

博士論文（要約）

**Synthesis of π -Conjugated Polycyclic Hydrocarbons
Using Successive Carbometalation of
Carbon–Carbon Unsaturated Bonds**

（炭素–炭素不飽和結合の連続的カルボメタル化反応を用いた
 π 共役多環炭化水素合成）

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General Introduction

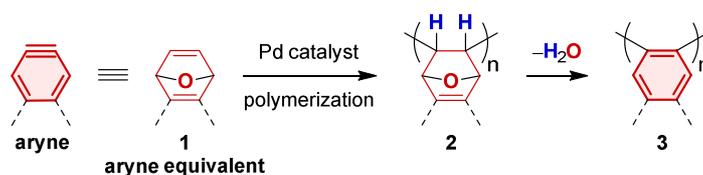
π -Conjugated polycyclic hydrocarbons have attracted much attention because of their utility in optical and electronic device applications. Therefore, the development of versatile methods for the synthesis of π -conjugated polycyclic hydrocarbons has been of utmost importance for decades.[1] Since the beginning, coupling reactions between preformed π -conjugated cycles have been employed as the most effective methods to produce extended π -conjugated molecules.[2] On the other hand, methods involving the formation of new π -conjugated cycles, such as Diels-Alder reaction and [2+2+2] cycloaddition, have also studied intensively.[3] These methods have also known as efficient methods for the synthesis of graphene nanoribbons.[4]

In this thesis, the author focuses on the successive carbometalation of carbon-carbon unsaturated bonds as a key reaction to construct π -conjugated polycyclic hydrocarbons. In the first part is described formal aryne polymerization to produce poly(*o*-arylene)s. In the second part, selective synthesis of various unsymmetric dibenzo[*a,e*]pentalenes by rhodium-catalyzed stitching reaction is described.

Synthesis of Poly(*o*-arylene)s by Pd-Catalyzed Formal Aryne Polymerization

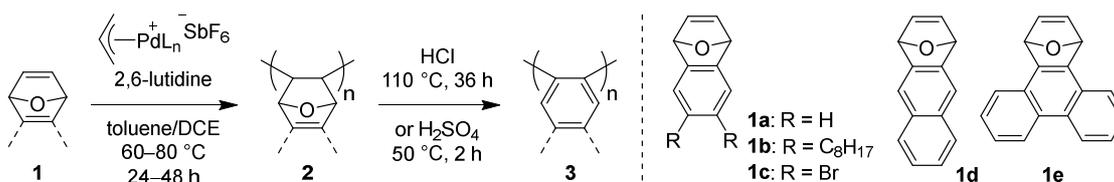
Aryne—1,2-didehydroarene—serves as a useful intermediate in organic synthesis. However, the polymerization of aryne leading to poly(*o*-arylene)s was regarded as a challenging reaction until recently because of difficulty in controlling the highly reactive aryne species.[5] Therefore, the author focuses on a synthetic equivalent of arynes, [2.2.1]oxabicyclic alkene, as a monomer for polymerization and discloses the formal chain-growth aryne polymerization based on palladium-catalyzed coordination-insertion polymerization of [2.2.1]oxabicyclic alkenes (**1**) followed by acid-promoted dehydration to synthesize various poly(*o*-arylene)s (**3**) (Scheme 1).

Scheme 1. Formal aryne polymerization



The polymerization of **1b** was successfully catalyzed by a complex prepared from a π -allylpalladium chloride dimer ($[\text{PdCl}(\eta^3\text{-allyl})]_2$) and silver hexafluoroantimonate (AgSbF_6) in the presence of 2,6-lutidine (Table 1). Whereas the use of toluene and 1,2-dichloroethane (DCE) as single solvent systems gave poor results, the combined use of toluene and DCE (1:1) afforded the polymer **2a** in 86% yield (entry 1). Using the optimized procedure, monomers **1b–1e** having various substituents were also polymerized to form the corresponding polymers **2b–2e** in good yields (entries 2–5). The polymerization method could also be applied to monomers with longer π -conjugated systems (entry 4 and entry 5), although the molecular weight of polymer **2e** remained low. Dehydration of polymers **2a–2e** was accomplished by treatment with hydrogen chloride in 1,4-dioxane at 110 °C (entries 1, 2, 4 and 5) or with conc. sulfuric acid at 50 °C (entry 3) to afford the corresponding poly(*o*-arylene)s.

