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$Pd(OAc)_2$/*o*-Chloranil/$M(OTf)_n$: A Catalyst for the Direct C−H Arylation of Polycyclic Aromatic Hydrocarbons with Boryl-, Silyl-, and Unfunctionalized Arenes

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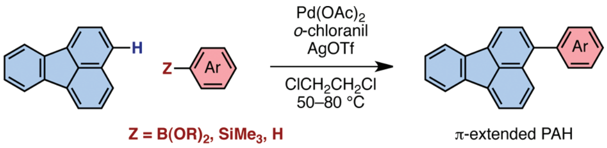
ABSTRACT



$Pd(OAc)_2$/*o*-chloranil/$M(OTf)_n$ can effectively promote the C−H arylation of fluoranthene with arylboron compounds or arylsilanes. The reaction takes place with high regioselectivity at the C3 position of fluoranthene. Moreover, the new catalytic system allows the use of unfunctionalized arenes as coupling partners in the arylation of polycyclic aromatic hydrocarbons.

The arylation of polycyclic aromatic hydrocarbons (PAHs) is a fundamental reaction in the synthesis of π-extended PAHs useful in the field of materials science and nanocarbon chemistry.[1] Typically arylation of PAHs has been executed by a two-step sequence consisting of either (i) halogenation of PAHs followed by Pd-catalyzed cross-coupling reactions,[2] or (ii) Ir-catalyzed C−H borylation of PAHs followed by Pd-catalyzed cross-coupling with aryl halides.[3] Very recently, we discovered that the combination of $Pd(OAc)_2$/*o*-chloranil catalyzes the direct C−H arylation at the 'armchair' edge of PAHs, such as pyrene, with arylboron compounds (Figure 1).[4−6] We also demonstrated that the sequence of Pd-catalyzed direct arylation of pyrene with *o*-biphenylboroxin followed by $FeCl_3$-mediated cyclodehydrogenation rapidly extends a

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pyrene π-system with high directionality along the armchair edge.[4]

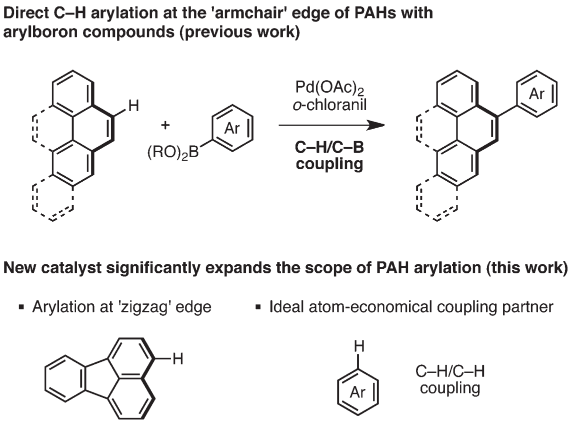
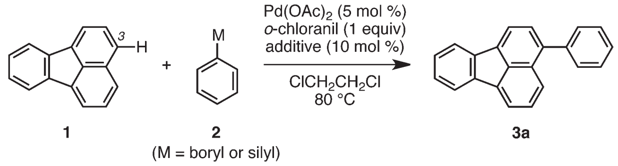


Figure 1. Direct C–H arylation of polycyclic aromatic hydrocarbons.

Although these studies established the viability of the direct PAH arylation process, there still exist several challenges (Figure 1). For example, new catalysts and/or reaction conditions that allow effective π-extension at the 'zigzag' edge of PAHs must be established for future applications to a controlled synthesis of graphene nanoribbons. In addition, it is extremely important to investigate whether unfunctionalized arenes, the ideal atom-economical arylating agents, undergo a catalyzed C–H coupling with PAHs (C–H/C–H cross-coupling). Herein we report our finding that a new catalytic system, Pd(OAc)$_2$/*o*-chloranil/M(OTf)$_n$, can effectively promote the C–H arylation of fluoranthene at the zigzag edge with arylboron compounds[7] or arylsilanes.[8] Moreover, we have found that the new system allows the use of unfunctionalized arenes as coupling partners in PAH arylation.

