Polycyclic Hydrocarbons

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9-Stannafluorenes: 1,4-Dimetal Equivalents for Aromatic Annulation by Double Cross-Coupling**

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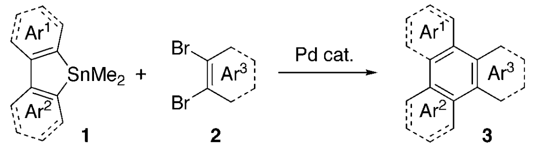
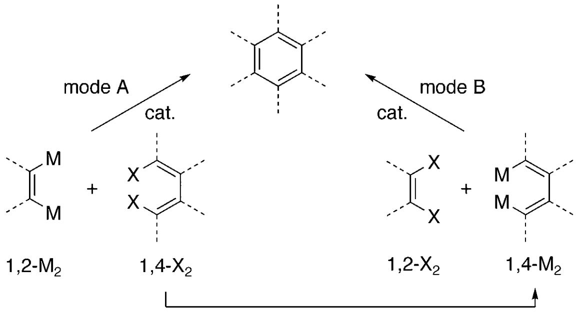
In the field of organic materials science, the design and characterization of polycyclic aromatic hydrocarbons (PAHs), which exhibit superior electronic, optical, and/or self-assembling properties, has been studied intensely.[1] Hence, efficient synthetic methods leading to functionalized PAHs are expected to assist the rapid developments of PAH-based functional materials.[2] The transition-metal-catalyzed cross-coupling reactions of organometals with organic halides are an efficient method for regio- and stereospecific formation of $C(sp^2)-C(sp^2)$ bond.[3] As a result, double cross-coupling reactions of organodimetallic reagents and dihalides would provide a straightforward and promising method for designing PAHs if the annulation reaction takes place efficiently in preference to the possible oligomerization and/or polymerization. However, the examples of such annulations are limited.[4]

Herein, we report that the palladium-catalyzed double cross-coupling reaction of 9-stannafluorenes **1** with 1,2-dihaloarenes **2** serves as a new entry to aromatic annulation and provides a variety of triply annulated benzene derivatives **3** in good to excellent yields [Eq. (1)]. Moreover, the approach is applicable to the synthesis of twisted PAHs[5] such as phenanthro[9,10-*b*]triphenylenes and diphenanthro[9,10-*b*:9′,10′-*d*]thiophene through double annulation with tetrabromoarenes, and the reaction can be extended to annulation with 1,1-dibromoalkenes leading to the production of dibenzofulvenes.



(1)

Our research group has recently demonstrated that the palladium-catalyzed double cross-coupling reaction of *vic*-bis(pinacolatoboryl)alkenes and -phenanthrenes is a versatile synthetic method for the preparation of functionalized phenanthrenes and dibenzo[*g*,*p*]chrycenes.[4i] As illustrated in Scheme 1, the annulation reaction can be categorized as the coupling of 1,2-dimetal reagents 1,2-M_2 and 1,4-dihalogenated compounds 1,4-X_2 (mode A). To expand the synthetic utility of palladium-catalyzed aromatic annulation using dimetal reagents, we were interested in the combination of 1,2-dihalogenated compounds 1,2-X_2 and 1,4-dimetal reagents 1,4-M_2 (umpolung of mode A) as an alternative approach (mode B). Considering that 1,4-M_2 can be readily prepared from the corresponding 1,4-X_2 and, in particular, the structural variation of available 1,2-X_2 is much broader than that of 1,2-M_2: thus mode B-type annulation could greatly expand the repertoire of accessible PAHs. However, the precedents of mode B-type annulation were limited to only the reactions of 2,2′-diborylbiphenyls,[4a] zirconacyclopentadienes,[4b–d] $[Zr(2,2'\text{-biphenyldiyl})_3][Li\cdot(THF)_4]_2$,[4e–g] 2,2′-distannylbinaphthyl,[4h] and 1,4-dilithiobutadienes[4j] with 1,2-dihalobenzenes, and there is still much room for improvement in the scope of the substrates and reagents, yields, and reaction conditions.



Scheme 1. Modes of [4+2]-type aromatic annulation using dimetal reagents and dihalogenated compounds.