Table 1. Polymerization of [2.2.1]oxabicyclic alkenes (**1**) followed by dehydration to form poly(*o*-arylene)s (**3**)



entry	monomer	polymerization step ^a					dehydration step ^b		
		temperature (°C)	time (h)	2 (%)	M_w^c	M_w/M_n^c	3 (%)	M_w^c	M_w/M_n^c
1	1a	60	24	86	5,600 ^d	1.2	94	3,900	2.0
2	1b	60	36	90	9,500	1.3	96	7,000	1.5
3 ^e	1c	80	48	76	3,500	1.4	85	1,200	1.9
4	1d	60	36	87	6,500 ^d	1.3	97	6,300 ^d	3.0
5	1e	100	36	86	700 ^d	1.4	96	800	1.6

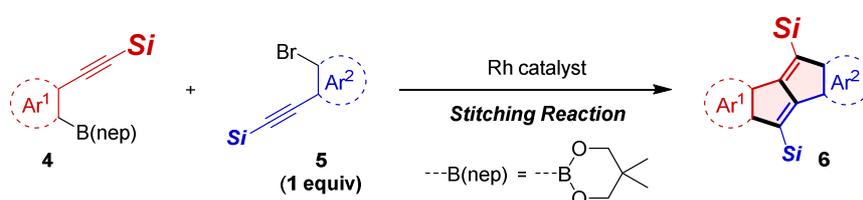
^a Catalyst was prepared by mixing $[\text{PdCl}(\eta^3\text{-allyl})]_2$, 2,6-lutidine, and AgSbF_6 in toluene/DCE followed by filtration to remove AgCl . Polymerization of **1** (10.0 mmol) was performed in toluene/DCE (40 mL). ^b A mixture of polymer **2** (1.0 mmol unit) and hydrogen chloride (4.0 M solution in dioxane; 10 mL) was stirred for 36 h at 110 °C, except for entry 3. ^c Determined by SEC analysis using THF as an eluent and polystyrene as an internal standard. ^d Soluble fractions in THF were analyzed. ^e Dehydration was performed with conc. sulfuric acid (instead of hydrogen chloride) for 2 h at 50 °C.

Selective Synthesis of Unsymmetric Dibenzo[*a,e*]pentalenes by Rh-Catalyzed Stitching Reaction

Despite significant advances in dibenzo[*a,e*]pentalene synthesis, synthesis of dibenzo[*a,e*]pentalene derivatives that are unsymmetrically fused by two different (hetero)arenes or the ones unsymmetrically substituted have been less

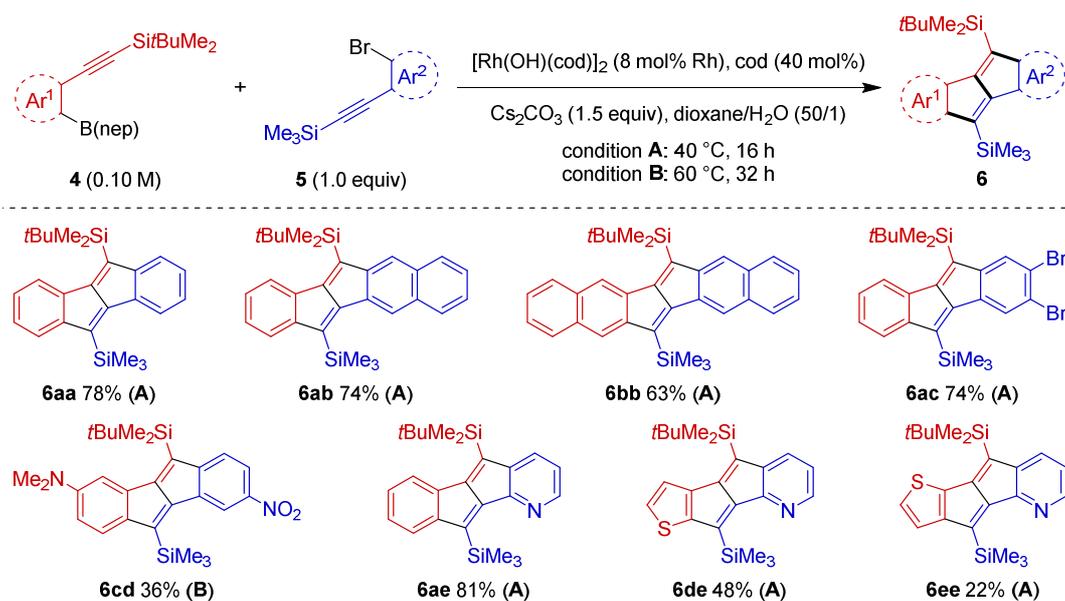
studied.[6] This could be mainly due to difficulty in selective cross annulations between two different substrates. In this context, the author focuses on the synthesis of unsymmetric pentalene derivatives through the use of rhodium-catalyzed stitching reaction, a novel strategy for the intermolecular synthesis of polycyclic π -conjugated ladder-type compounds via successive insertion of alkynes.[7] Herein the author describes the successful synthesis of various unsymmetric dibenzo[*a,e*]pentalenes by the stitching reaction between alkyne **4** bearing an arylboron moiety and alkyne **5** bearing bromoarene moiety in the presence of a rhodium catalyst (Scheme 2).

