# Synthesis of a Contrapositionally Substituted Cyclohexa-metaphenylene: A Ready-to-Use Precursor for Cyclohexa-meta-phenylene-Based Materials

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**Abstract** A contrapositionally substituted derivative of cyclohexameta-phenylene ([6]CMP) was synthesized by an intramolecular Yamamoto coupling reaction of an appropriate terphenyl unit containing a trimethylsilyl substituent. lododesilylation of the trimethylsilyl groups of the product with iodine monochloride was used to incorporate iodo groups, an important functionality for metal-catalyzed coupling reactions. The iodo groups were also converted into a (pinacolato)boryl groups, another important functionality for coupling reactions. The diborylated [6]CMP is expected to be a versatile potential comonomer and a precursor for the synthesis of CMP-based materials. The synthetic route to the disubstituted [6]CMP included lithiation, Pd-catalyzed borylation, Suzuki coupling, and Yamamoto coupling. The structure of the product was established by NMR spectroscopy and mass spectrometry.

Key words cyclohexaphenylene, Yamamoto coupling, borylation

[*n*]Cyclo-*meta*-phenylenes ([*n*]CMPs) are polycyclic aromatic compounds containing *meta*-linked benzene rings. The first CMP was synthesized by Staab and Binnig in 1960,<sup>1</sup> and some later work on CMP-based cation hosts was carried by Cram and co-workers.<sup>2</sup> During the next few decades, except for a few syntheses, very little was discovered about the chemistry of CMPs, even though their unique cyclic structure has potential applications in electronics, optoelectronic devices, and supramolecular chemistry.<sup>3</sup> Despite the simple structure of CMPs, few groups have succeeded in one-pot or sequential syntheses of substituted derivatives, and there have been no reports of CMPs bearing substituents in the contra positions. Synthesis of unsubstituted and polysubstituted CMP molecules bearing trimethylsilyl, alkyl, alkoxy, or trifluoromethyl groups (Figure 1) have been reported by Chan and Swager,<sup>4a</sup> by the Müllen group,<sup>4b</sup> and, recently, by Isobe and co-workers.<sup>4c</sup> The Müllen group also demonstrated a synthesis of a phenylenebridged 6[CMP] as a hexa-peri-hexabenzocoronene precursor.<sup>5</sup> Given the recent interest in the design of various novel functional materials, molecules with functionalities at selective positions are needed for the design of useful materials. The introduction of functional groups primed for coupling reactions to CMPs would permit the preparation of various CMP-based structures with diverse properties and functions.

Here, we report an efficient approach to a 1<sup>5</sup>,4<sup>5</sup>-diborylated [6]CMP (Figure 2), potentially useful as precursor for variety of architectures containing a CMP core unit. This disubstituted [6]CMP motif might also be useful as a comonomer to form polymeric ribbons, and the attached pinacolatoboryl group might be replaced by variety of substituents to provide new [6]CMP-based motifs.







The 1<sup>5</sup>,4<sup>5</sup>-diborylated [6]CMP was synthesized in stepwise fashion, starting from the commercially available 1.3.5-tribromobenzene. The major precursor to the macrocycle, (3,3"-dibromo-1,1':3',1"-terphenyl-5'-yl)(trimethyl)silane (3), and was prepared as shown in Scheme 1. First, 1.3.5-tribromobenzene was lithiated with tert-butyllithium and converted into (3,5-dibromophenyl)(trimethyl)silane (1) by treatment with chloro(trimethyl)silane.<sup>6</sup> Treatment of 1 with bis(pinacolato)diborane in the presence of 6 mol% of  $Pd(dppf)_2Cl_2$  [dppf = dichlorobis(1,1'-diphenylphosphino)ferrocene] catalyst and KOAc afforded the diboryl derivative 2.7 Suzuki cross coupling of 2 with a fivefold amount of 1,3-dibromobenzene at 90 °C in 3:2:1 toluene-ethanolwater gave the *m*-terphenyl derivative  $3.^8$  This large excess of 1,3-dibromobenzene was used to prevent polymerization of the *m*-terphenyl unit.

