JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Pd-Catalyzed Cascade Crossover Annulation of *o*-Alkynylarylhalides and Diarylacetylenes Leading to Dibenzo[*a*,*e*]pentalenes

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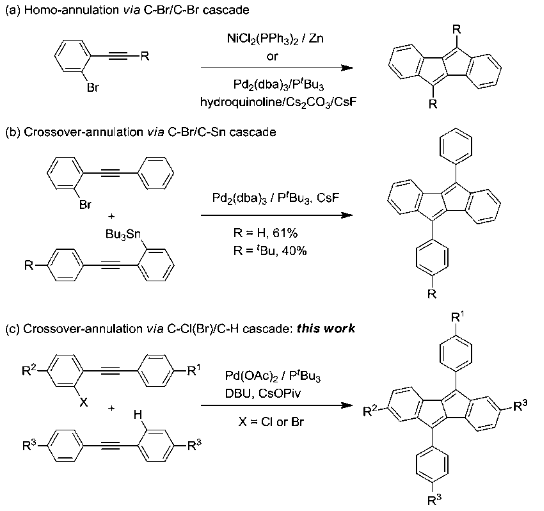
Supporting Information

ABSTRACT: A novel and selective Pd-catalyzed cascade crossover-annulation of *o*-alkynylarylhalides and diarylacetylenes for the synthesis of dibenzo[*a*,*e*]pentalenes has been reported. Various arylacetylenes with a wide range of functional groups were tolerated, producing the corresponding multisubstituted dibenzopentalenes with the different substituents on the aromatic rings in good to high yields under the optimized reaction conditions. The reaction proceeds through a Pd-catalyzed cascade carbopalladation and C−H activation. The use of the combined DBU and CsOPiv bases is crucial for the successful implementation of the present cross-annulation.

Cyclopenta-fused π-conjugated linear acene-type polycyclic compounds have attracted increasing interest due to their distinct physical and chemical properties.[1] Recent investigations revealed that those fused polycyclic compounds embedding cyclopentadiene moieties such as dibenzo-fused *s*-indacenes and pentalenes have narrow energy gaps[1,2] relative to the linear acenes such as pentacene,[3] which have been utilized as the active organic semiconductors in optical and electronic device applications.[2] The planar structure of dibenzo[*a*,*e*]pentalene framework possessing two five-membered rings and two external benzene rings has the increased stability and more extended π-conjugation than the simple pentalenes,[4] and hence the synthetic methods of its versatile derivatives are of growing recent interest.[5a] Especially, the multisubstituted dibenzopentalenes bearing functional groups at the 5- and 10-positions exhibited high stability and drastically changed electronic and structure properties compared to the parent dibenzopentalene.[2a,4]

Since the first synthesis in 1912, a number of the improved methods of dibenzopentalene derivatives have been reported.[4,5] For example, Yamaguchi et al. reported the reductive cyclization of *o*,*o*′-bis(arylcarbonyl)diphenylacetylenes with lithium naphthalenide[4c] and Saito et al. reported the reductive cyclization of phenyl(tri-*i*-propylsilyl)acetylene with lithium followed by iodine.[4a] More recently, Tilley and Kawase groups reported independently the simple synthetic protocols through the Pd- or Ni-catalyzed C−Br/C−Br homoannulation of *o*-alkynylarylbromides (Scheme 1a).[4b,5h] However those reactions provide the efficient ways for the synthesis of benzopentalenes with symmetric substituents at 5-, and 10-positions, only a limited number of approaches for the synthesis of the unsymmetrically 5,10-disubstituted dibenzopentalenes have been reported; for example, except for the multistep procedures,[6] Tilley et al. reported two examples of the Pd-catalyzed C−Br/C−Sn crossover-annulation of 1-bromo-2-(phenylethynyl)benzene and *o*-(alkynyl)phenyl-tributylstannanes (Scheme 1b).[5h] However, it is highly desirable that, if the crossover-annulation proceeds through the C−H activation[7] instead of the C−Sn activation, which may provide an attractive and general synthetic method for the construction of the multisubstituted benzopentalenes with a wide range of the functional groups on aromatic rings. Herein, we report a novel Pd-catalyzed crossover-annulation of *o*-alkynylarylhalides and diarylacetylenes *via* C−Cl(Br)/C−H cascade to afford the corresponding multisubstituted dibenzo[*a*,*e*]pentalenes in good to high yields (Scheme 1c).