We began our study by examining various arylboron compounds and additives in the Pd(OAc)$_2$/*o*-chloranil-catalyzed C–H arylation of fluoranthene (**1**) (Table 1). When the reaction was conducted with PhB(OH)$_2$, C3-phenylation product **3a** was obtained only in 28% yield (entry 1).[9] The structure of **3a** was unambiguously determined by an X-ray diffraction study (see the Supporting Information for details). The presence of one minor regioisomer was indicated from GC analysis, but it was extremely difficult to identify the structure of the isomer unambiguously since there exists no reliable method to synthesize all other possible isomers selectively (1-, 2-, 7-, and 8-phenylfluoranthenes). During these studies, we also found that trimethylphenylsilane could also be used for the C–H phenylation of fluoranthene (entry 2).[8] Although high regioselectivity was secured, the low reactivity was the bane of the original Pd(OAc)$_2$/*o*-chloranil system.

Table 1. Discovery of Pd(OAc)$_2$/*o*-Chloranil/M(OTf)$_n$ as Catalytic System for the C3-Selective C–H Arylation of Fluoranthene with Arylboron Compounds or Arylsilanes[a]



entry	**2**	additive	**3a** (%)[b]	selectivity[c] (%)
1	PhB(OH)$_2$	none	28	92
2	PhSiMe$_3$	none	32	85
3	PhB(OH)$_2$	AgBF$_4$	23	91
4	PhB(OH)$_2$	AgOCOCF$_3$	18	94
5	PhB(OH)$_2$	AgOTf	36	92
6	PhSiMe$_3$	AgOTf	52 (41)	89
7	PhB(neo)[d]	AgOTf	50	90
8	(PhBO)$_3$	AgOTf	55 (50)	88
9	(PhBO)$_3$	Y(OTf)$_3$	55 (42)	89
10	(PhBO)$_3$	Sc(OTf)$_3$	54 (38)	89
11	(PhBO)$_3$	LiOTf	47 (43)	87
12	(PhBO)$_3$	HOTf	39	87

[a] Conditions: **1** (0.20 mmol, 1.0 equiv), **2** (0.40 mmol for boronic acid, neopentyl glycol ester, and silane, 0.13 mmol for boroxin) Pd(OAc)$_2$ (10 μmol, 5 mol %), *o*-chloranil (0.20 mmol, 1.0 equiv), additive (20 μmol, 10 mol %), 1,2-dichloroethane (1 mL), 80 °C, 2–16 h. [b] Yield of **3a** was determined by GC analysis using *n*-dodecane as an internal standard. The number in the parentheses is the yield of **3a** after silica gel chromatography. [c] Regioselectivity of reaction determined by GC analysis (calibration curve of **3a** was tentatively used for that of minor regioisomer). [d] PhB(neo) = phenylboronic acid neopentyl glycol ester.

Expecting that silver salts might activate an arylboron compound,[10] arylsilanes,[11] or an assumed arylpalladium intermediate,[4] we added various silver salts to the Pd(OAc)$_2$/*o*-chloranil system. While most of the examined silver salts, such as AgBF$_4$ and AgOCOCF$_3$, only had a negative effect, it was found that silver triflate (AgOTf) did improve the efficiency of the reaction (Table 1, entries 5 and 6). Though arylboron compounds were not as efficient as arylsilanes at this point, we elected to focus

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(7) For examples of C–H/C–B biaryl coupling, see refs 4 and 6g, and references therein.

(8) For examples of C–H/C–Si biaryl coupling, see: (a) Yang, S.; Li, B.; Wan, X.; Shi, Z. *J. Am. Chem. Soc.* **2007**, *129*, 6066. (b) Hachiya, H.; Hirano, K.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 2202. (c) Liang, Z.; Yao, B.; Zhang, Y. *Org. Lett.* **2010**, *12*, 3185. (d) Han, W.; Mayer, P.; Ofial, A. R. *Chem.—Eur. J.* **2011**, *17*, 6904.

