327 Hz, after Gaussian multiplication: t, $J = 120$ Hz); IR (KBr, nujol): $\tilde{\nu} =$ 1571, 1491, 1308, 1261, 1172, 1154, 1095, 887, 802, 742, 651, 466 cm^{-1}; MS (EI): *m*/*z* (%): 242 (17, Bu_4N), 142 (100, Bu_2NCH_2); negative-ion FAB-MS (NBA matrix): *m*/*z* (%): 95 (70, Me_2AlF_2); elemental analysis calcd for $C_{18}H_{42}AlF_2N$ (337.51): C 64.1, H 12.5, N 4.2; found: C 62.8, H 12.1, N 4.2.

2: A solution of $TrisAlMe_2 \cdot THF$ (3.00 g, 8.32 mmol) was added dropwise to a solution of TBADF (2.34 g, 8.32 mmol) in THF (40 mL) at room temperature, and the mixture was stirred for 12 h. The solvent was removed in vacuo, and the residue was redissolved in toluene (30 mL). The solution was then filtered, and recrystallization at 0 °C for 3 d yielded 4.20 g (7.00 mmol, 84 %) of **2** as rhombic crystals. M.p. 108 °C; ^1H NMR (200 MHz, C_6D_6, TMS): $\delta = -0.29$ (t, $J = 2.8$ Hz, 3H, $AlCH_3$), 0.69 (s, 27H, Me_3Si), 0.91 (t, $J = 6.5$ Hz, 12H, CH_3), 1.12–1.31 (m, 16H, $C^{3/7/11/15}H_2$, $C^{2/6/10/14}H_2$), 2.91 (m, 8H, $C^{1/5/9/13}H_2$); ^{19}F NMR (235 MHz, C_6D_6, $CFCl_3$): $\delta = -145.93$ (s); ^{29}Si NMR (79.5 MHz, C_6D_6, TMS): $\delta = -3.71$ (t, $J =$ 1.5 Hz, Me_3Si); IR (KBr): $\tilde{\nu} = 2965$, 2898, 2878, 1488, 1466, 1382, 1243, 1179, 1029, 869, 787, 754, 741, 709, 680, 664, 640, 575, 316 cm^{-1}; EI-MS: *m*/*z* (%): 242 (100, Bu_4N), 100 (4, $Bu(Me)NCH_2$); negative-ion FAB-MS (NBA matrix): *m*/*z* (%): 311 (100, $Tris(Me)AlF_2$), 231 (9, Tris); elemental analysis calcd for $C_{30.5}H_{70}AlF_2NSi_3$ (600.13; crystallized with 0.5 molecules of C_7H_8): C 61.0, H 11.8, Al 4.5, F 6.3, N 2.3; found: C 61.8, H 11.5, Al 3.4, F 5.5, N 2.8.

3: $GaMe_3$ (1.71 g, 14.9 mmol) was cooled to −196 °C, and THF (10 mL) was added. The solution was warmed to −30 °C, and a solution of TBADF (4.08 g, 14.5 mmol) in THF (10 mL) was added dropwise. The mixture was then stirred for 30 min. Crystallization at 4 °C for 3 d yielded 4.35 g (11.4 mmol, 79 %) of **3** as rhombic crystals. M.p. 132 °C; ^1H NMR (500 MHz, CD_3CN, TMS): $\delta = -0.74$ (s, 6H, $GaCH_3$), 0.96 (t, $J = 7.3$ Hz, 12H, CH_3), 1.34 (qt, $J = 7.5$ Hz, 8H, $C^{3/7/11/15}H_2$), 1.60 (tt, $J = 7.5$ Hz, 8H, $C^{2/6/10/14}H_2$), 3.09 (m, 8H, $C^{1/5/9/13}H_2$); ^{13}C NMR (126 MHz, CD_3CN, TMS): $\delta = -6.63$ (s, $GaCH_3$), 13.80 (CH_3), 20.35 ($C^{3/7/11/15}H_2$), 24.42 ($C^{2/6/10/14}H_2$), 59.36 ($C^{1/5/9/13}H_2$); ^{19}F NMR (235 MHz, CD_3CN, $CFCl_3$): $\delta = -164.76$ (s); IR (KBr, nujol): $\tilde{\nu} = 1576$, 1494, 1261, 1181, 1152, 1109, 1024, 887, 802, 563, 518, 494 cm^{-1}; EI-MS: *m*/*z* (%): 242 (34, Bu_4N), 142 (100, Bu_2NCH_2), 101 (19, Me_2Ga), 99 (29, Me_2Ga); negative-ion FAB-MS (NBA matrix): *m*/*z* (%): 139 (25, Me_2GaF_2), 137 (38, Me_2GaF_2); elemental analysis calcd for $C_{18}H_{42}F_2GaN$ (380.25): C 56.9, H 11.1, Ga 18.3, N 3.7; found: C 57.0, H 10.6, Ga 18.3, N 3.7.