Scheme 2. Rhodium-catalyzed stitching reaction to synthesize unsymmetric dibenzo[*a,e*]pentalene derivatives



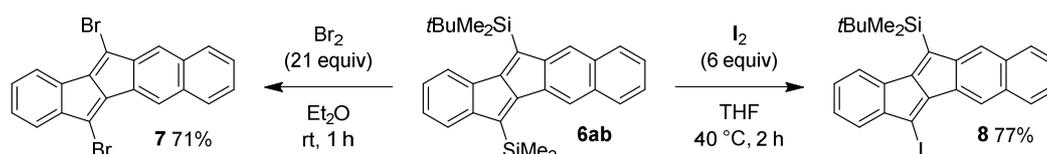
The reaction of 2-[(*tert*-butyldimethylsilyl)ethynyl]phenylboronates (**4a**) with an equimolar amount of [(2-bromophenyl)ethynyl]trimethylsilane (**5a**) was conducted in the presence of di- μ -hydroxido-bis[(1,5-cyclooctadiene)rhodium] (8 mol% Rh), 1,5-cyclooctadiene (40 mol%), and cesium carbonate (1.5 equiv) in 1,4-dioxane/water (50/1) at 40 °C to afford the desired dibenzo[*a,e*]pentalene **6aa** in 78% yield (Scheme 3). The

Scheme 3. Scope of rhodium-catalyzed stitching reaction for the synthesis of dibenzo[*a,e*]pentalene derivatives.



present method was also effective for the synthesis of π -extended pentalenes (**6ab** and **6bb**) and various unsymmetric pentalenes with different substituents on the fused benzene rings (**6ac** and **6cd**). In addition, the present method could also be extended to the synthesis of pentalenes fused by heteroarenes (**6ae**, **6de** and **6ee**). Treatment of the obtained benzonaphthopentalene **6ab** with bromine in diethyl ether at room temperature smoothly converted both of the silyl groups into bromides to give 5,12-dibromobenzo[*a*]naphtho[2,3-*e*]pentalene **7** in 71% yield, while the reaction of **6ab** with iodine in tetrahydrofuran at 40 °C selectively converted only the trimethylsilyl group to an iodide to give compound **8** in 77% yield (Scheme 4). This demonstrates that the present rhodium catalysis and subsequent derivatization would be an efficient method for the preparation of pentalene-based functional molecules.

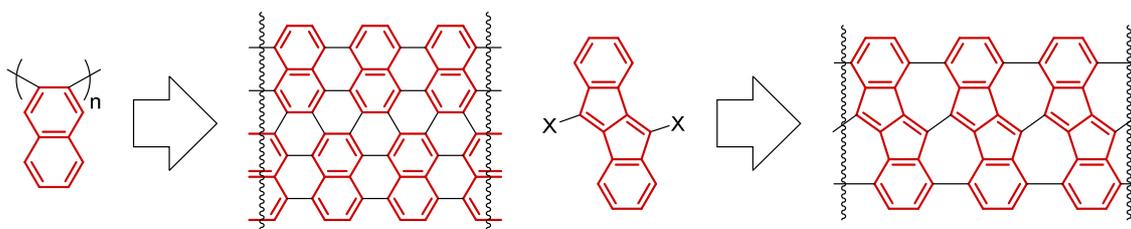
Scheme 4. Desilylative halogenation of benzonaphthopentalene **6ab**



Perspective

In this thesis, two methods for the construction of π -conjugated polycyclic hydrocarbons have been developed based on the successive carbometalation of carbon–carbon unsaturated bonds. The obtained π -conjugated polycyclic hydrocarbons would be precursors of further extended π -conjugated systems, such as graphene nanoribbons (Scheme 5).

Scheme 5. Applications of the present methods for construction of further extended π -conjugated systems.



[References]

[1] Jin, T.; Zhao, J.; Asao, N.; Yamamoto, Y. *Chem. Eur. J.* **2014**, *20*, 3554. [2] (a) Bura, T.; Blaskovits, J. T.; Leclerc, M. *J. Am. Chem. Soc.* **2016**, *138*, 10056. (b) Kawasumi, K.; Zhang, Q.; Segawa, Y.; Scott, L. T.; Itami, K. *Nat. Chem.* **2013**, *5*, 739. [3] (a) Vij, V.; Bhalla, V.; Kumar, M. *Chem. Rev.* **2016**, *116*, 9565. (b) Weding, N.; Hapke, M. *Chem. Soc. Rev.* **2011**, *40*, 4525. [4] Narita, A.; Wang, X.-Y.; Feng, X.; Mullen, K. *Chem. Soc. Rev.* **2015**, *44*, 6616. [5] (a) Ihara, E.; Kurokawa, A.; Koda, T.; Muraki, T.; Itoh, T.; Inoue, K. *Macromolecules* **2005**, *38*, 2167. (b) Mizukoshi, Y.; Mikami, K.; Uchiyama, M. *J. Am. Chem. Soc.* **2015**, *137*, 74. [6] Zhao, J.; Oniwa, K.; Asao, N.; Yamamoto, Y.; Jin, T. *J. Am. Chem. Soc.* **2013**, *135*, 10222. [7] Shintani, R.; Iino, R.; Nozaki, K. *J. Am. Chem. Soc.* **2016**, *138*, 3635.

[Publications related to this thesis]

1. Ito, S.; Takahashi, K.; Nozaki, K. *J. Am. Chem. Soc.* **2014**, *136*, 7574.
2. Takahashi, K.; Ito, S.; Shintani, R.; Nozaki, K. *Chem. Sci.* **2017**, *8*, 101.