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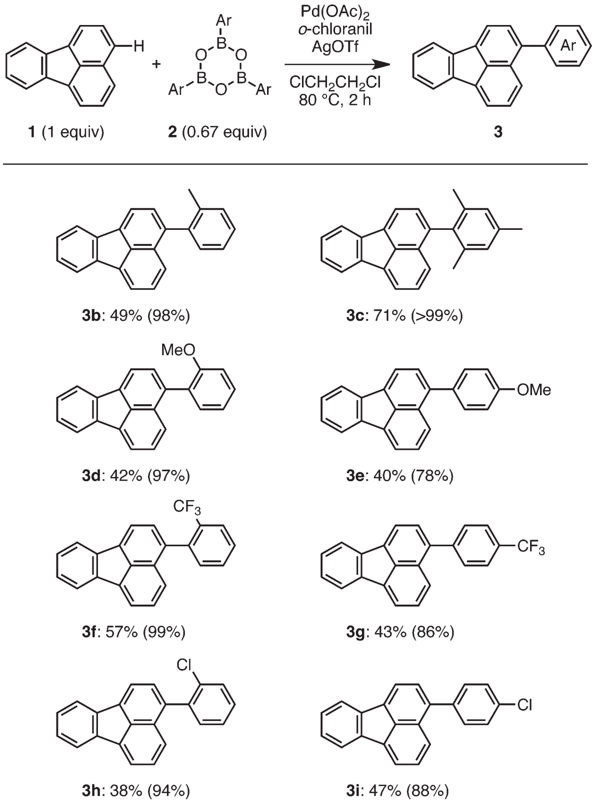
on arylboron compounds given their ease of preparation and widespread commercial availability. Gratifyingly, the use of phenylboronic acid neopentyl glycol ester or phenylboroxin provided **3a** in 50% and 55% yield, respectively (entries 7 and 8). It was also found that some other metal triflates such as $Y(OTf)_3$, $Sc(OTf)_3$, and LiOTf also promoted the reaction of **1** and phenylboroxin (entries 9–11), whereas triflic acid (HOTf) did not function as a promoter (entry 12). In view of efficiency, cost, and availability, we selected AgOTf as our first choice additive for the coupling.

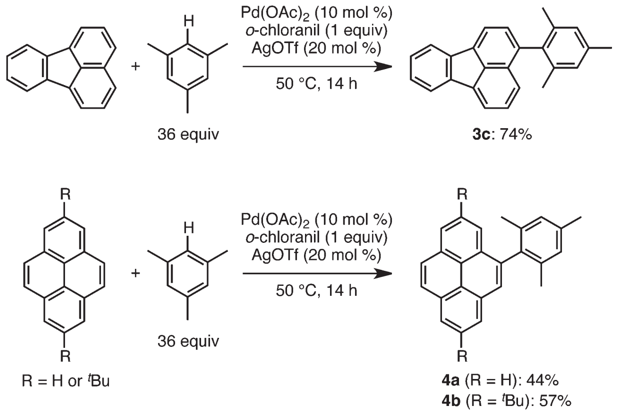
Table 2. Scope of C3-Selective C–H Arylation of Fluoranthene with Arylboroxins Catalyzed by $Pd(OAc)_2$/*o*-Chloranil/AgOTf.[a]



[a] Conditions: **1** (0.20 mmol, 1.0 equiv), **2** (0.13 mmol, 0.67 equiv), $Pd(OAc)_2$ (10 μmol, 5 mol %), *o*-chloranil (0.20 mmol, 1.0 equiv), AgOTf (20 μmol, 10 mol %), 1,2-dichloroethane (1 mL), 80 °C, 2 h. Yields after silica gel chromatography are given below the structures and the number in the parentheses is the regioselectivity of reaction.