4: A solution of TBADF (0.931 g, 3.31 mmol) in THF (5 mL) was added dropwise to a solution of $InMe_3$ (1.06 g of a 50 % solution in diethyl ether, 3.30 mmol) in THF (5 mL) at room temperature. A white precipitate formed immediately upon the addition of the TBADF and subsequently redissolved upon further addition of TBADF. The mixture was stirred for 30 min after the addition was complete. Crystallization at room temperature for 3 h yielded 0.470 g (1.10 mmol, 33 %) of **4** as rhombic crystals. M.p. 147 °C; ^1H NMR (500 MHz, [D_8]THF, TMS): $\delta = -0.56$ (s, 6H, $InCH_3$), 0.99 (t, $J = 7.4$ Hz, 12H, CH_3), 1.41 (qt, $J = 7.4$ Hz, 8H, $C^{3/7/11/15}H_2$), 1.73 (tt, $J = 7.5$ Hz, 8H, $C^{2/6/10/14}H_2$), 3.47 (m, 8H, $C^{1/5/9/13}H_2$); ^{13}C NMR (126 MHz, [D_8]THF, TMS): $\delta = -7.35$ (br, $InCH_3$), 14.08 (CH_3), 20.66 ($C^{3/7/11/15}H_2$), 24.84 ($C^{2/6/10/14}H_2$), 59.22 ($C^{1/5/9/13}H_2$); ^{19}F NMR (235 MHz, [D_8]THF, $CFCl_3$): $\delta = -180.87$ (s); IR (KBr, nujol): $\tilde{\nu} = 1582$, 1495, 1306, 1262, 1153, 1144, 1107, 1053, 1025, 888, 803, 738, 693, 507, 450, 430 cm^{-1}; EI-MS: *m*/*z* (%): 242 (50, Bu_4N), 142 (100, Bu_2NCH_2), 115 (14, In); negative-ion FAB-MS (NBA matrix): *m*/*z* (%): 183 (18, Me_2InF_2); elemental analysis calcd for $C_{18}H_{42}F_2InN$ (425.35): C 50.8, H 9.9; found: C 50.8, H 9.6.