Scheme 1. Catalytic Homoannulations and Crossover Annulations for the Synthesis of the Multisubstituted Dibenzo[*a*,*e*]pentalene Derivatives

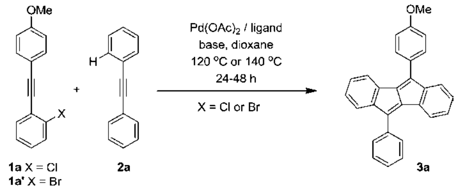


We initiated our investigation by examining various base additives in the reaction of 1-bromo-2-((4-methoxyphenyl)-ethynyl)benzene (**1a′**) and 1,2-diphenylacetylene (**2a**) (5 equiv) in the presence of $Pd(OAc)_2$ (5 mol %) and P^tBu_3 (15 mol %) in 1,4-dioxane (0.2 M) at 120 °C for 24 h (Table 1 and Supporting Information, Table S1). Among the inorganic bases, such as Cs_2CO_3, CsOPiv, and K_2CO_3 tested, only a small amount of the corresponding product **3a** was obtained (entries 1−3) with decomposition of **1a′**. The use of organic bases, such as DBU

Received: April 11, 2013
Published: June 28, 2013

dx.doi.org/10.1021/ja403382d | *J. Am. Chem. Soc.* 2013, 135, 10222−10225

Table 1. Optimization of Reaction Conditions[a]

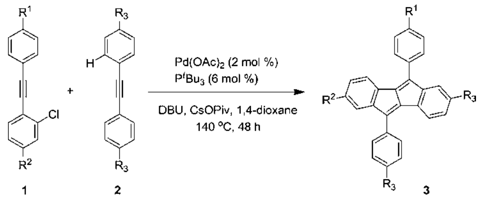


entry	X	ligand (15 mol %)	base (3 equiv)	yield (%)[b]
1	Br	P^tBu_3	Cs_2CO_3	38
2	Br	P^tBu_3	CsOPiv	7
3	Br	P^tBu_3	K_2CO_3	trace
4	Br	P^tBu_3	DBU	28
5	Br	P^tBu_3	DABCO	trace
6	Br	P^tBu_3	Pyridine	trace
7	Br	P^tBu_3	Cs_2CO_3/PivOH[c]	24
8	Br	P^tBu_3	DBU/Cs_2CO_3[c]	19
9	Br	P^tBu_3	DBU/CsOPiv[c]	78 (66)
10[d]	Cl	P^tBu_3	DBU/CsOPiv[c]	81 (75)
11[d]	Cl	P^iBu_3	DBU/CsOPiv[c]	trace
12[d]	Cl	P^iPr_3	DBU/CsOPiv[c]	trace
13[d]	Cl	PCy_3	DBU/CsOPiv[c]	trace
14[d]	Cl	$P(Tol)_3$	DBU/CsOPiv[c]	19
15[d]	Cl	dppf	DBU/CsOPiv[c]	40
16[d,e]	Cl	P^tBu_3	DBU/CsOPiv[c]	87 (81)
17[d,e,f]	Cl	P^tBu_3	DBU/CsOPiv[c]	87 (82)
18[d,e,f]	Cl	P^tBu_3	DBU/CsOPiv[g]	70

[a] Reaction conditions: **1a** or **1a′** (0.4 mmol), **2a** (5 equiv), $Pd(OAc)_2$ (5 mol %), P^tBu_3 (15 mol %), base (3 equiv), solvent (0.2 M), under Ar atmosphere, 120 °C for 24 h. [b] ^{1}HNMR yield determined using CH_2Br_2 as an internal standard. The isolated yield is shown in parentheses. [c] An amount of 1.1 equivalent was used. [d] Reaction time is 48 h, [e] Reaction temperature is 140 °C and concentration is 0.1 M. [f] Concentrations of 2 mol % of $Pd(OAc)_2$ and 6 mol % of $P(^tBu)_3$ were used. [g] CsOPiv (0.5 equiv) was used.

