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2,7-Diborylanthracene as a Useful Building Block for Extended π-Conjugated Aromatics

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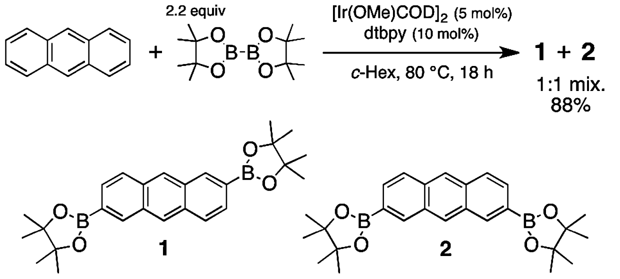
Ir-catalyzed direct diborylation of anthracene produced a 1:1 mixture of 2,6- and 2,7-diborylanthracenes, which could be separated by recrystallization. The Suzuki–Miyaura cross-coupling using 2,7-diborylanthracene gave extended π-conjugated 2,7-disubstituted anthracene derivatives as building blocks for macrocycles. A 1:1 mixture of 2,7-di(4-pyridyl)anthracene and [Pd(dppp)(OTf)$_2$] self-assembled into a [3 + 3] macrocycle.

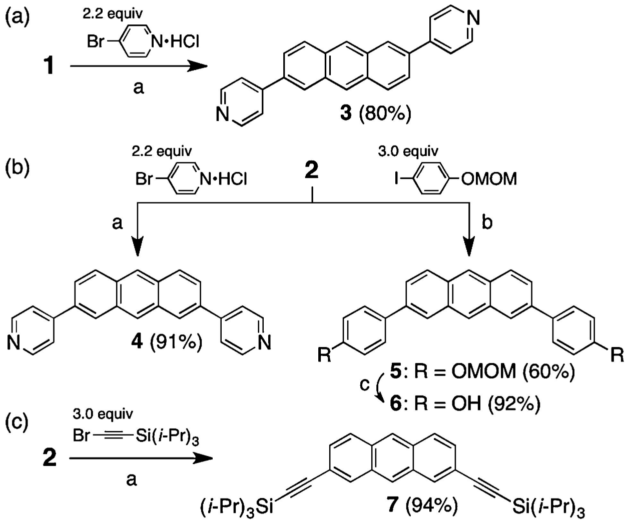
Ir-catalyzed direct borylation of aromatic compounds using bis(pinacolato)diboron is a very useful reaction for the synthesis of arylboronic acid pinacol esters,[1] which are reagents for the Suzuki–Miyaura cross-coupling reaction.[2] Marder et al. first observed the synthesis of 2,6- and 2,7-diborylnaphthalenes.[3] Recently, using this reaction, we have reported on the selective synthesis of 2,8- and 2,9-diboryltetracenes, which are very useful building blocks for the regiospecific synthesis of extended π-conjugated tetracene derivatives of organic semiconductors used in organic field-effect transistors.[4]

It is well known that the *meta*-phenylene unit and its derivatives are useful building blocks for the construction of extended π-conjugated macrocycles[5] and self-assembled macrocycles.[6] An extended version of the *meta*-phenylene unit is the 2,7-anthracene unit.[7,8] Anthracene derivatives are materials for use in optoelectronics.[9] In addition, 2,7-dibromoanthracene should be useful as a building block for the synthesis of extended π-conjugated anthracene macrocycles. However, the synthesis of 2,7-dibromoanthracene is difficult, because it requires a six-step synthetic procedure from anthrone and only gives a 9% yield in total.[10] Our work was concerned with the efficient synthesis of 2,7-difunctionalized anthracenes. Herein, we report on: (1) the Ir-catalyzed direct diborylation of anthracene to give a 1:1 mixture of 2,6- and 2,7-diborylanthracenes **1** and **2**, (2) the Suzuki–Miyaura cross-coupling using **2** to give extended π-conjugated 2,7-disubstituted anthracene derivatives, and (3) the self-assembly of 2,7-dipyridylanthracene and [Pd(dppp)(OTf)$_2$] into a [3 + 3] macrocycle as an application of this reaction.

The reaction of anthracene with 2.2 equiv of bis(pinacolato)diboron in the presence of [Ir(OMe)(COD)]$_2$ (5 mol %) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy, 10 mol %)[1,3,4] in cyclohexane at 80 °C for 18 h under Ar in the dark gave a 1:1 mixture of 2,6- and 2,7-bis[(pinacolato)boryl]anthracenes **1** and **2** in 88% yield (Scheme 1). Recrystallization of an initial 1:1 mixture of **1** and **2** followed by repeated recrystallizations of the **2**-rich mixture from hot toluene gave pure **2** (41% yield in total from anthracene). Similarly, repeated recrystallizations of the **1**-rich mixture from hot benzene yielded pure **1** (39% yield in total from anthracene).[11] The NMR spectra of both products revealed the positions of the diborylation of anthracene. In the ^{1}H NMR spectra, **1** and **2** showed two and three singlet aromatic signals, respectively, and in the ^{13}C NMR spectra, **1** and **2** exhibited six and seven aromatic signals, respectively (the carbon atom attached to the boron atom was not observed).[11]

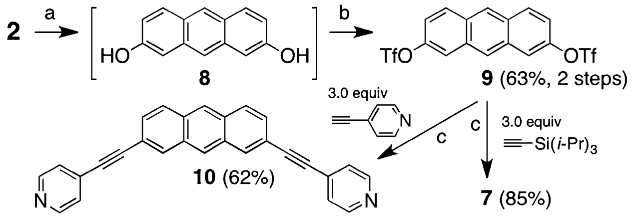


Scheme 1. Synthesis of diborylanthracenes **1** and **2**.



