Polycyclic Aromatic Hydrocarbons **Hot Paper**

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One-Step Annulative π-Extension of Alkynes with Dibenzosiloles or Dibenzogermoles by Palladium/*o*-chloranil Catalysis

Kyohei Ozaki, Keiichiro Murai, Wataru Matsuoka, Katsuaki Kawasumi, Hideto Ito, and Kenichiro Itami**

***Abstract:** Reliable and short synthetic routes to polycyclic aromatic hydrocarbons and nanographenes are important in materials science. Herein, we report an efficient one-step annulative π-extension reaction of alkynes that provides access to diarylphenanthrenes and related nanographene precursors. In the presence of a cationic palladium/o-chloranil catalyst system and dibenzosiloles or dibenzogermoles as π-extending agents, a variety of diarylacetylenes are transformed successfully into 9,10-diarylphenanthrenes in a single step with good functional-group tolerance. Furthermore, double π-extension reactions of 1,4-bis(phenylethynyl)benzene and diphenyl-1,3-butadiyne are demonstrated, affording oligoarylene products, which show potential for application in the synthesis of larger polycyclic aromatic hydrocarbons and nanographenes.*

Nanographenes have recently received a considerable amount of attention in synthetic chemistry, nanocarbon science, and organic electronics.[1] The chemical and physical properties of nanographenes depend on their size, shape, and peripheral structure,[2] and, therefore, efficient and precise synthetic routes to structurally uniform nanographenes are in high demand. To date, cyclodehydrogenation (also known as graphitization or graphenization) through a FeCl$_3$-mediated Scholl reaction, photocyclization, and oxidative coupling have been employed frequently for the syntheses of oligo- and polyarylene precursors for nanographenes.[3] Among the various possible synthetic approaches to oligo- and polyarylenes, the annulative π-extension (APEX) of alkynes[4–7] is generally regarded as one of the most powerful and reliable methods for the construction of not only small oligophenylene derivatives[5–7] but also ladder polyphenylenes that are precursors for graphene nanoribbons (GNRs).[4] Therefore, the development of efficient one-step APEX reactions of alkynes is an important synthetic goal in the field of nanocarbon sciences.

Recently, we have reported the palladium-catalyzed one-step APEX reaction of polycyclic aromatic hydrocarbons (PAHs) with dibenzosiloles for the synthesis of structurally uniform nanographenes (Figure 1).[8] We have also discovered that the K-region (convex armchair edge) selectivity stems from the favorable coordination of the carbon–carbon double bond at the K-region to a cationic palladium (K-region is the most olefinic site within PAH structures).[8a] While the π-coordination of PAHs (e.g., phenanthrene and pyrene) to a metal is usually not strong, an electron-deficient and cationic arylpalladium species (the key intermediate in our APEX catalysis[8a]) can facilitate the π-coordination more efficiently.

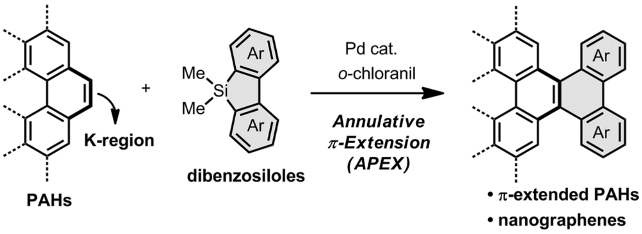

Figure 1. Palladium-catalyzed K-region-selective annulative π-extension (APEX) of polycyclic aromatic hydrocarbons (PAHs).

Building on these mechanistic studies, we envisaged that this catalytic APEX reaction with dibenzosiloles could be potentially extended to other substrates containing multiple carbon–carbon bonds such as alkynes,[9,10] providing access to extremely facile and short synthetic routes to oligoarylenes and nanographenes. Among the related examples of APEX reactions of diphenylacetylene with various π-extension units giving 9,10-diphenylphenanthrenes,[9,10] most recently, the group of Fukushima has elegantly demonstrated the power of their two-step alkyne APEX reaction in the synthesis of exotic planar/nonplanar π-conjugated molecules.[9p] Herein, we report a novel one-step APEX reaction of diarylacetylenes with dibenzosiloles or dibenzogermoles catalyzed by a palladium/*o*-chloranil catalyst system.