(1,8-diazabicycloundec-7-ene), DABCO (1,4-diazabicyclo-[2.2.2]octane), and pyridine also produced very low yields of **3a** (entries 4–6). However, it should be noted that, in contrast to the inorganic bases, the strong organic base DBU produced **3a** in 28% yield with a 72% yield of the recovered **1a′** (entry 4), indicating the good compatibility of arylbromide substrates with DBU base. The combination of Cs_2CO_3 base with PivOH (pivalic acid) (1.1 equiv) or DBU with Cs_2CO_3 (1.1 equiv) did not increase the yield of **3a** (entries 7 and 8). To our delight, DBU combined with CsOPiv (1.1 equiv) showed a high activity, affording the crossover-annulation product **3a** in 66% isolated yield together with the homoannulation product of **1a′** in less than 10% yield, implying the involvement of the pivalate-assisted C−H bond cleavage in this reaction (entry 9).[8] We thought that the use of arylbromide as a substrate might be favorable for the formation of a homoannulation product due to the ease of the intramolecular oxidative addition of the *in situ* formed vinyl-palladium to arylbromide. As expected, when 1-chloro-2-((4-methoxyphenyl)ethynyl)benzene (**1a**) was used as a substrate instead of arylbromide **1a′**, the yield of **3a** was increased to 75% isolated yield with about 2–3% yield of homoannulation product, although a prolonged reaction time (48 h) was needed (entry 10). The reaction with other ligands, such as P^iBu_3, P^iPr_3, and PCy_3 were almost completely inactive (entries 11–13). Although other ligands, such as $P(Tol)_3$ and dppf [bis-(diphenylphosphino)ferrocene] were active, the yields of **3a** were lower than 40% (entries 14 and 15). Moreover, the use of toluene as a solvent gave a slightly lower yield of **3a** than that of 1,4-dioxane, whereas the polar solvents, such as *N*,*N*-dimethylformamide or *N*,*N*-dimethylacetamide gave very low yields of **3a** (see Table S1). The reaction with other palladium catalysts, such as $Pd_2(dba)_3$ (dba = diphenylbenzylideneacetone) and $Pd(P^tBu_3)_2$ (without additional P^tBu_3) were also active, affording **3a** in 69% and 73% yields, respectively, while $Pd(PPh_3)_4$ catalyst was inactive (see Table S1). The yield of **3a** was further increased to 81% yield when 1,4-dioxane was diluted to 0.1 M at the higher temperature of 140 °C (entry 16). The use of a lower catalytic loading of $Pd(OAc)_2/P^tBu_3$ (2/6 mol %) did not affect the yield of **3a** (entry 17). The yield of **3a** was decreased slightly when 0.5 equiv of CsOPiv was used (entry 18). Overall, the use of $Pd(OAc)_2/P^tBu_3$ catalyst systems with a mixture of DBU and CsOPiv bases has been proved to be the most efficient and selective condition for the formation of the crossover-annulation product.

Table 2. Pd-catalyzed Crossover Annulation of Various *o*-Alkynylarylchlorides with 1,2-Diarylacetylenes[a]



entry	1	2	3	yield (%)[b]
1	**1b** $R^1 = NMe_2$, $R^2 = H$	**2a** $R^3 = H$	**3b**	74
2	**1c** $R^1 = n\text{-}C_4H_9$, $R^2 = H$	**2a** $R^3 = H$	**3c**	83
3	**1d** $R^1 = CO_2Me$, $R^2 = H$	**2a** $R^3 = H$	**3d**	58[c]
4	**1e**[d] $R^1 = COMe$, $R^2 = H$	**2a** $R^3 = H$	**3e**	70[e]
5	**1f** $R^1 = CN$, $R^2 = H$	**2a** $R^3 = H$	**3f**	76[e]
6	**1g** $R^1 = OMe$, $R^2 = F$	**2a** $R^3 = H$	**3g**	68[c,e]
7	**1h** $R^1 = n\text{-}C_4H_9$, $R^2 = OMe$	**2a** $R^3 = H$	**3h**	89
8	**1a** $R^1 = OMe$, $R^2 = H$	**2b** $R^3 = Me$[f]	**3i**	75
9	**1c** $R^1 = n\text{-}C_4H_9$, $R^2 = H$	**2b** $R^3 = Me$[f]	**3j**	86
10	**1a** $R^1 = OMe$, $R^2 = H$	**2c** $R^3 = OMe$[f]	**3k**	73
11	**1c** $R^1 = n\text{-}C_4H_9$, $R^2 = H$	**2c** $R^3 = OMe$[f]	**3l**	74
12	**1i** $R^1 = F$, $R^2 = H$	**2c** $R^3 = OMe$[f]	**3m**	76[e]
13	**1a** $R^1 = OMe$, $R^2 = H$	**2d** $R^3 = CN$[f]	**3n**	71[e]