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[3] Crystal structure analysis: The data were collected on a Stoe Siemens four-circle diffractometer with $Mo_{K\alpha}$ radiation on rapidly cooled crystals suspended in oil with profile optimized $2\theta/\omega$ scans. The structures were solved using direct methods (SHELXS-97) and refined on F^2 (SHELXL-97).[6] A psi-scan absorption correction was used for **3** and **4**. – **1**: $C_{18}H_{42}AlF_2N$, $M_r = 337.51$, monoclinic, space group $P2_1/n$, $a = 10.744(2)$, $b = 12.124(2)$, $c = 17.203(3)$ Å, $\beta = 96.09(3)°$, $V =$ 2228.1(7) Å^3, $Z = 4$, $\rho_{calcd} = 1.006$ Mg m^{-3}, $F(000) = 752$, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.105$ mm^{-1}, $T = -123$ °C, crystal size $0.7 \times 0.7 \times 0.2$ mm^3. Of the 9616 reflections collected ($7.0 \leq 2\theta \leq 50.0°$), 3921 were independent; max./min. residual electron density 237/−187 e nm^{-3}, $R1 =$ 0.0431 ($I > 2\sigma(I)$) and $wR2 = 0.1187$ (all data). – **2**: $C_{30.5}H_{70}AlF_2NSi_3$ (including 0.5 molecules of toluene), $M_r = 600.13$, monoclinic, space group $P2_1/c$, $a = 17.618(3)$, $b = 12.917(2)$, $c = 17.681(3)$ Å, $\beta =$ 101.32(2)°, $V = 3945.1(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.010$ Mg m^{-3}, $F(000) =$ 1332, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.170$ mm^{-1}, $T = -60$ °C, crystal size $0.8 \times 0.8 \times 0.6$ mm^3. Of the 9891 reflections collected ($7.0 \leq 2\theta \leq 45.0°$), 5134 were independent; max./min. residual electron density 1373/−426 e nm^{-3}, $R1 = 0.1204$ ($I > 2\sigma(I)$), $wR2 = 0.3726$ (all data). – **3**: $C_{18}H_{42}F_2GaN$, $M_r = 380.25$, monoclinic, space group $P2_1/n$, $a =$ 10.8088(11), $b = 12.0465(11)$, $c = 17.336(2)$ Å, $\beta = 96.73(1)°$, $V =$ 2241.7(4) Å^3, $Z = 4$, $\rho_{calcd} = 1.127$ Mg m^{-3}, $F(000) = 824$, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 1.241$ mm^{-1}, $T = -70$ °C, $0.7 \times 0.6 \times 0.2$ mm^3. Of the 3265 reflections collected ($7.0 \leq 2\theta \leq 45.0°$), 2924 were independent; max./min. residual electron density 499/−387 e nm^{-3}, $R1 = 0.0398$ ($I >$ $2\sigma(I)$), $wR2 = 0.1156$ (all data). – **4**: $C_{18}H_{42}F_2InN$, $M_r = 425.35$, monoclinic, space group $P2_1/n$, $a = 10.8943(12)$, $b = 11.984(2)$, $c =$ 17.483(3) Å, $\beta = 96.20(1)°$, $V = 2269.2(6)$ Å^3, $Z = 4$, $\rho_{calcd} =$ 1.245 Mg m^{-3}, $F(000) = 896$, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 1.055$ mm^{-1}, $T = -70$ °C, crystal size $0.90 \times 0.80 \times 0.40$ mm^3. Of the 6863 reflections collected ($7.0 \leq 2\theta \leq 45.0°$), 3985 were independent; max./min. residual electron density 666/−722 e nm^{-3}, $R1 = 0.0371$ ($I > 2\sigma(I)$), $wR2 =$ 0.0960 (all data). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-127535 (**1**), -127536 (**2**), -127537 (**3**), -127538 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Palladium-Catalyzed Intermolecular Controlled Insertion of Benzyne-Benzyne-Alkene and Benzyne-Alkyne-Alkene—Synthesis of Phenanthrene and Naphthalene Derivatives

Eiji Yoshikawa and Yoshinori Yamamoto*

Alkynes are frequently used as a substrate for the transition metal catalyzed inter- and intramolecular carbometalation reaction.[1] However, arynes have hardly been utilized in transition metal catalyzed organic synthesis, although stoichiometric reactions of zirconium–benzyne and nickel–benzyne complexes were studied.[2] Quite recently, Castedo and his co-workers reported the efficient palladium-catalyzed cyclotrimerization of arynes[3a] and cocyclization of arynes with alkynes.[3b] During our continuing studies on the catalytic

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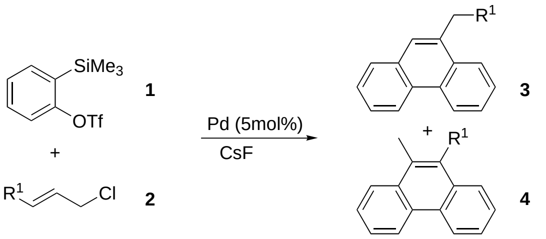
[*] Prof. Y. Yamamoto, E. Yoshikawa
Department of Chemistry
Graduate School of Science, Tohoku University
Aoba, Sendai 980-8578 (Japan)
Fax: (+81) 22-217-6784
E-mail: yoshi@yamamoto1.chem.tohoku.ac.jp