Through a screen of the reaction conditions, we were able to establish that the alkyne APEX reaction is possible. Treatment of diphenylacetylene (**1a**, 1.0 equiv) with dibenzosilole **2a** (1.2 equiv), PdCl$_2$ (5 mol%), AgOTf (10 mol%), and *o*-chloranil (2.0 equiv) in 1,2-dichloroethane at 80°C for 2 h provided 9,10-diphenylphenanthrene (**3aa**) in 63% yield (Table 1, entry 1). The use of *o*-chloranil was found to be crucial in this reaction. While 3,5-di-*tert*-butyl-*o*-benzoquinone provided the desired APEX product **3aa** in 25% yield, other common oxidants such as DDQ, *p*-benzoquinone, *p*-

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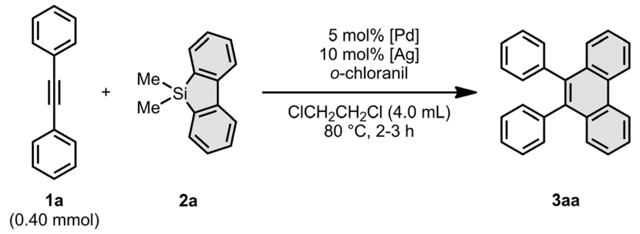
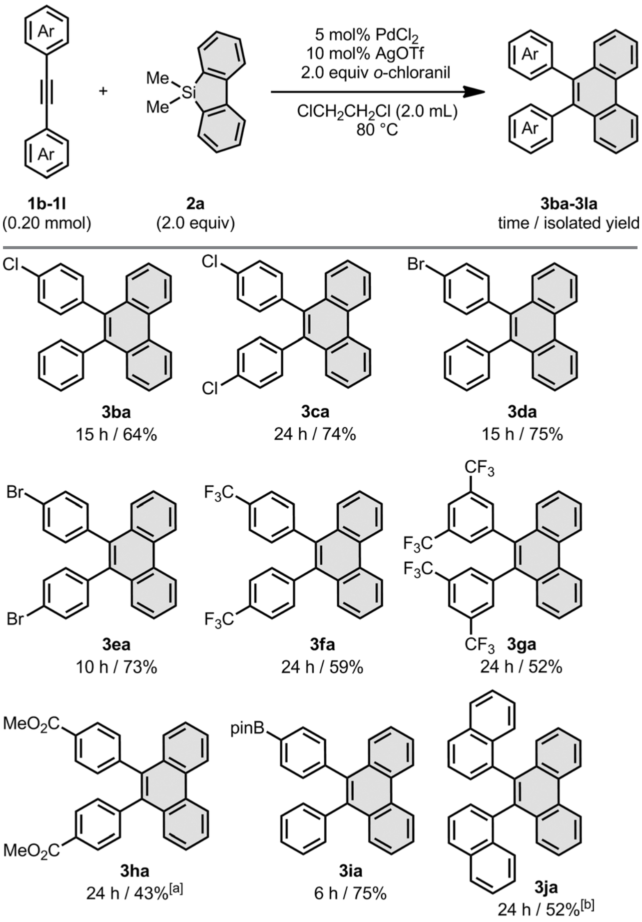
Table 1: Effect of varying representative reaction conditions in Pd-catalyzed APEX reaction of diphenyleacetylene **1a** with dibenzosilole **2a**.



Entry	**2a** [equiv]	[Pd]	[Ag]	*o*-Chloranil [equiv]	Yield of **3aa**[a]
1[b]	1.2	$PdCl_2$	AgOTf	2.0	(63 %)[d]
2[c]	2.0	$PdCl_2$	AgOTf	2.0	91 % (94 %)[d]
3[b]	1.2	$PdCl_2$	–	2.0	2 %
4[c]	2.0	$Pd(OAc)_2$	–	2.0	15 %
5[b]	2.0	$Pd(CH_3CN)_4(SbF_6)_2$	–	2.0	46 %
6[c]	2.0	$PdCl_2$	AgOTf	1.5	87 %

[a] Yield determined by ^1H NMR spectroscopy using dibromomethane as an internal standard. [b] Reaction time: 2 h. [c] Reaction time: 3 h. [d] Yield of isolated product in parentheses.

Table 2: Pd-catalyzed APEX reaction of various diarylacetylenes (**1b**–**1j**) with dibenzosilole **2a**.



[a] 3,5-Di-*tert*-butyl-*o*-benzoquinone (*o*-DTBQ) (2.0 equiv) was used instead of *o*-chloranil. [b] The product was obtained as a 1:1 mixture of rotamers.

