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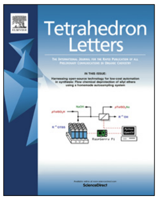

From propargylic biscarbonate to diaryl[n]dendralenes

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ABSTRACT

An efficient cross-coupling reaction using a low cost carbon-supported palladium (Pd/C) catalyst for the synthesis of cross-conjugated compounds, diaryl[n]dendralenes, has been developed. The reaction of a propargylic biscarbonate with phenylboronic acid using Pd/C and phosphine ligand (S-Phos) gave 2,3-diphenyl[2]dendralene in high yield. We found that Pd/C was an effective catalyst for the synthesis of dialyl[n]dendralenes. The synthesis of various dendralenes was successfully achieved under the optimized conditions, giving dialyl [2] and [4] dendralenes in good yields.

π-Conjugated compounds such as polyarylenes, polyenes and acenes have wide applications in biology and electronics.[1,2] These compounds are recognized as model parts of graphene being a zero-band gap semimetal. Common conjugated compounds, namely *through-conjugated compounds*,[3] which have alternating single and multiple bonds, are composed of unbranched π-electron frameworks. Many of such compounds show semiconducting properties.

On the other hand, *cross-conjugated compounds* are constructed by branched π-electron frameworks and the typical examples are dendralenes and radialenes.[4a] In contrast to huge examples of through-conjugated compounds, the studies on cross-conjugated compounds have been quite limited so far. In recent years, however, the cross-conjugated compounds have received increasing attention as unique properties such as π-electron communication and charge separation.[4b,4c] [n]Dendralenes are one of cross-conjugated compounds. The simplest dendralene is [3]dendralene (Scheme 1). 2,3-Diaryl-1,3-butadienes, which are formally [4]dendralenes, have attracted their molecular structures and electronic features.[4]

In general, 1,3-butadiene prefers an *s-trans* conformation, but Walree and co-workers reported that 2,3-diphenyl[2]dendralene (2,3-diphenyl-1,3-butadiene) has an *s-gauche* conformation mainly in the crystal state.[5] This [2]dendralene would exist in equilibrium between two conformational states at room temperature since the energies of the *s-gauche* and *s-trans* conformations are very similar.[5d]

The synthesis of oligomeric dendralenes is a challenging topic because multi-step reactions are usually requiered.[6] The Pd(0)-catalyzed Suzuki-Miyaura reaction with 1,3-butadiene-2,3-bis(pinacolatoborane) and the Stille reaction with 1,3-butadiene-2,3-bis(tri-*n*-butyltin) are key processes to access [2–8]dendralene derivatives. Various 2,3-diaryl[2]dendralenes were also synthesized by Cu, Pd or Ni-catalyzed cross-coupling reaction.[4] Ishino et al. reported that the reaction of 1,4-dimethoxy-2-butyne with aryl Grignard reagents in the presence of CuBr gave 2,3-diaryl[2]dendralenes.[4h] The Pd(0)-catalyzed synthesis of diaryl[2]dendralenes from propargyl carbonates and aryl boronic acids was reported by Grigg.[4g] We have recently succeeded in the synthesis of cross-conjugated polymers based on [2]dendralenyl (1,3-butadiene-2,3-diyl) skeleton via a palladium(0)-catalyzed cross-coupling polycondensation between propargylic biscarbonate **1** and aryl diboronic acids.[7] The efficient polymerization was achieved by a catalytic system composed of $Pd_2(dba)_3{\cdot}CHCl_3$ as the palladium source and dicyclohexyl(2′,6′-dimethoxybiphenyl-2-yl)phosphine (S-Phos) as the electron-donating ligand. The [2]dendralenyl skeleton is generated efficiently and selectively from **1**. Propargylic biscarbonates are thus powerful precursors for the synthesis of [2]dendralene derivatives.

Solid-supported transition-metal catalysts have significant advantages such as stability, reusability, and reduction of residual metal catalysts in the products.[8] For these reasons, such catalysts enable the production of organic materials to become efficient and cost-effective processes in chemical industry. Recently, heterogeneous Pd(0)-catalytic systems have accomplished many important carbon–carbon cross-coupling reactions such as Mizoroki-Heck, Suzuki-Miyaura, Sonogashira, Stille, and

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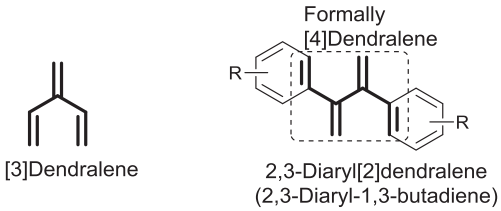
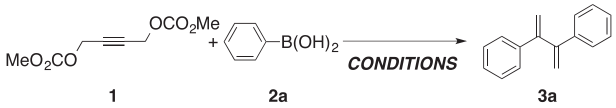


Scheme 1. Dendralenes.