[a] Reaction conditions: **1** (0.4 mmol), **2a** (2 mmol), $Pd(OAc)_2$ (2 mol %), P^tBu_3 (6 mol %), DBU (1.2 mmol), CsOPiv (0.44 mmol), 1,4-dioxane (4 mL), Ar atmosphere, 140 °C, 48 h. [b] Isolated yield. [c] Reaction time was 3 days. [d] 1-(4-((2-Bromophenyl)ethynyl)phenyl)-ethanone (**1e**) was used as arylhalide. [e] $Pd(OAc)_2$ (4 mol %) and P^tBu_3 (12 mol %) were used. [f] Diarylacetylenes **2b**,**c** (2 equiv) was used.

Under optimized conditions, the scope of Pd-catalyzed crossover-annulation of various *o*-alkynylarylhalides and diarylacetylenes was examined (Table 2). In each case, a very small amount of homoannulation products (~2%) and side-products derived from the decomposition of both two alkynes were observed, but they were separated by silica gel chromatography. A variety of functional groups, such as *N*,*N*-dimethyl, *n*-butyl, ester, ketone, and cyano groups at R^1, were tolerated, affording the crossover-annulated products **3b**–**f** in good to high yields (entries 1–5). Relative to the good reactivity of the arylchlorides **1a**–**c** with an electron-donating group at R^1, the arylhalides **1d**–**f** bearing an electron-withdrawing group at R^1 required a longer reaction time or higher catalytic loading. As a representative determination of the dibenzo[*a*,*e*]pentalene products, the structure of **3e** was unambiguously confirmed by X-ray crystal-structure analysis (Figure 1).[9]

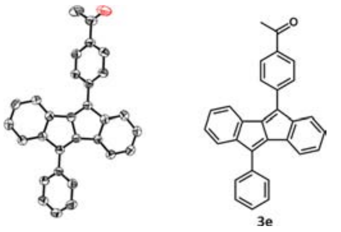


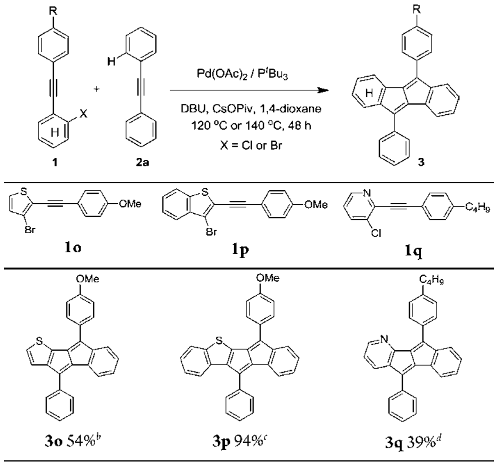
Figure 1. ORTEP drawing of the crossover-annulation product **3e**. Hydrogen atoms are omitted for clarify. Red: oxygen atom.