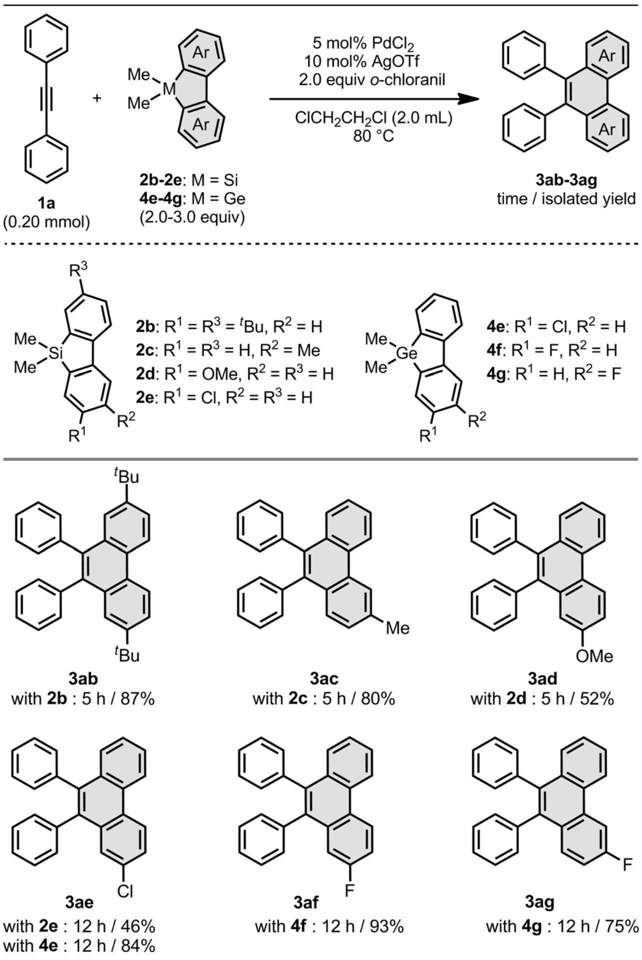
chloranil, $K_2S_2O_8$, and $CuCl_2$ were found to be completely ineffective (see Table S1 in the Supporting Information for the overview of the oxidant screening results). In the next step, the effect of changing other reaction parameters such as the nature of the palladium catalyst and silver salt, and the number of equivalents of dibenzosilole and *o*-chloranil was investigated. Judging from the results listed in Table 1, the most critical parameter was found to be the number of equivalents of dibenzosilole. Namely, 2.0 equivalents of dibenzosilole increased the yield of **3aa** dramatically to 94 % (entry 2). The absence of AgOTf or the use of $Pd(OAc)_2$ catalyst in place of $PdCl_2$/AgOTf diminished the reaction yield noticeably (entries 3 and 4). Therefore, these results suggest that the generation of the cationic palladium species contributes significantly to the success of the alkyne APEX reaction. The use of a preformed cationic complex $Pd(CH_3CN)_4(SbF_6)_2$—i.e., the optimal catalyst for APEX of PAHs—resulted in a decrease in the yield of **3aa** to 46 % (entry 5). Similarly, decreasing the amount of *o*-chloranil to 1.5 equivalents resulted in a somewhat lower yield of **3aa** (87 %, entry 6). Thus, the optimized conditions for the APEX of diphenylacetylene were established as: heating the mixture of **1a** (1.0 equiv) and **2a** (2.0 equiv) in 1,2-dichloroethane at 80 °C in the presence of $PdCl_2$ (5 mol %), AgOTf (10 mol %), and *o*-chloranil (2.0 equiv).[11]

With the optimal reaction conditions successfully established, various diarylacetylenes were subjected to the APEX reaction with **2a** (Table 2). Interestingly, chloro, bromo, and boryl groups were well tolerated in this reaction, affording the corresponding diarylphenanthrenes **3ba**, **3ca**, **3da**, **3ea**, and **3ia**, equipped with functional groups that could be used for further functionalization and π-extension, in high yields. Diphenylacetylenes bearing trifluoromethyl groups (**1f** and **1g**) afforded **3fa** and **3ga** in moderate yields. The use of 3,5-di-*tert*-butyl-*o*-benzoquinone (*o*-DTBQ) instead of *o*-chloranil in the reaction employing a substrate equipped with a methyl ester group (**1h**) resulted in a higher yield (**3ha**, 43 % yield). The reaction of dinaphthylacetylene **1j** also proceeded well, affording the sterically congested 9,10-dinaphthylphenanthrene (**3ja**) as a 1:1 mixture of rotamers.