Tsuji-Trost reactions.[9] Especially, palladium on carbon (Pd/C) supplied from commercial sources is one of the most frequently used catalyst for the cross-coupling reactions with good efficiency.[9b–d] In general, Pd/C is more stable and cheaper than other homogeneous Pd catalysts. The handling is also easier. Moreover, some cases using Pd/C have successfully demonstrated its reusability.[9a] In contrast to the previous works, to the best of our knowledge, there is no report on the coupling reaction of propargylic carbonates by the use of Pd/C. It would be a useful Pd/C-catalyzed synthesis of cross-conjugated ([2]dendralenyl) compounds via a cross-coupling reaction between propargylic biscarbonates and aryl boronic acids. In this letter, we report the synthesis of diaryl[2]dendralenes by a Pd/C-catalyzed reaction of propargylic biscarbonate **1** with boronic acids.

The cross-coupling reaction of propargylic biscarbonate **1** with arylboronic acids **2** was carried out with Pd/C, 10% Palladium on carbon (wetted with 55% water) supplied by Tokyo Chemical Industry (TCI) Corporation, and 2 M K_2CO_3 aq. at 100 °C. The Pd/C used was easily removed by filtration after the reaction. The yields of the products **3** were estimated by ^{1}H NMR spectroscopy in $CDCl_3$ using nitromethane as a standard. The products **3** were separated by silica-gel column chromatography (hexane as an eluent).

Table 1
Cross-coupling of **1** with Phenylboronic Acid **2a** using Palladium on Carbon as Catalyst.[a]



Entry	Phosphine Ligand	Pd/L	Solvent	Yield[b] (%)
1	–	1:2	Toluene	2
2	PPh_3	1:2	Toluene	0
3	P(*o*-Tolyl)$_3$	1:2	Toluene	20
4	P(*o*-Anisoyl)$_3$	1:2	Toluene	33
5	$PCy_3{\cdot}HBF_4$	1:2	Toluene	33
6	$P^tBu_3{\cdot}HBF_4$	1:2	Toluene	20
7	X-Phos	1:2	Toluene	15
8	John-Phos	1:2	Toluene	8
9	$P^tBu_2Me{\cdot}HBF_4$	1:2	Toluene	57
10	S-Phos	1:2	Toluene	57
11	$P^tBu_2Me{\cdot}HBF_4$	1:3	Toluene	58
12	S-Phos	1:3	Toluene	73
13	S-Phos	1:4	Toluene	45
14[c]	S-Phos	1:3	Toluene	74 (70)[d]
16	S-Phos	1:3	THF	0
17	S-Phos	1:3	DMF	0
18[e]	S-Phos	1:3	Toluene	12
19[f]	S-Phos	1:3	Toluene	67
20[g]	S-Phos	1:3	Toluene	9
21[h]	S-Phos	1:3[g]	Toluene	3

[a] Conditions: **1** (1.0 mmol), **2a** (2.0 mmol), Pd/C (2.5 mol%), ligand (5.0–10.0 mol%), 2 M K_2CO_3 aq. (1.0 mL), solvent (2.0 mL), 100°C, under argon.

[b] NMR yield of **3a**.

[c] $Pd_2(dba)_3{\cdot}CHCl_3$ (1.25 mol%).

[d] Isolated yield.

[e] Pd/C (1.25 mol%), Ligand (3.75 mol%).

[f] Pd/C (5.0 mol%), Ligand (15.0 mol%).

[g] An equimolar amount of 3-mercaptopropyl silica gel (ca. 0.5 mmol/g, TCI) to Pd/C was added to the reaction media.

[h] The Pd/C collected from the reaction mixture (Entry 12) was used.