We focused our attention on 9-stannafluorene derivatives as equivalents of 1,4-dimetal reagents, which are available from the corresponding 2,2′-dihalobiphenyls and are often used as precursors of 9-borafluorenes[6] but never employed for the synthesis of PAHs.[7] We anticipated that the cyclic form would have a beneficial effect on the reactivity toward the first coupling of the annulation owing to the strain.[8] In addition, the use of 9-stannafluorenes is favorable for lowering metal waste as compared with the corresponding 2,2′-distannylbiphenyls.

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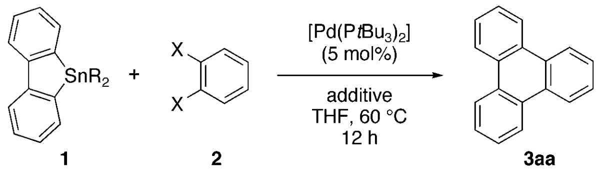
Initially, we chose 9,9-dimethyl-9-stannafluorene (**1a**) and 1,2-dibromobenzene (**2a**) as the coupling partners. After conducting extensive experiments,[9] we found that the expected product triphenylene (**3aa**) was isolated in 90% yield when the reaction was conducted in the presence of [Pd(P*t*Bu$_3$)$_2$] (5 mol%) in THF at 60°C (Table 1, entry 1).[10]

Table 1: Palladium-catalyzed annulation of **1a**–**1b** with **2a**–**2c** leading to **3aa**.[a]



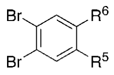
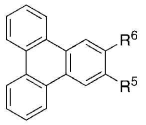
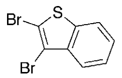
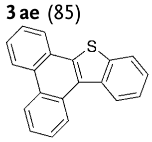
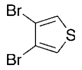
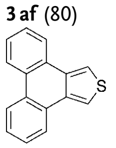
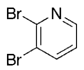
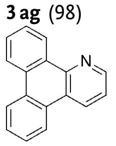
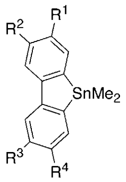
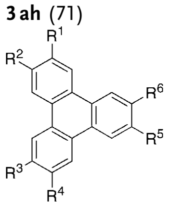
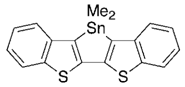
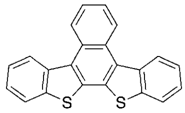
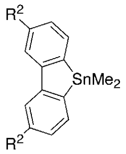
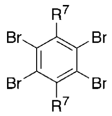
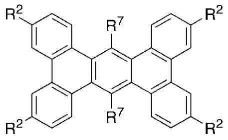
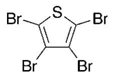
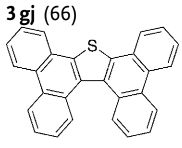
Entry	1	2	Additive (equiv)	3 Yield [%][b]
1	**1a** (R = Me)	**2a** (X = Br)	–	87 (90)[c]
2	**1a**	**2a**	CsF (5)	84
3	**1a**	**2a**	CuI (0.1)	68
4	**1a**	**2a**	CsF (5), CuI (0.1)	8
5	**1a**	**2a′** (X = I)	–	0
6	**1a**	**2a′**	CsF (5)	87
7	**1a**	**2a″** (X = Cl)	–	0
8	**1a**	**2a″**	CsF (5)	21
9	**1b** (R = Bu)	**2a**	–	0
10	**1b**	**2a**	CsF (5)	90

[a] Reaction conditions: **1** (0.050 mmol), **2** (0.050 mmol), [Pd(P*t*Bu$_3$)$_2$] (2.5 μmol, 5 mol%), additive as shown in Table, THF, 60°C. [b] Yield based on ^{1}H NMR spectroscopy. [c] The value in parentheses is the yield of the isolated product.