In the next step, a variety of π-extension units were tested for the APEX reaction of alkyne **1a** (Table 3). In the APEX reactions examined, the dibenzosiloles equipped with electron-donating groups, 3,7-di-*tert*-butyldibenzosilole **2b** and 2-methyldibenzosilole **2c**, were found to work effectively as π-extending agents, affording the corresponding phenanthrenes **3ab** and **3ac** in an 87 % and 80 % yield, respectively. Dibenzosilole **2d** bearing a methoxy group was also able to produce the corresponding APEX product **3ad** in 52 % yield. In contrast to the dibenzosiloles bearing electron-donating groups, the electron-deficient dibenzosiloles such as 3-chlorodibenzosilole **2e** displayed a somewhat lower reactivity (**3ae**, 46 %). In such circumstances, the use of dibenzogermole **4e**, which has a superior reactivity over dibenzosilole **2e**, furnished the same product **3ae** in a much higher yield (84 %). Similarly, dibenzogermoles bearing a fluoro group (**4f** and **4g**) afforded the corresponding APEX products **3af** and **3ag** in high yields.

Exploiting $PdCl_2$/AgOTf/*o*-chloranil as the catalyst system, we found that double APEX reactions of dialkyne

Table 3: Pd-catalyzed APEX reaction of diphenylacetylene **1a** with various dibenzosiloles (**2b**–**2e**) or dibenzogermoles (**4e**–**4g**).[a]



[a] Reaction conditions: diphenylacetylene (**1a**) (0.20 mmol), dibenzosilole **2** (3.0 equiv) or dibenzogermole **4** (2.0 equiv), $PdCl_2$ (5 mol%), AgOTf (10 mol%), o-chloranil (2.0 equiv), 1,2-dichloroethane (2.0 mL), 80°C.

substrates were also possible. For example, 1,4-bis(phenylethynyl)benzene (**1k**) and 1,4-diphenyl-1,3-butadiyne (**1l**) underwent double APEX reaction with dibenzosilole **2a** (Figure 2a,b). In these reactions, the addition of larger quantities of dibenzosilole **2a** and *o*-chloranil was necessary in order to produce the double APEX products (**3ka** and **3la**) in reasonable yields. In particular, these additional reagents were necessary because the dibenzosilole and *o*-chloranil were being consumed through homo-dimerization, desilylation, and decomposition faster than in the APEX reactions of **1k** and **1l**. The sterically congested structures of **3ka** and **3la** were confirmed by X-ray crystallographic analysis (Figure 2c).[12]

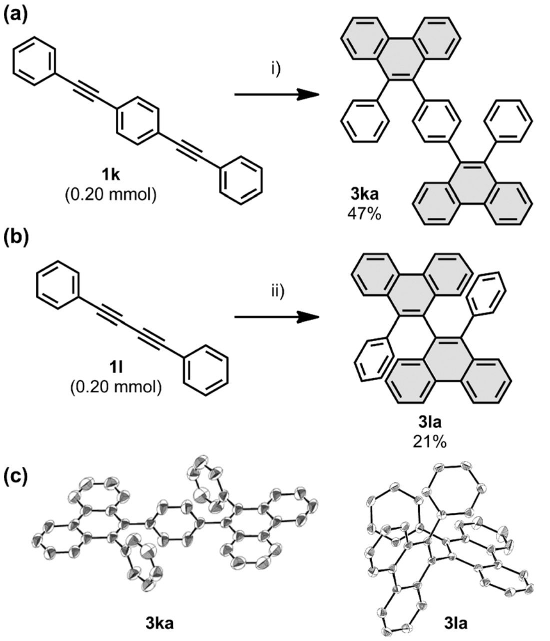


Figure 2. Double APEX reaction of diynes. a) Reaction of diyne **1k**: Conditions i) **1k** (0.20 mmol), **2a** (8.0 equiv), *o*-chloranil (6.0 equiv), $PdCl_2$ (10 mol%), AgOTf (20 mol%), $ClCH_2CH_2Cl$ (2.0 mL), 80°C, 18 h. b) Reaction of diyne **1l**: Conditions ii) **1l** (0.20 mmol), **2a** (8.0 equiv), *o*-chloranil (6.0 equiv), $PdCl_2$ (10 mol%), AgOTf (20 mol%), $ClCH_2CH_2Cl$ (2.0 mL), 80°C, 16.5 h. c) Thermal ellipsoid representations (50%) of the X-ray crystal structures of **3ka** and **3la**, as obtained with ORTEP.[12] Hydrogen atoms and solvent are omitted for clarity.

