ORGANIC
LETTERS

2012
Vol. 14, No. 13
3284–3287

Selective Synthesis and Crystal Structure of [10]Cycloparaphenylene

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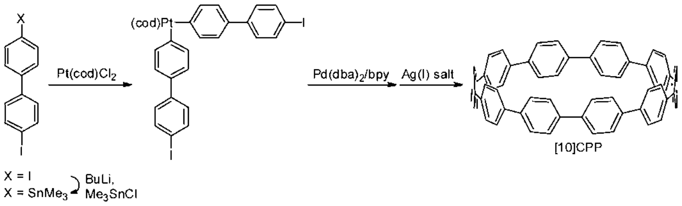
Received May 7, 2012

ABSTRACT



[10]Cycloparaphenylene ([10]CPP) was selectively synthesized in four steps in 13% overall yield from commercially available 4,4′-diiodobiphenyl by using mono-I–Sn exchange, Sn–Pt transmetalation, I–Pd exchange, and subsequent oxidative coupling reactions. The single-crystal X-ray structure of [10]CPP is described.

Cycloparaphenylenes (CPPs), which consist of *para*-connected phenylene rings (Figure 1), have recently attracted a great deal of attention from synthetic and theoretical viewpoints because of their potential applications in electronics, photonics, and host–guest chemistry.[1−6] Due to the recent progress in the synthesis of CPPs, as described below, their unique properties, such as size-dependent photophysical, electronic, and redox properties[7−9] and size-selective host–guest chemistry,[10] are being unveiled.

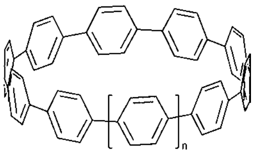


Figure 1. Structure of [*n*]CPPs.

Despite their simple structure and the intensive synthetic efforts devoted to them over a half century,[11,12] CPPs only became available recently because of the work of three research groups, including our own. Jasti and Bertozzi utilize cyclohexa-2,5-diene-1,4-diyl as the key units for the construction of the cyclic structure, and the diyl is aromatized in the final step to afford [9]-, [12]-, and [18]CPPs.[7] More recently, Jasti applied this strategy to selectively synthesize [7]-[13] and [6]CPPs.[14] Itami and co-workers utilize cyclohexane-1,4-diyl as the key component and

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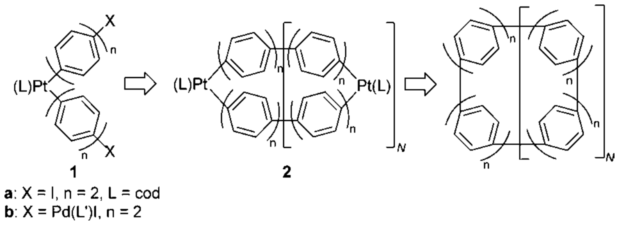
10.1021/ol301242t

have size-selectively synthesized [9]-, [12]-, [14]-, [15]-, and [16]CPPs[15−19] and their derivatives.[20−22] In contrast, we utilize cyclic, *cis*-bisaryl-platinum complexes as precursors for CPPs, and reductive elimination from the complexes selectively affords [8]- and [12]CPPs.[23] In addition, we have reported that the same strategy is effective for the random synthesis of [8]−[13]CPPs.[8] Isobe has utilized our strategy to prepare the first optically active, simplest structural unit of helical single-walled carbon nanotubes.[24] Despite these developments, the availability of CPPs in terms of size and quantity has been quite limited. Therefore, a size-selective and high-yielding synthetic route for CPPs is needed.

We envisioned that L-shaped *cis*-substituted bis(*para*-haloaryl) platinum complex **1** could be used as a precursor for a cyclic platinum intermediate, such as **2**, by selective C−C bond formation through selective C−X bond manipulation (Scheme 1). Once **2** forms, reductive elimination of the platinum from **2** should give a CPP. We report here the selective synthesis of [10]CPP from **1a** (X = I, *n* = 2, L = cyclooctadiene [cod]) by using the palladium-mediated coupling reaction developed by Osakada as the key step.[25,26] In addition, we report the X-ray crystal structure of [10]CPP for the first time. During our investigation, Itami and co-workers reported the selective synthesis of [9]−[11]- and [13]CPPs by using their *cis*-1,4-diphenylcyclohexane-1,4-diyl based strategy.[27]