No formation of oligomeric or polymeric by-products was observed. The addition of CsF or CuI was found to be less effective for the annulation reaction (Table 1, entries 2 and 3), whereas using these two additives simultaneously resulted in far from satisfactory results (Table 1, entry 4). This outcome sharply contrasts to those of Baldwin and co-workers, who reported the palladium-catalyzed reaction of arylstannanes with aryl halides.[11] The presence of CsF was essential in the case of 1,2-diiodobenzene (**2a′**; compare Table 1, entries 5 and 6), whereas the reaction with dichlorobenzene (**2a″**) was unsuccessful both in the absence and presence of CsF (Table 1, entries 7 and 8). Dibutylstannafluorene **1b** underwent the annulation reaction efficiently when CsF was added as in the case of **2a** (compare Table 1, entries 9 and 10). Bulkier atoms/substituents such as iodine and the butyl group appeared to slow down the transmetalation process, while the addition of fluorides probably accelerates the transmetalation process by generating stannates.[12]

The scope of the present annulation reaction is summarized in Table 2. Substituted dibromobenzenes **2b**–**2e** reacted with **1a** to produce triphenylenes **3ab**–**3ae** in high to excellent yields (Table 2, entries 1–4). Both electron-withdrawing and -donating substituents on **2** were tolerated. The annulation reaction carried out with dibromothiophenes **2f** and **2g** proceeded smoothly at the 2,3- and 3,4-positions to produce benzo[*b*]phenanthro[9,10-*d*]thiophene (**3af**) and phenanthro-[9,10-*c*]thiophene (**3ag**) in 78–98% yield (Table 2, entries 5–7). Thus, the fusion mode of a thiophene ring was easily

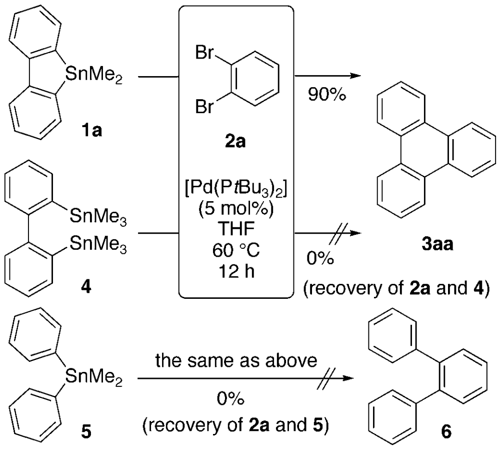
Table 2: Pd-catalyzed annulation of **1** with dibromoarenes **2**.[a]

Entry	1	2	3 (yield [%])[b]
			
1	**1a**	**2b** (R^5 = CF$_3$; R^6 = H)	**3ab** (99)
2	**1a**	**2c** (R^5, R^6 = F)	**3ac** (85)
3[c]	**1a**	**2d** (R^5 = OMe; R^6 = H)	**3ad** (95)
4[d]	**1a**	**2e** (R^5, R^6 = Me)	**3ae** (85)
			
5	**1a**	**2f**	**3af** (78)
6[d]	**1a**	**2f**	**3af** (80)
			
7	**1a**	**2g**	**3ag** (98)
			
8	**1a**	**2h**	**3ah** (71)
			
9	**1c** (R^1,R^4 = H; R^2,R^3 = OMe)	**2a** (R^5,R^6 = H)	**3ca** (99)
10	**1d** (R^1,R^2,R^3,R^4 = Me)	**2a** (R^5,R^6 = H)	**3da** (77)
11	**1e** (R^1,R^2 = OMe; R^3,R^4 = H)	**2c** (R^5,R^6 = F)	**3ec** (97)
			
12	**1f**	**2a**	**3fa** (74)
			
13	**1a** (R^2 = H)	**2i** (R^7 = O*n*C$_{10}$H$_{21}$)	**3ai** (80)
14	**1g** (R^2 = O*n*C$_6$H$_{13}$)	**2j** (R^7 = H)	**3gj** (66)
			
15	**1a**	**2k**	**3ak** (85)

[a] Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), [Pd(P*t*Bu$_3$)$_2$] (50 μmol, 5 mol%), THF, 60°C, 12 h. [b] Yield of isolated product. [c] **1** (1.0 mmol), **2** (1.0 mmol), [Pd(P*t*Bu$_3$)$_2$] (50 μmol, 5 mol%), CsF (5 mmol), 1,4-dioxane, 130°C, 12 h. [d] CsF (5 mmol) was used as the additive.