Scheme 2. Synthesis of **3**–**7**. (a) Method A: [Pd(PPh$_3$)$_4$] (4 mol %), Na$_2$CO$_3$ (10 equiv), toluene–EtOH–H$_2$O (4:2:1 for **3** and **4** or 10:5:1 for **7**), 80 °C, 42 h for **3** and **4** and 13 h for **7**. (b) Method B: [Pd(OAc)$_2$] (4 mol %), SPhos (4 mol %), K$_3$PO$_4$ (4 equiv), THF–H$_2$O (9:1), 60 °C, 42 h. (c) 2 M HCl–*i*-PrOH–THF (1:2:2), 40 °C, 22 h.

The 2,6- and 2,7-diborylanthracenes **1** and **2** are very useful building blocks for the regiospecific synthesis of extended π-conjugated anthracenes. The Suzuki–Miyaura cross-coupling reaction of **1** and **2** with 2.2 equiv of 4-bromopyridine hydrochloride catalyzed by [Pd(PPh$_3$)$_4$] (4 mol %) in the presence of Na$_2$CO$_3$ (10 equiv) in toluene–EtOH–H$_2$O at 80 °C (Method A) for 42 h gave 2,6- and 2,7-di(4-pyridyl)anthracenes **3** and **4** in 80% and 91% yields, respectively (Schemes 2a and 2b). The reaction of **2** with 4-bromopyridine catalyzed by Pd(OAc)$_2$ (4 mol %), SPhos (4 mol %),[12] and K$_3$PO$_4$ (4 equiv) in



Scheme 3. Synthesis of **7**–**10**. (a) Oxone (4 equiv), THF–acetone–H_2O (10:2:1), rt, 3 h. (b) Tf_2O (3 equiv), Et_3N (4 equiv), CH_2Cl_2, 0 °C to rt, 18 h. (c) $[PdCl_2(PPh_3)_2]$ (8 mol %), CuI (8 mol %), PPh_3 (16 mol %), toluene–Et_3N (1:1), rt, 2 h to 60 °C, 2 h to 80 °C, 12 h.

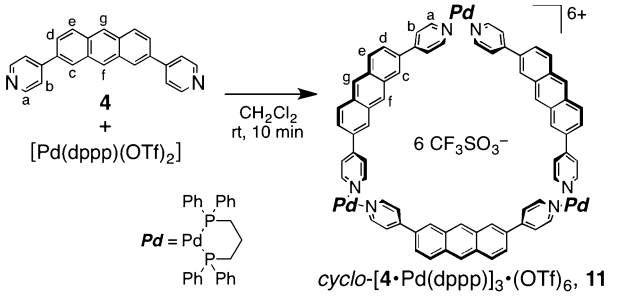
THF–H_2O at 60 °C (Method B) for 42 h produced **4** in 41% yield. On the other hand, the coupling reaction of **2** with 3 equiv of 1-iodo-4-(methoxymethoxy)benzene based on Methods A and B gave **5** in 38% and 60% yields, respectively (Scheme 2b). Compound **5** was hydrolyzed by HCl (aq) to produce 2,7-bis(4-hydroxyphenyl)anthracene (**6**) in 92% yield. The Suzuki–Miyaura cross-coupling reaction can be applied to 1-bromoalkynes,[13] which is an alternative method to the Sonogashira cross-coupling reaction. Thus, the coupling reaction of **2** with 3 equiv of bromo(triisopropylsilyl)acetylene[13b] using Method A gave 2,7-bis[(triisopropylsilyl)ethynyl]anthracene (**7**) in 94% yield (Scheme 2c).

The transformation of 2,7-diborylanthracene **2** into 2,7-bistriflate **9** would further enhance the utility of **2** as a synthetic building block, because **9** can be used in the Sonogashira cross-coupling (Scheme 3). Thus, the reaction of **2** with Oxone® produced crude 2,7-dihydroxyanthracene (**8**),[14a] which was treated with Tf_2O to give **9** (63% yield in two steps).[14b] The Sonogashira cross-coupling reaction of **9** with 3 equiv of 4-ethynylpyridine and triisopropylsilylacetylene gave 2,7-bis(4-pyridylethynyl)anthracene (**10**) and **7** in 62% and 85% yields, respectively.