The Pd/C-catalyzed cross-coupling reaction of **1** with phenylboronic acid (**2a**) was conducted under ligand-free conditions to afford a very low yield of 2,3-diphenyl-1,3-butadiene (diphenyl [2]dendralene) **3a** (Table 1, Entry 1). Although the reaction with PPh_3 as a ligand did not give **3a** (Entry 2), a 20% yield of **3a** was obtained when P(*o*-tolyl)$_3$ was used as a ligand (Entry 3). P(*o*-anisoyl)$_3$, $PCy_3{\cdot}HBF_4$, $P^tBu_3{\cdot}HBF_4$, dicyclohexyl(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)phosphine (X-Phos), and di-*tert*-butyl [2-(diphenylphosphino)phenyl]phosphine (John-Phos) also gave **3a**, but the yields were not good (entries 4–8). Among the ligands tested, $P^tBu_2Me{\cdot}HBF_4$ and dicyclohexyl(2′,6′-dimethoxybiphenyl-2-yl)phosphine (S-Phos) raised the yield of **3a** up to 57% (Entries 9 and 10).

We next examined the ratio of phosphine ligand to Pd. Although changing the ratio of Pd to $P^tBu_2Me{\cdot}HBF_4$ from 1:2 to 1:3 did not increase the yield of **3a** (Table 1, Entries 9 and 11), the Pd/S-Phos ratio of 1:3 raised the yield to 73% (Entry 12). We reported that $Pd_2(dba)_3{\cdot}CHCl_3$ is an effective palladium source for the cross-coupling reaction with **1**.[7] To compare with the results with Pd/C, the reaction of **1** with **2a** was carried out using $Pd_2(dba)_3{\cdot}CHCl_3$ instead of Pd/C. The yield (74%) of **3a** was similar to the case with Pd/C (Entry 14). The results show that Pd/C as well as $Pd_2(dba)_3{\cdot}CHCl_3$ is highly effective for the reaction. The kind of solvent affected the reaction largely. THF and DMF were not suitable (Entries 16 and 17). The higher Pd/C catalyst loading (5.0 mol%) did not increase the yield of **3a** (Entries 18 and 19). Thus, the optimized reaction conditions were found to be as follows: **1** (1.0 mmol), **2** (2.0 mmol), Pd/C (2.5 mol%), S-Phos (7.5 mol%), 2 M K_2CO_3 aq. (1.0 mL), toluene (2.0 mL) at 100 °C.

It is known that a solid-supported metal catalyst acts as a soluble metal source by leaching of the metal into solution. [9a,10] In order to learn whether the Pd/C used plays a role as a heterogeneous catalyst, the reaction of **1** with **2a** was carried out under the optimized conditions in the presence of an equimolar amount of 3-mercaptopropyl-functionalized silica gel (2.5 mol% of SH), which is known to be a good palladium scavenger,[10] to Pd/C. A dramatic decrease of yield (9%) of **3a** was observed (Table 1, Entry 20). The leached Pd species would be captured by the scavenger. This result suggests that the Pd/C used would play a homogeneous catalyst under our optimized conditions because the phosphine ligand leads to leaching of Pd atoms on carbon to form the phosphine-ligated palladium species in the bulk solution.[9a] The reusability was tested by the use of the used Pd/C. The yield of **3a** dropped to 3%, probably due to the decrease of amount of the palladium atoms supported on the carbon surface (Entries 12 and 21).

With the optimized conditions in hand, the coupling reaction of **1** with a variety of aryl boronic acids **2** was investigated by using Pd/C or $Pd_2(dba)_3{\cdot}CHCl_3$ (Table 2).[12,13] 4-Methylphenylboronic acid (**2b**) and 3,5-dimethylphenylboronic acid (**2c**) gave dendralenes **3b** and **3c** in good yields (Entries 1 and 2). In the reaction using $Pd_2(dba)_3{\cdot}CHCl_3$ as a catalyst, 4-methoxyphenylboronic acid (**2d**) and 3-acetylphenylboronic acid (**2e**) afforded **3d** and **3e** in good yields, but the use of Pd/C catalyst results in lower yields of **3d** and **3e** (Entries 3 and 4). Although 4-chlorophenyl-substituted dendralene **3f**[11] was obtained from 4-chlorophenylboronic acid (**2f**), the yields were not good in the cases using the both palladium sources (Entry 5). The reaction of **1** with 2-thienylboronic acid (**2g**) gave **3g** in 41% (Entry 6). 3-Thienylboronic acid (**2h**) was a much better reaction partner than **2g**, and gave **3h** in 89% (Entry 7). The yield of **3h** was higher in the reaction with Pd/C. Potassium(4-pyridinyl) trifluoroborate was also used, but the product was not formed at all.

We next tried to synthesize [4]dendralenes from **1** and vinylboronic acids under the optimized conditions. The reaction of **1**