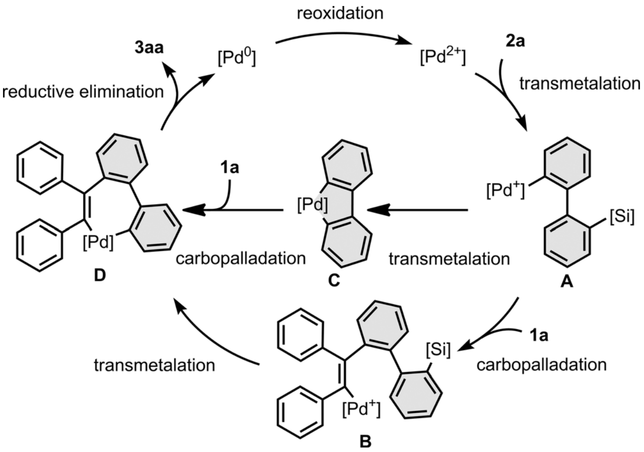


Figure 3. Proposed mechanisms for the Pd-catalyzed APEX reaction of diphenylacetylene (**1a**) with dibenzosilole **2a**.

Two possible reaction mechanisms for the APEX reaction of alkynes are shown in Figure 3. Based on our previous mechanistic studies of APEX reactions of PAHs,[8a] the reaction is most likely to be initiated by a transmetalation of dibenzosilole **2a** with a cationic palladium(II) to give a biphenylpalladium intermediate **A**. Subsequent π-coordination of alkyne **1a** and carbopalladation afford alkenylpalladium intermediate **B**, which undergoes intramolecular transmetalation to generate palladacycle **D**. Alternatively, palladacycle **D** might be formed through a transmetalation–carbonpalladation sequence from **A** (via **C**). The product of the APEX reaction, **3aa**, would be obtained by the reductive elimination from intermediate palladacycle **D** along with Pd^0 species, which can be oxidized by *o*-chloranil to regenerate the Pd^{II} species.

In summary, palladium-catalyzed APEX reactions of alkynes with dibenzosiloles or dibenzogermoles have been demonstrated. The $PdCl_2$/AgOTf/*o*-chloranil catalyst system enables transformation of diarylacetylenes to diarylphenanthrenes in one step with a good functional-group tolerance. The use of dibenzogermoles bearing an electron-deficient substituent expanded the scope of the APEX reaction significantly. Moreover, the double APEX reaction of diynes was also established as an efficient route to sterically congested diphenanthrylenes. The alkyne APEX technology described here has immense potential for application in the precise synthesis of large polycyclic aromatic hydrocarbons and nanographenes.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkynes · dibenzosiloles · palladium · polycyclic aromatic hydrocarbons · π-extension

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[11] While it is well known that diarylacetylenes can be transformed into dibenzopentalenes through a catalytic dimerization reaction in *N*,*N'*-dimethylacetamide under the same reaction conditions without dibenzosiloles, the present reaction with dibenzosiloles in 1,2-dichloroethane did not result in the production of any corresponding by-products. For details of the synthesis of dibenzopentalenes from diarylacetylenes by the $PdCl_2$/AgOTf/*o*-chloranil catalyst system, see: a) T. Maekawa, Y. Segawa, K. Itami, *Chem. Sci.* **2013**, *4*, 2369; b) T. Maekawa, H. Ueno, Y. Segawa, M. M. Haley, K. Itami, *Chem. Sci.* **2016**, *7*, 650.

[12] CCDC 1510553 (**3ka**·0.5MeOH), 1510554 (**3la**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Communications

Polycyclic Aromatic Hydrocarbons

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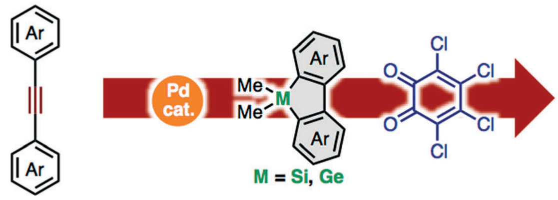

Extending circumstances: An efficient one-step annulative π-extension reaction of alkynes provides facile access to diarylphenanthrenes and related nanographene precursors. In the presence of a cationic palladium/*o*-chloranil catalyst system, a variety of diarylacetylenes are transformed through the use of dibenzosiloles or dibenzogermoles as π-extending agents into 9,10-diarylphenanthrenes with good functional-group tolerance.