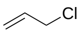
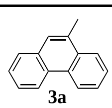
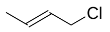
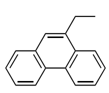
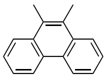
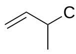
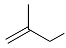
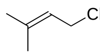
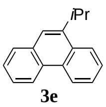
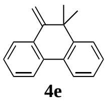
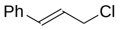
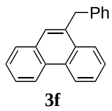
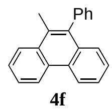
hydro- and/or carbopalladation of allenes,[4a] enynes,[4b] methylenecyclopropanes,[4c] and alkynes[4d, e] it occurred to us that arynes may be utilized as a partner in catalytic carbopalladation. It is well known that aryl– and vinyl–palladium complexes readily undergo intra- and intermolecular carbopalladation with alkynes by, for example, a Heck-type reaction. However, to the best of our knowledge, there is no report on the intermolecular carbopalladation of π-allyl palladium complexes with alkynes, although several examples of the corresponding intramolecular reactions are known.[5, 6] We now report that benzyne is actually very reactive as a carbopalladation partner of π-allyl palladium chloride: the palladium-catalyzed reaction of allyl chlorides **2** with benzyne precursor **1** produces phenanthrene derivatives **3**, along with their minor regioisomers **4**, in good yields [Eq. (1), Table 1].

After a series of optimization experiments on the reaction of allyl chloride **2a** we settled on the following two best methods: Method A: the reaction of allyl chloride **2** (1.0 equiv) and benzyne precursor **1** (2.0 equiv) in the presence of $[Pd_2(dba)_3]\cdot CHCl_3$ (2.5 mol%), dppf (5 mol%), and CsF (4.0 equiv) in CH_3CN/THF (1/1) at 60°C gave **3a** in 69% yield (entry 1). Method B: the reaction of allyl chloride **2** (1.0 equiv) and benzyne precursor **1** (4.0 equiv) in the presence of $[Pd_2(dba)_3]\cdot CHCl_3$ (2.5 mol%) and CsF (8.0 equiv) in CH_3CN at 80°C gave **3a** in 70% yield (entry 2).[7] The catalytic system of $[Pd_2(dba)_3]\cdot CHCl_3$ with PPh_3 or dppe gave slightly lower yields, and the other catalysts such as $\{(\eta^3\text{-allyl})$ palladium chloride$\}_2$ and $[Pd(PPh_3)_4]$ were not so effective. The reaction of crotyl chloride (**2b**) with **1** under the conditions of Method A gave a 58:42 mixture of **3b** and **4b** in 66% combined yield (entry 3). The ratio of **3b** to **4b** increased up to 70:30 under the conditions of Method B (entry 4). The reaction of α-methyl allyl chloride **2c** gave a 65:35 mixture of **3b** and **4b** in 70% yield (entry 5). It should be noted that the isomer ratio of the products obtained from the reaction of **2c** is almost same as that of **2b**. Methyl allyl chloride **2d** did not produce phenanthrene derivatives at all (entry 6).[8] The reaction of prenyl chloride (**2e**) under the conditions of Method A gave an 80:20 mixture of **3e** and **4e** in 44% yield (entry 7). However, the isomer ratio and the chemical yield increased up to greater than 95:5 and 68% yield, respectively, under the conditions of Method B (entry 8). The reaction of cinnamyl chloride (**2f**) afforded an approximately 7:3 mixture of **3f** and **4f** under the conditions of both Methods, but Method B gave a higher chemical yield than Method A (entries 9 and 10).