2,7-Di(4-pyridyl)anthracene (**4**) serves as a building block for self-assembled macrocycles.[6,15] A 1:1 mixture of **4** and square-planar $[Pd(dppp)(OTf)_2]$ self-assembled into a [3 + 3] macrocycle, *cyclo*-$[\mathbf{4}\cdot Pd(dppp)]_3\cdot(OTf)_6$ (**11**), via Pd–pyridyl coordination bonds (Scheme 4). The ^1H NMR spectrum of a 1:1 mixture of **4** and $[Pd(dppp)(OTf)_2]$ in CD_2Cl_2 at room temperature after 10 min showed a highly symmetric new species, along with the disappearance of **4** and $[Pd(dppp)(OTf)_2]$, suggesting the formation of **11** (Figure 1). The pyridyl α-proton was shifted downfield by 0.33 ppm relative to that of free **4**, indicative of Pd–pyridyl coordination bonds being formed. The UV–vis spectrum also supported the formation of a Pd–pyridyl bond, where the longest wavelength λ_{max} of this mixture in CH_2Cl_2 was red-shifted by 6 nm relative to that of free **4**.[11] A 2:1 mixture of **4** and $[Pd(dppp)(OTf)_2]$ gave a mixture of **11**, free **4**, and unknown species (Figure 1d), indicating that **11** is not stable. Finally, the molecular structure of **11** was confirmed from single-crystal X-ray diffraction analysis, although the final *R* indices were poor because the triflate ions and inclusion solvents were highly disordered.[11,16]

Single crystals of *cyclo*-$[\mathbf{4}\cdot Pd(dppp)]_3\cdot(OTf)_6$ (**11**) suitable for X-ray diffraction analysis were obtained by slow evaporation of a $CHCl_3$ solution of **11**. Figure 2 shows the molecular structure of **11**, wherein there are two types of slightly different conformations for both the **4** unit (ant-A and ant-B) and the [Pd(dppp)] unit (Pd1 and Pd2) to form a triangular structure. The lengths of sides of the triangular cavity are Pd1···Pd2 = 18.8 Å and Pd1···Pd1 = 18.4 Å. The distances between the anthracene rings are C10···C10 (between the ant-A rings) = 15.9 Å and C10···C10′ (between the ant-A and ant-B rings) = 15.6 Å for the upper rim and C9···C9 = 11.8 Å and C9···C9′ = 12.0 Å for the lower rim.

In summary, we have demonstrated the Ir-catalyzed direct diborylation of anthracene to form 2,6- and 2,7-diborylanthracenes **1** and **2**. The Suzuki–Miyaura cross-coupling using **2** gave extended π-conjugated 2,7-disubstituted anthracene derivatives as building blocks for macrocycles. A study on the synthesis of



Scheme 4. Self-assembly of **4** and $[Pd(dppp)(OTf)_2]$ into **11**.

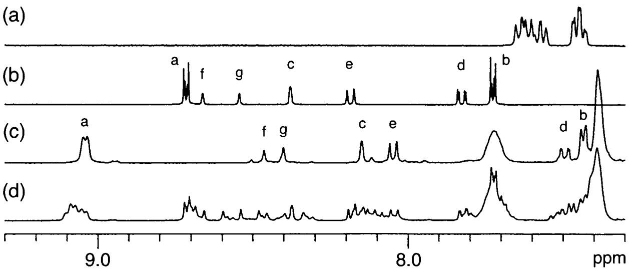


Figure 1. ^1H NMR spectra of (a) $[Pd(dppp)(OTf)_2]$, (b) **4**, (c) a 1:1 mixture of **4** and $[Pd(dppp)(OTf)_2]$ (formation of **11**), and (d) a 2:1 mixture of **4** and $[Pd(dppp)(OTf)_2]$ in CD_2Cl_2 at rt.

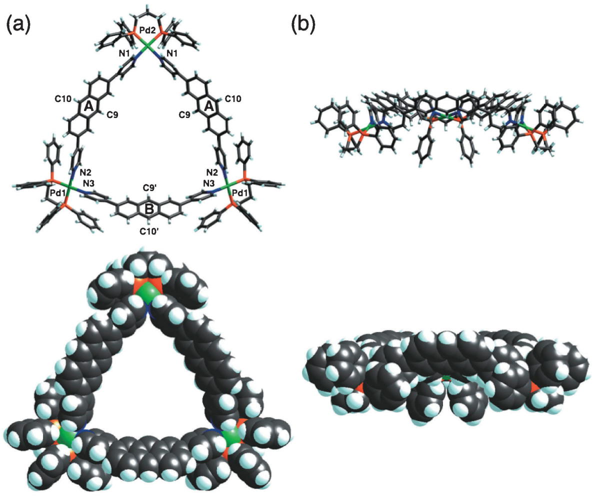


Figure 2. X-ray crystal structure of **11**: (a) front and (b) side views. Triflate ions are omitted for clarity.

an extended π-conjugated anthracene macrocycle based on **2**, **7**, and **9** is currently in progress.

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16 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-824622. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).