The next and most critical step was the conversion of the *m*-terphenyl unit **3** into the corresponding disubstituted cyclohexa-*meta*-phenylene **4** through dimerization by using the Yamamoto coupling reaction (Scheme 2). As expected, the reaction was greatly influenced by the concentration of the reaction mixture, and dilution was necessary



**Scheme 1** Synthesis of (3,3''-dibromo-1,1':3',1''-terphenyl-5'-yl)-(trimethyl)silane (**3**). *Reagents and conditions*: (i) BuLi, TMSCl, Et<sub>2</sub>O, -78 °C, 94%; (ii) (pinB)<sub>2</sub>, Pd(dppf)Cl<sub>2</sub> (6 mol%), KOAc, DMF, 90 °C, 90%; (iii) Pd(PPh<sub>3</sub>)<sub>4</sub> (3 mol%), K<sub>2</sub>CO<sub>3</sub>, 3:2:1 toluene–EtOH–H<sub>2</sub>O, 90 °C, 81%.

to avoid polymerization of **3**. Therefore, **3** was subjected to macrocyclization under dilute conditions with bis(cyclooc-ta-1,5-diene)nickel(0), 1,5-cyclooctadiene (cod), and 2,2'-bipyridine at a concentration of  $3 \times 10^{-2}$  mol·L<sup>-1</sup> in DMF under an inert atmosphere at 90 °C for three days.<sup>9</sup> The product was identified by MALDI-TOF MS analysis of the crude mixture, which indicated the presence of **4**, as well as incompletely closed species and oligomers. Column chromatography was used to remove these byproducts and to isolate **4** in a yield of 61%.

The structure of **4** was confirmed by high-resolution MALDI-TOF MS (Figure 3; left) and by NMR spectroscopy (Figure 4a). The recorded MS spectrum (blue line) agrees with the calculated one (red line) in both the isotopic dis-

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Scheme 2 Synthesis of diborylated [6]CMP (6). Reagents and conditions: (iv) cod, 2,2'-bipyridine, [Ni(cod)<sub>2</sub>] (2 equiv), 61%; (v) ICl, 86%; (vi) (pinB)<sub>2</sub>, Pd(dppf)Cl<sub>2</sub> (6 mol%), KOAc, DMF, 90 °C; 58%.

tribution and the mass-to-charge-ratio. The <sup>1</sup>H NMR spectrum of **4** exhibits a set of signals corresponding to only five different types of aromatic protons, indicating a highly symmetric structure. The trimethylsilyl groups of **4** were converted into iodo substituents by iododesilylation with iodine monochloride in darkness for eight hours. The resulting diiodo[6]CMP **5** was a sparingly soluble white solid that could not be characterized.



**Figure 3** High-resolution MALDI-TOF MS spectra of structures **4** and **6** measured with tetracyanoquinodimethane (TCNQ) as a matrix. The solid blue lines represent the measured mass spectra and the solid red lines are calculated spectra based on the molecular structures.

The next step was the conversion of the diiodo derivative **5** into corresponding diborylated [6]CMP **6** (Scheme 2). High dilution was necessary to prevent polymerization reactions. The diiodo derivative 5 was added to  $(pinB)_2$ , KOAc, and Pd(dppf)Cl<sub>2</sub> in DMF, and the mixture was degassed by bubbling argon. It was then refluxed for 48 hours at 110 °C.<sup>10</sup> The product was precipitated by addition of cold methanol. After precipitation, MALDI-TOF MS analysis of the crude product indicated the presence of **6**. Column chromatography was used to remove byproducts and to isolate **6** in a yield of 58%. The high-resolution MALDI-TOF mass spectrum (Figure 3, right) and <sup>1</sup>H NMR spectrum (Figure 4b) clearly confirmed the structure of the product.

In summary, we have synthesized and characterized the diborylated cyclohexa-*meta*-phenylene **6**, as a unique precursor that should provide smooth access to many new polyaromatic structures based on [6]CMP with various substituents. The diborylated [6]CMP **6** is a versatile building block that might lead to materials with various applications and properties, and we expect it to make a fruitful contribution to the synthesis of CMP-based scaffolds and in the syntheses of more planar molecules.