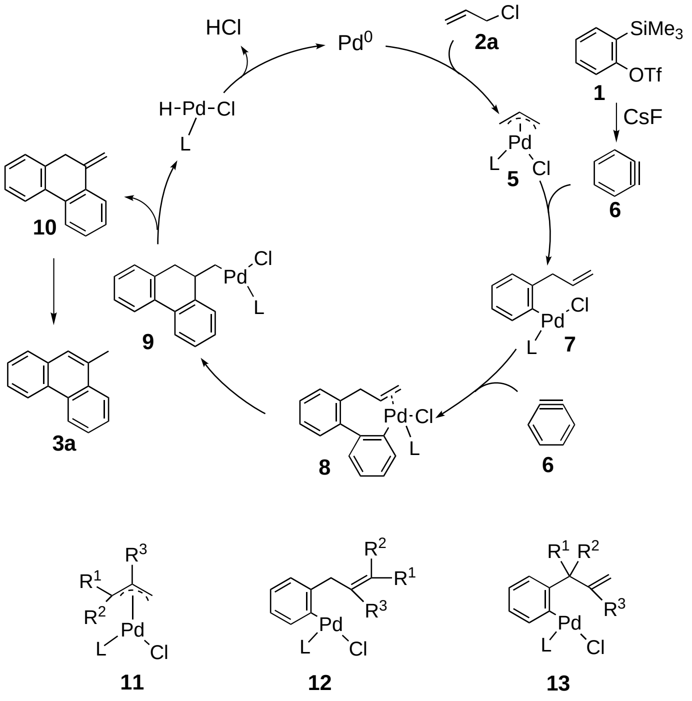
(1)

Table 1. Palladium-catalyzed reaction of **1** with **2**.

Entry	2	Method[a]	Product	Yield [%][b] (**3**:**4**)[c]
1	 **2a**	A	 **3a**	69
2	**2a**	B		70
3	 **2b**	A	 +  **3b** **4b**	66 (58:42)
4	**2b**	B		70 (70:30)
5	 **2c**	A	**3b** + **4b**	70 (65:35)
6	 **2d**	B		–
7	 **2e**	A	 +  **3e** **4e**	44 (80:20)
8	**2e**	B		68 (>95:5)
9	 **2f**	A	 +  **3f** **4f**	56 (70:30)
10	**2f**	B		71 (73:27)

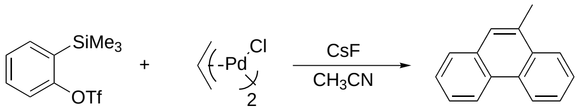
[a] for a description of the methods see the text. [b] Isolated yield based on **2**. [c] Ratio determined by ^1H NMR spectroscopy on the crude product.

A plausible mechanism for this unprecedented intermolecular benzyne-benzyne-alkene insertion reaction is shown in Scheme 1. Initially π-allyl palladium chloride **5** would be formed from Pd^0 and **2a**. Benzyne **6**, which is generated from the reaction of CsF and **1**,[3c] would insert into **5** to afford the aryl palladium intermediate **7**. In the case of substituted allylic chlorides **2b**, **c**, **e**, **f**, two regioisomers **12** and **13** would be produced at this stage. A second benzyne insertion into **7** would produce **8** and subsequent carbopalladation to the alkene would afford the cyclized intermediate **9**. A β-hydride



Scheme 1. Proposed mechanism for the palladium-catalyzed benzyne-benzyne-alkene insertion cascade. L = phosphane ligand.

