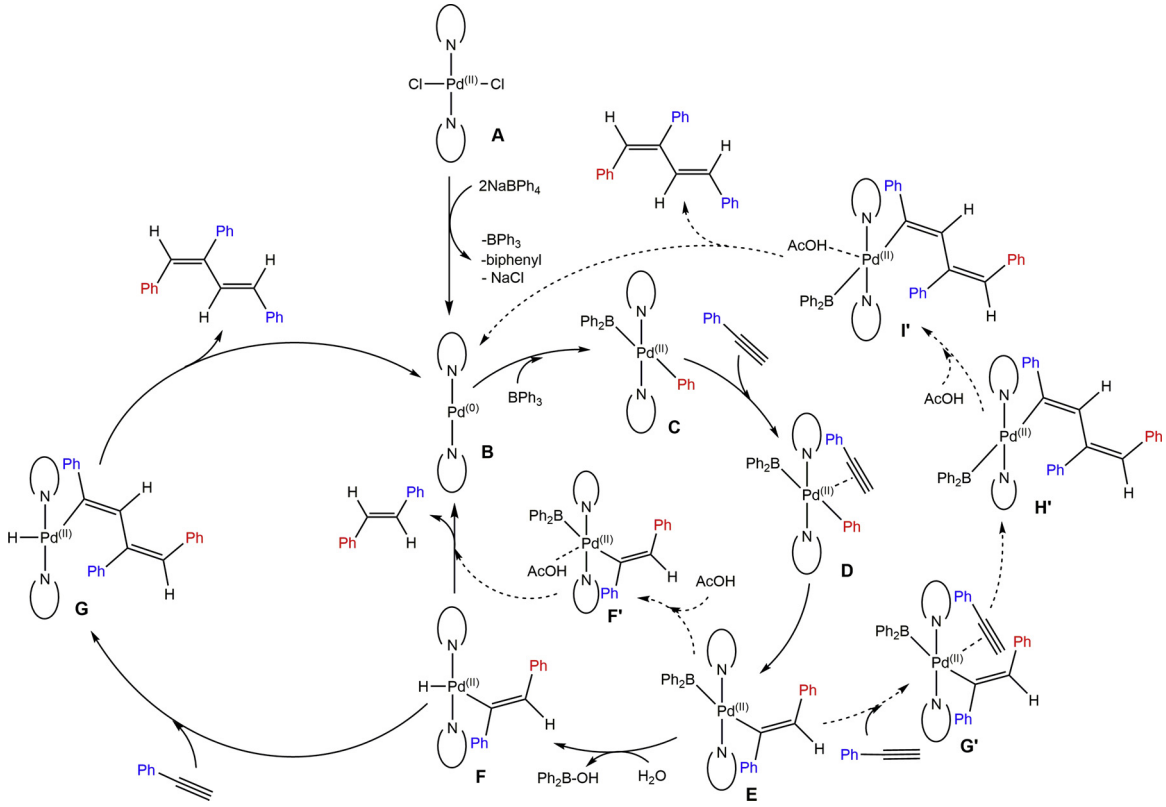


Fig. 10. Proposed reaction mechanism for the hydroarylation of alkynes.

stilbene (**2**) and coordination of the second phenylacetylene to palladium.

Further mechanistic studies will be needed to verify the proposed reaction mechanism. At this point, we wanted to highlight the molecular reaction pathway based on the activity of palladium complexes bearing imidazole ligands during the whole catalytic process. Their presence is an advantage over phosphine (PPh_3) which results in higher yield of products. Moreover, PPh_3 provided similar amounts of both products, **2** and **3**, while excess of **3** was obtained in reaction with imidazole palladium catalyst.

5. Conclusions

In summary, we developed an effective Pd-catalysed method of terminal alkyne hydroarylation with sodium tetraphenylborate. The present procedure works efficiently in water under mild conditions. Depending on the alkyne structure, stilbenes and aryl-substituted dienes were formed. Higher steric hindrance of alkyne substrate promoted formation of stilbene, while less substituted alkynes were hydroarylated to dienes as the main products. In contrast, alkynols reacted with sodium tetraphenylborate forming exclusively arylalkenes with excellent yield. To the best of our knowledge, this is the first effective palladium catalytic system for alkynols hydroarylation. The reactivity of alkynols depended on the distance between the OH group and the triple bond with a preference for a shorter one. Mechanistic studies revealed that water was not only a solvent but also a hydride source in the studied hydroarylation. A similar conclusion was recently formulated for diboron mediated alkyne hydroarylation [28]. One limitation of the presented method should be noted. Because sodium tetraphenylborate was used as an arylating agent, only phenylated derivatives could be prepared.

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