The reaction was further extended to the synthesis of the multisubstituted debenzopentalene derivatives. The reaction using arylchloride **1g** having an electron-withdrawing group at R^2, such as fluorine group, furnished the corresponding product **3g** in 68% yield, whereas the arylchloride **1h** bearing an electron-donating group at R^2, such as methoxy group, gave the multisubstituted product **3h** in 89% yield (entries 6 and 7). The reactions of various arylchlorides **1a**, **1c**, and **1i** also worked well with the diarylacetylenes **2b−d** having two symmetric electron-donating or electron-withdrawing groups at R^3, affording the expected products **3i−n** in good to high yields (entries 8−13), while **1i** or **2d** with a fluorine group at R^2 or two cyano groups at R^3 required a higher catalytic loading (entries 12 and 13). It was noted that the reaction of **1a** with the unsymmetric diarylacetylenes, such as 1-fluoro-4-((4-methoxyphenyl)ethynyl)benzene, gave the desired product as a mixture of two regioisomers (see Supporting Information). The alkyl-substituted arylchloride, such as 1-chloro-2-(dec-1-yn-1-yl)benzene, was not compatible for the present reaction, giving a mixture of the unidentified products.

The increasing interests of heteroacenes and heterocycle-fused polyaromatic compounds in electronic device applications as organic semiconducting materials,[10] led us to examine the construction of heterocycle-fused pentalene derivatives (Table 3). The reaction of 3-bromo-2-alkynylthiophene **1o** with diphenylacetylene **2a** afforded the corresponding product **3o** in moderate yield because of the low stability of the substrate **1o** which has no substituent at 2′-position of thiophene moiety. In contrast, 3-bromo-2-alkynylbenzothiophene **1p** showed a very high stability under the present conditions, which furnished the corresponding product **3p** in 94% yield. Although the 3-chloro-2-alkynylpyridine **1q** showed a low stability, we were able to obtain the crossover-annulated product **3q** in 39% yield.

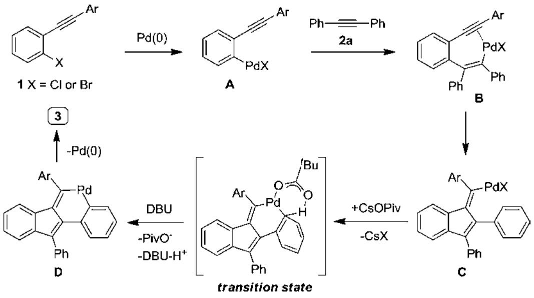
On the basis of these observations, the present crossover-annulation mechanism is proposed as shown in Scheme 1. Initially, the oxidative addition of the strong electron rich Pd(0)/Ln to arylhalide **1** forms arylpalladium intermediate **A**. The intermolecular alkyne carbopalladation of the intermediate **A**,[11] followed by the intramolecular 5-*exo-dig* carbopalladation of the vinylpalladium intermediate **B** affords the second vinylpalladium intermediate **C**. The electron-donating groups at R^1, R^2, and R^3 in the substrates **1** and **2** not only facilitate the smooth carbopalladation paths but also stabilize the two vinypalladium species in intermediates **B** and **C**, which resulted in high chemical yields of the desired products. The result that only CsOPiv combined with DBU showed the significantly increased yields of the products **3** (Table 1, entry 9), strongly suggests that the reaction involves the pivalate-promoted C(sp^2)-H activation transition state.[8] Moreover, the use of DBU as a strong and non-nucleophilic base is crucial for removing the pivalic acid to form the six-membered palladacycle **D**. Reductive elimination of **D** produces the corresponding products **3**.

Table 3. Pd-Catalyzed Crossover Annulation of Heteroaromatic Alkynes with 1,2-Diphenylacetylene[a]



[a]Reaction conditions: **1** (0.4 mmol), **2a** (2.0 mmol), $Pd(OAc)_2$, P^tBu_3, DBU (1.2 mmol), CsOPiv (0.44 mmol), 1,4-dioxane (4 mL), Ar atmosphere, 120 °C, 48 h. [b]$Pd(OAc)_2$ (4 mol %) and P^tBu_3 (12 mol %). [c]$Pd(OAc)_2$ (5 mol %) and P^tBu_3 (10 mol %) at 120 °C. [d]$Pd(OAc)_2$ (10 mol %) and P^tBu_3 (20 mol %) at 140 °C.