Under the optimized reaction conditions (Table 1, entry 8), the scope with respect to arylboroxins **2** was investigated. As shown in Table 2, various arylboroxins **2** react with fluoranthene (**1**) to give the corresponding C3-arylated fluoranthenes **3**. Both electron-rich (**3b**–**3e**) and electron-deficient (**3f**–**3i**) aryl groups could be installed onto the fluoranthene ring with high C3-regioselectivity. It was found that phenylboroxins with ortho substitution (**3b**–**3d**, **3f**, and **3h**) showed higher regioselectivity. As a striking example, 3-mesitylfluoranthene (**3c**) was obtained in 71% yield with virtually complete regioselectivity. Except for ortho substituted products, the major C3-arylated fluoranthenes **3** could be isolated in a pure form by simple recrystallization from hexane/CH_2Cl_2. Notably, halogen-containing arylboroxins underwent cross-coupling, leaving carbon–halogen bonds intact (**3h** and **3i**). The tolerance of the reaction for carbon–halogen bonds makes it attractive for the rapid and selective assembly of arene units in combination with carbon–halogen bond cross-couplings such as the Suzuki–Miyaura reaction.

Scheme 1. Discovery of C–H/C–H Cross-Coupling Reaction of Polycyclic Aromatic Hydrocarbons and Unfunctionalized Arenes



In addition to C–H/C–B and C–H/C–Si couplings, we found that the oxidative C–H/C–H cross-coupling[5d,12,13] of PAHs and unfunctionalized aromatic compounds is also possible with our newly developed catalytic conditions. Representative results are shown in Scheme 1. For example, fluoranthene (1.0 equiv) was reacted with mesitylene (36 equiv) at 50 °C under the influence of $Pd(OAc)_2$/*o*-chloranil/AgOTf to afford 3-mesitylfluoranthene (**3c**) in 74% yield with virtually complete regioselectivity. Furthermore, it was found that pyrene and 2,7-di-*tert*-butylpyrene also react with mesitylene to furnish the corresponding C4-mesitylated pyrenes (**4a** and **4b**) in 44% and 57% yield, respectively (Scheme 1). In both cases, arylation occurred exclusively at the C4-position of

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(12) For reports of C–H/C–H biaryl coupling of naphthalene and benzene derivatives, see: (a) Li, R.; Li, J.; Lu, W. *Organometallics* **2006**, *25*, 5973. (b) Dohi, T.; Ito, M.; Morimoto, K.; Iwata, M.; Kita, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 1301. (c) Kita, Y.; Morimoto, K.; Ito, M.; Ogawa, C.; Goto, A.; Dohi, T. *J. Am. Chem. Soc.* **2009**, *131*, 1668.

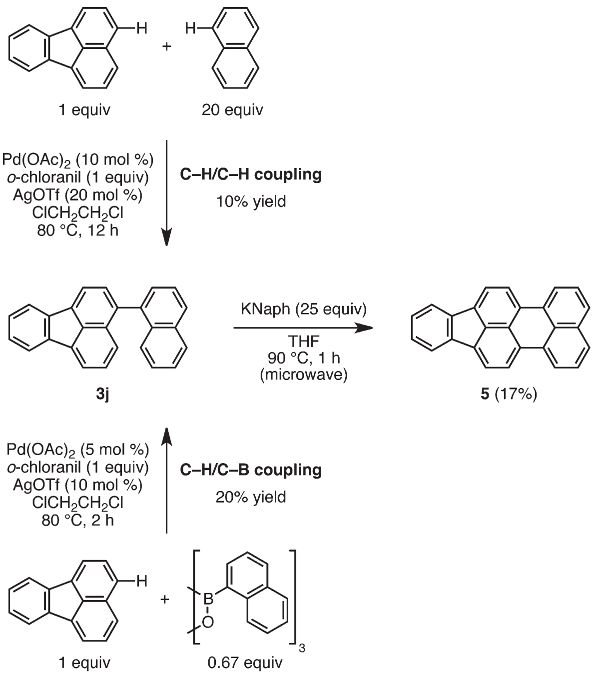
(13) For selected examples of C–H/C–H biaryl coupling using simple substrates, see: (a) Stuart, D. R.; Fagnou, K. *Science* **2007**, *316*, 1172. (b) Cho, S. H.; Hwang, S. J.; Chang, S. *J. Am. Chem. Soc.* **2008**, *130*, 9254. (c) Deprez, N. R.; Sanford, M. *J. Am. Chem. Soc.* **2009**, *131*, 11234. (d) Li, Y.; Wang, W.-H.; Yang, S.-D.; Li, B.-J.; Feng, C.; Shi, Z.-J. *Chem. Commun.* **2010**, *46*, 4553. (e) Potavathri, S.; Pereira, K. C.; Gorelsky, S. I.; Pike, A.; LeBris, A. P.; DeBoef, B. *J. Am. Chem. Soc.* **2010**, *132*, 14676. (f) Xi, P.; Yang, F.; Qin, S.; Zhao, D.; Lan, J.; Gao, G.; Hu, C.; You, J. *J. Am. Chem. Soc.* **2010**, *132*, 1822. (g) Zhao, X.; Yeung, C. S.; Dong, V. M. *J. Am. Chem. Soc.* **2010**, *132*, 5837. (h) Han, W.; Mayer, P.; Ofial, A. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 2178. (i) Kitahara, M.; Umeda, N.; Hirano, K.; Satoh, T.; Miura, M. *J. Am. Chem. Soc.* **2011**, *133*, 2160. (j) Reference 6h. (k) Reference 6j.