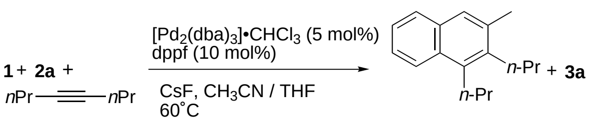
elimination from **9** would give the phosphane-substituted HPdCl species and **10**. The latter would then undergo isomerization to 9-methylphenanthrene (**3a**). In the case of the substituted allylic chlorides benzyne (**6**) would react predominantly at the less-substituted terminus of the π-allyl chloride complex **11** to produce **12** preferentially over its regioisomer **13**. Accordingly, **3b**, **e**, **f** were in general formed predominantly over their isomers **4b**, **e**, **f**, respectively. The formation of **4e** strongly supports the β-elimination-rearrangement processes (**9** → **10** → **3**) in the proposed mechanism; the rearrangement of the double bond of **4e** to form the phenanthrene ring is not possible. As is apparent from the result of the experiment with **2d**, the carbopalladation step (**8** → **9**) is hampered if there is a substituent at the 2-position (for example, $R^3 = Me$) of **11**. As mentioned above the lack of an example for the intermolecular carbopalladation of π-allyl palladium complexes toward alkynes was strange for us. Accordingly, the reaction of the π-allyl palladium chloride dimer **14** with 4-octyne was examined under various reaction conditions. However, no addition products were obtained, instead the starting materials were recovered. On the other hand, the reaction of **14** (1 equiv) with **1** (1 equiv) in the presence of CsF (2 equiv) in CH_3CN at room temperature gave **3a** in 22% yield [Eq. (2)]. This result clearly indicates a very high reactivity of the benzyne triple bond, compared to the ordinary triple bond, toward the π-allyl–Pd bond.



(2)

1 **14** **3a** 22%

Encouraged by the successful controlled insertion of benzyne-benzyne-alkene, we next examined the controlled insertion of benzyne-alkyne-alkene. The reaction of **1** (1 equiv), **2a** (1 equiv), and 4-octyne (2 equiv) under slightly modified conditions[9] of Method A gave **15** in 47% yield along with small amounts (3%) of **3a** [Eq. (3)]. As mentioned



(3)

15 47% 3%

above, π-allyl palladium chloride (**5**) would be very sluggish toward the insertion into the ordinary alkyne, 4-octyne, to give **7** at the first stage of carbopalladation. The second stage of carbopalladation would take place through the Heck-type arylpalladation, so that 4-octyne could participate selectively in this step.

It is now clear that the benzyne triple bond is highly reactive toward carbopalladation processes, and the controlled carbopalladation enables the production of phenanthrene and naphthalene derivatives from π-allyl palladium species. The reactions of benzyne with other organopalladium derivatives are currently under investigation.

Experimental Section

The general procedures for the conversions of the allylic chlorides are described using allyl chloride **2a**.

Method A: **2a** (32.6 μL, 0.4 mmol) was added to a suspension of anhydrous CsF (243 mg, 1.6 mmol), $[Pd_2(dba)_3] \cdot CHCl_3$ (10.4 mg, 0.01 mmol), and dppf (11 mg, 0.02 mmol) in CH_3CN (1 mL) and THF (1 mL), and the mixture was stirred at room temperature for a few minutes. Benzyne precursor **1** (182.8 μL, 0.8 mmol) was added and the resulting mixture was stirred at 60°C for 1 day. The mixture was cooled to room temperature, extracted with diethyl ether, dried with $MgSO_4$, and concentrated. The product was purified by column chromatography on silica gel to give **3a** in 69% yield (53.1 mg).

Method B: **2a** (32.6 μL, 0.4 mmol) was added to a suspension of anhydrous CsF (486 mg, 3.2 mmol) and $[Pd_2(dba)_3] \cdot CHCl_3$ (10.4 mg, 0.01 mmol) in CH_3CN (2 mL) and the mixture was stirred at room temperature for 15 min. Four equivalents of **1** (365.6 μL, 1.6 mmol) were added and the mixture was stirred at 80°C for 3 h. The same work-up procedure as above was used, and **3a** was obtained in 70% yield (53.9 mg).

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[7] Significant amounts of triphenylene (20–30%) were produced as a by-product in Method B (entry 2), but only a trace amount of it was detected in Method A (entry 1).

[8] An unidentified compound having *m*/*z* 282 was obtained. This molecular weight corresponds to a molecule composed of three benzynes and one $CH_2{=}CH(CH_3)CH_2$ unit.

[9] A mixture of $[Pd_2(dba)_3] \cdot CHCl_3$ (5 mol%), dppf (10 mol%), and CsF (0.8 mmol) in CH_3CN (1 mL) and THF (1 mL) was treated with **1** (0.4 mmol) at 60°C for 1 day. Further CsF (0.8 mmol) was then added and the resulting mixture was st irred at 60°C for 1 day.