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## Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690676.

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- (8) (3,3"-Dibromo-[1,1':3',1"-terphenyl]-5'-yl)(trimethyl)silane (3)

Argon was bubbled through a solution of the diborylated derivative **2** (1 g, 2.48 mmol, 1 equiv), 1,3-dibromobenzene (2.92 g, 12.43 mmol, 5 equiv), and K<sub>2</sub>CO<sub>3</sub> (1.46 g, 15 mmol, 5 equiv) in 3:2:1 toluene–EtOH–H<sub>2</sub>O. Pd(PPh<sub>3</sub>)<sub>4</sub> (71 mg, 2.5 equiv) was added, and the mixture was stirred at 90 °C for 24 h. The organic phase was separated, washed with H<sub>2</sub>O, dried (MgSO<sub>4</sub>), and concentrated. The residue was purified by column chromatography (silica gel, hexane;  $R_f$  = 0.50) to give a colorless powder; yield: 0.92 g (81%); mp 230 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.76 (t, *J* = 1.7 Hz, 2 H), 7.66 (s, 3 H), 7.56 (dd, *J* = 1.7, 1.1 Hz, 1 H), 7.54 (dd, *J* = 1.7, 1.1 Hz, 1 H), 7.52 (dd, *J* = 1.9, 1.0 Hz, 1 H), 7.50 (dd, *J* = 1.9, 1.0 Hz, 1 H), 7.33 (t, *J* = 7.8 Hz, 2 H), 0.36 (s, 9 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 143.9, 143.0, 138.1, 133.8, 132.9, 132.0, 128.0, 127.4, 125.9, 121.5, 1.2.

#### (9) 1<sup>5</sup>,4<sup>5</sup>-Bis(trimethylsilyl)cyclohexa-meta-phenylene (4)

2,2'-bipyridine (312 mg, 2.0 mmol), cod (216 mg, 2.0 mmol), and [Ni(cod)<sub>2</sub>] (550 mg, 2.0 mmol) were placed in a well-dried Schlenk flask and dissolved in anhyd DMF (80 mL). The mixture was then stirred for 30 min at 80 °C in darkness. A solution of the dibromo compound **3** (500 mg, 1.08 mmol) in degassed anhyd toluene (150 mL) was added quickly, and the resulting mixture was stirred at 80 °C for 3 d. The reaction was stopped by adding 10% aq HCl, and the organic phase was separated, washed with H<sub>2</sub>O, dried (MgSO<sub>4</sub>) and concentrated in vacuo. The residue was purified by column chromatography [silica gel, PE-CH<sub>2</sub>Cl<sub>2</sub> (20:1); *R<sub>f</sub>* = 0.29] to give a colorless crystalline solid; yield: 397 mg (61%, 0.66 mmol).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.34 (s, 4 H), 8.31 (s, 2 H), 7.86 (d, *J* = 1.7 Hz, 4 H), 7.75 (t, *J* = 8.8 Hz, 8 H), 7.58 (t, *J* = 7.6 Hz, 4 H), 0.39 (s, 18 H).

#### (10) 1<sup>5</sup>,4<sup>5</sup>-Bis(pinacolatoboryl)cyclohexa-meta-phenylene (6)

A 50 mL flask containing the diiodo compound **5** (1.0 g, 2.1 mmol), bis(pinacolato)diborane (1.42 g, 5.6 mmol), KOAc (2.06 g, 21 mmol), and Pd(dppf)Cl<sub>2</sub> (73.2 mg, 0.1 mmol) was evacuated and refilled with argon three times. DMF (30 mL) was then transferred into the flask from a syringe under argon at r.t., and the mixture was stirred at 110 °C for 48 h. The crude product was purified by column chromatography [silica gel, PE-CH<sub>2</sub>Cl<sub>2</sub> (4:1)] to give a white solid; yield: 0.8 g (58%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.19 (d, *J* = 1.7 Hz, 6 H), 7.84 (d, *J* = 8.7 Hz, 4 H), 7.73 (d, *J* = 7.1 Hz, 8 H), 7.56 (t, *J* = 7.7 Hz, 4 H), 1.41 (s, 24 H).