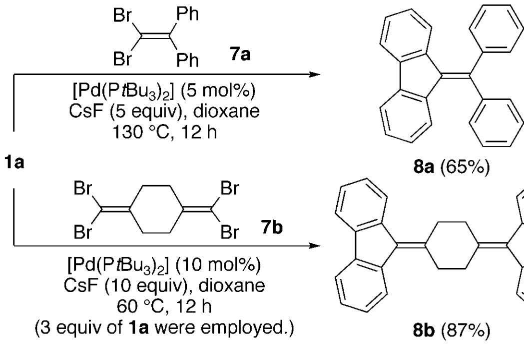
controlled. Dibenzo[*f,h*]quinoline (**3ah**) was obtained in 71 % yield from **1a** and 2,3-dibromopyridine (**2h**; Table 2, entry 8).[13] Substituted 9-stannafluorenes **1c**–**1e** also participated in the annulation reaction to give symmetrical triphenylenes **3ca** and **3da** as well as an unsymmetrical one **3ec** in high to excellent yields (Table 2, entries 9–11). Dithienostannole **1f** also underwent the double cross-coupling reaction as the equivalent of 2,2′-dimetalbithiophene with **2a** to produce **3fa** in 74 % yield (Table 2, entry 12). Moreover, a double annulation reaction that allows the facile synthesis of twisted PAHs was performed by using tetrabromoarenes as an electrophile (Table 2, entries 13–15). Thus, 1,2,4,5-tetrabromobenzenes **2i** and **2j** and 2,3,4,5-tetrabromothiophene (**2k**) were coupled with two equivalents of **1** to produce phenanthro[9,10-*b*]triphenylenes **3ai** and **3gj**,[4e] and diphenanthro[9,10-*b*:9′,10′-*d*]thiophene **3ak**,[14] respectively, in good to high yields. The present annulation reaction is, to the best of our knowledge, the first demonstration of **1** to be utilized as 2,2′-dimetalobiaryl equivalents for C–C bond-forming annulation.

To gain understanding of the characteristic reactivity patterns of **1**, we subjected 2,2′-bis(trimethylstannyl)biphenyl (**4**) and dimethyldiphenylstannane (**5**) to the reaction conditions ([Pd(P*t*Bu$_3$)$_2$], THF, 60 °C, 12 h) that were optimized for **1**, in the presence of **2a**. However, no coupling reaction took place and with only quantitative recovery of the stannyl reagents in both cases (Scheme 2).[15] These results clearly indicate that **1** is much more reactive than **4** or **5**. Meanwhile, the Pd^0 catalyst which is regenerated in the cross-coupling reaction of 1,2-dibromobenzenes and arylboronic acids with the aid of [Pd$_2$(dba)$_3$]/P*t*Bu$_3$ was reported to undergo oxidative addition exclusively with the remaining C–Br bond of the initial product over the diffusion process.[16] Therefore, the success of the present annulation reaction may be ascribed to both the high reactivity of **1**, induced by the cyclic structure, and the unique behavior of **2** with regard to the second oxidative addition process.



Scheme 2. Attempts at the coupling reaction of **4** and **5** with **2a**.

Furthermore, 1,1-dibromoalkenes **7a** and **7b** were also found to undergo a double cross-coupling reaction with **1** (Scheme 3). Although the addition of CsF at a higher reaction temperature (in the case of **7a**) was necessary to promote the formation of a five-membered ring, the expected products dibenzofulvenes **8a**[17] and **8b**[18] were isolated in 65 % and 87 % yield, respectively.



Scheme 3. Annulation of **1a** with 1,1-dibromoalkenes **7**.

In summary, we have developed a palladium-catalyzed double cross-coupling reactions of 9-stannafluorenes and dithienostannole with 1,2-dihaloarenes and 1,1-dibromoalkenes, by which diverse polycyclic aromatic hydrocarbons can be synthesized in good to excellent yields. We have also disclosed that the reactivity of 9,9-dimethyl-9-stannafluorene toward this palladium-catalyzed cross-coupling reaction is much higher than that of 2,2′-bis(trimethylstannyl)biphenyl. Further studies on the elucidation of the mechanism and the development of functional organic materials using the present annulation reaction are in progress.

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Keywords: arenes · cross-coupling · palladium · stannanes · synthetic methods

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