Scheme 2. Proposed Reaction Mechanism



The UV−vis absorption spectra of the dibenzopentalene products were measured in chloroform (Supporting Information, Figure S1). Dibenzopentalene derivatives with various functional groups exhibit similar absorption pattern in the 250−380 nm and 400−600 nm regions, where the compounds having an electron-donating group on an aromatic ring showed a red-shifted absorption maximum (λ_{max}) compared to that of dibenzopentalenes having an electron-withdrawing group on an aromatic ring. Solution/thin-film absorption spectra of the selected dibenzopentalenes with a longer wavelength are shown in Figure 2. In $CHCl_3$ (Figure 2a), **3b** with a *N*,*N*-dimethylamino group at R^1 showed a most red-shifted λ_{max} of 472 nm. **3n** having a methoxy and two cyano groups, and pentalene derivatives fused with thienyl (**3o**) or benzothienyl (**3p**) moiety also exhibited an enhanced λ_{max} compared to **3a** having a methoxy group at R^1. Thin film optical absorptions of the present compounds were recorded on spin-coated films on the quartz plates (Figure 2b). The film absorption maxima are red-shifted by ∼15−30 nm (from 472 to 502 nm for **3b**) versus the corresponding solution absorption maxima, indicating the existence of the intermolecular $\pi-\pi$ stacking in the solid state. The highest occupied

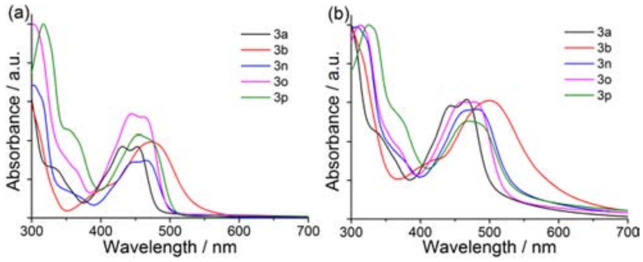


Figure 2. UV−vis absorption spectra of **3a**, **3b**, **3n**, **3o**, and **3p** in chloroform (a) and as-spun thin films on the quartz plates (b).

molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of **3a**, **3b**, **3n**, **3o**, and **3p** were estimated by electrochemical cyclic voltammetry (CV) in CH_2Cl_2 (Supporting Information, Figure S2 and Table S2). The HOMO energy level of dibenzopentalene **3b** is calculated to be −5.18 eV, which is much higher than that of **3a** (−5.76 eV), indicating the dramatic influence of the electron-donating *N*,*N*-dimethylamino-group on increasing HOMO energy level. Pentalene derivatives **3o** and **3p** having thiophene or benzothiophene moiety exhibit the relatively high HOMO energy levels of −5.34 eV and −5.25 eV, respectively, which are also effective for pushing up the HOMO energy level. Dibenzopentalene **3n** exhibits the lowest LUMO energy level of −3.42 eV among the five products (−3.08 eV for **3a**, −3.07 eV for **3b**, −3.23 eV for **3o**, and −3.29 eV for **3p**) due to the strong electron-withdrawing cyano-substituent on **3n**. Those optical and electrochemical data demonstrate that the HOMO/LUMO energies of the present pentalene derivatives can be easily tuned by the functional group modification.

In summary, we have described a novel and selective Pd-catalyzed crossover-annulation of *o*-alkynyl arylhalides with 1,2-diarylacetylenes through a C−Cl(Br)/C−H cascade cyclization. A wide range of the functional groups were tolerated, producing the corresponding multisubstituted dibenzopentalene and heterocycle-fused pentalene derivatives in good to high yields. The use of DBU combined with CsOPiv is indispensable for the selective implementation of the present crossover annulation efficiently. This methodology provides a valuable and general synthetic tool for the construction of various dibenzo[*a*,*e*]-pentalene structures that are expected to be useful in electronic device applications. Further design and synthesis of appropriate dibenzopentalene derivatives using this methodology and application in the electronic device are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a Scientific Research (B) from Japan Society for Promotion of Science (JSPS) (No. 25288043), and World Premier International Research Center Initiative (WPI), MEXT, Japan. This work is dedicated to Professor Irina Petrovna Beletskaya for her contribution to metal-catalyzed reactions.

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