the pyrene ring, which is consistent with our previous C−H/C−B coupling.[4]

A more challenging C−H/C−H cross-coupling between two different PAHs is also possible. For example, fluoranthene (1.0 equiv) reacts with naphthalene (20 equiv) in the presence of Pd(OAc)$_2$ (10 mol %), *o*-chloranil (1.0 equiv), and AgOTf (20 mol %) in 1,2-dichloroethane at 80 °C to furnish 3-(1-naphthyl)fluoranthene (**3j**) in 10% yield (Scheme 2). Though low yielding, the reaction takes place with complete regioselectivity for both coupling partners (C3 position for fluoranthene and C1 position for naphthalene). The regiochemistry of **3j** was unambiguously confirmed by X-ray crystal structure analysis (see the Supporting Information for details). However, it is clear that catalytic activity needs to be increased before the C−H/C−H cross-coupling between two PAHs becomes synthetically useful. When 1-naphthylboroxin was used as an arylating agent, **3j** was produced in 20% yield (Scheme 2). Thus, under the present catalytic conditions, the C−H/C−B cross-coupling is still better for such a challenging coupling in terms of reaction efficiency.

Apart from low efficiency, the successful installation of a 1-naphthyl group to the 'zigzag' edge of fluoranthene ring is encouraging. The application of a cyclodehydrogenation method[14] to close the resultant 'fjord' region of **3j** would set the stage for controlled π-growth in the 'zigzag' direction through the sequential integration of C−H arylation and cyclodehydrogenation. It was found that the anionic cyclodehydrogenation developed by the group of Scott[15] is suitable for such a purpose. When a THF solution of **3j** (1.0 equiv) and potassium naphthalenide (25 equiv) was heated at 90 °C for 1 h under microwave irradiation, the desired indeno[1,2,3-*cd*]perylene (**5**) was obtained in 17% yield.[16] We believe that such a sequence would be complementary to our previous methods for a controlled π-extension in the 'armchair' direction using pyrene or phenanthrene as a template.[4]

Scheme 2. 'Zigzag' Extension at 'Zigzag' Edge



In summary, a new Pd(OAc)$_2$/*o*-chloranil/M(OTf)$_n$ catalytic system has been developed for the C−H arylation of fluoranthene with arylboron compounds or arylsilanes. The reaction takes place with high regioselectivity at the C3 position of the fluoranthene ring. More interestingly, we have discovered that the oxidative C−H/C−H cross-coupling of PAHs and unfunctionalized aromatic compounds is also possible with the Pd(OAc)$_2$/*o*-chloranil/AgOTf catalyst. We believe that this 'ideal' arene-assembling reaction will find use in the atom- and step-economical synthesis of π-extended PAHs for various applications. The application of Pd(OAc)$_2$/*o*-chloranil/AgOTf catalysis to various planar and geodesic PAHs and the development of a third-generation catalyst with much higher activity are currently ongoing in our laboratory.

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Supporting Information Available. Experimental procedures and characterization data for all new compounds; CIF files of **3a** and **3j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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