Commercially available 4,4′-diiodobiphenyl (**3c**) was treated with BuLi (1.0 equiv) in THF at −78 °C, followed by Me_3SnCl (1.0 equiv), to afford monostannylated biphenyl **3d** in 84% yield (Scheme 2). Subsequent treatment of **3d** with $Pt(cod)Cl_2$ (0.50 equiv) in THF at 60 °C for 8 h afforded the desired **1a** in 96% yield. Then, **1a** was treated with $Pd(dba)_2$ (2.0 equiv, dba = dibenzylideneacetone) and 2,2′-bipyridyl (bpy) in THF at 50 °C for 8 h. After the solvent and free dba were removed by filtration, the resulting solid material was treated with $AgBF_4$ (2.2 equiv) at room temperature in CH_2Cl_2/acetone for 12 h. Although we anticipated the formation of [8]-, [12]-, or [16]CPP via the selective dimerization, trimerization, or tetramerization of **1a**, respectively, we found that [10]CPP formed exclusively from ^1H NMR and mass spectroscopies. [10]CPP was isolated, by using silica gel chromatography, in 16% overall yield from **1a** (13% from **3c**) and was fully characterized by using ^1H NMR (7.56 ppm in $CDCl_3$), ^{13}C NMR (127.5 and 138.3 ppm), and MALDI TOF mass spectroscopies (m/z = 760.3136), the results of which are identical to those in our previous report.[8] Although a considerable amount of insoluble black solid, presumably linear oligomers of biphenyls, was observed, no other CPPs, besides [10]CPP, formed. Use of $AgSbF_6$ or AgOTf instead of $AgBF_4$ gave [10]CPP selectively in 10% or 14% yield from **1a**, respectively. In contrast, treatment of **1a** with $Ni(cod)_2$ instead of $Pd(dba)_2$ gave a mixture of

Scheme 1. Working Hypothesis on a New Synthetic Route for CPPs



Scheme 2. Selective Synthesis of [10]CPP

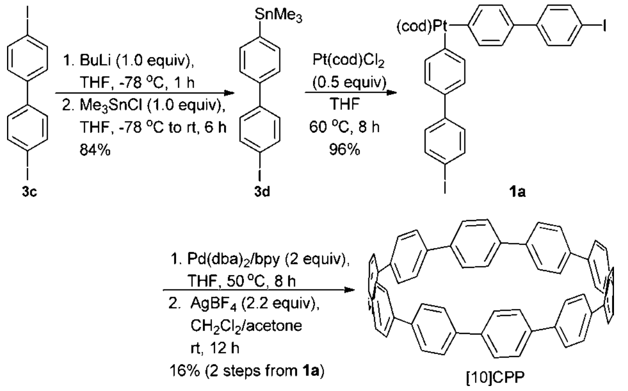


Figure 2. ORTEP drawing of [10]CPP·hexane. Thermal ellipsoids are shown at 50% probability, and all hydrogen atoms are omitted for clarity.

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[8]-, [10]-, [12]-, and [16]CPPs in 2, 0.5, 2, and 0.9% yields, respectively.

The structure of [10]CPP was determined by using single-crystal X-ray analysis. Suitable crystals were obtained by slow vapor diffusion of *n*-hexane into a solution of [10]CPP in CH_2Cl_2 at room temperature. An ORTEP drawing is shown in Figure 2. In the solid state, [10]CPP is slightly distorted to an ellipsoidal structure with major and minor axes of 13.9 and 13.5 Å, respectively. The cavity of [10]CPP is occupied by a hexane molecule, which was highly disordered. Although the D_{5h} structure with a dihedral angle between two paraphenylene units of 32°−33° was calculated to be the most stable conformer,[8] the structure is closer to a D_{2h} conformer with alternating triphenylene and biphenylene units. The dihedral angles between two paraphenylene units were approximately 20° and 45°, respectively. The lower symmetry in the solid state has been observed for [12]CPP[18] and could be due to the crystal packing and/or inclusion of solvent molecules. The average $C_{ipso}-C_{ipso}$, $C_{ipso}-C_{ortho}$, and $C_{ortho}-C_{ortho}$ bond lengths are 1.484(1), 1.399(2), and 1.385(9) Å, respectively, and the bond lengths are consistent with theoretical calculations (Table 1).[8] A difference in their bond length is very small within experimental errors, but the difference is presumebly due to the strain of the benzene ring.

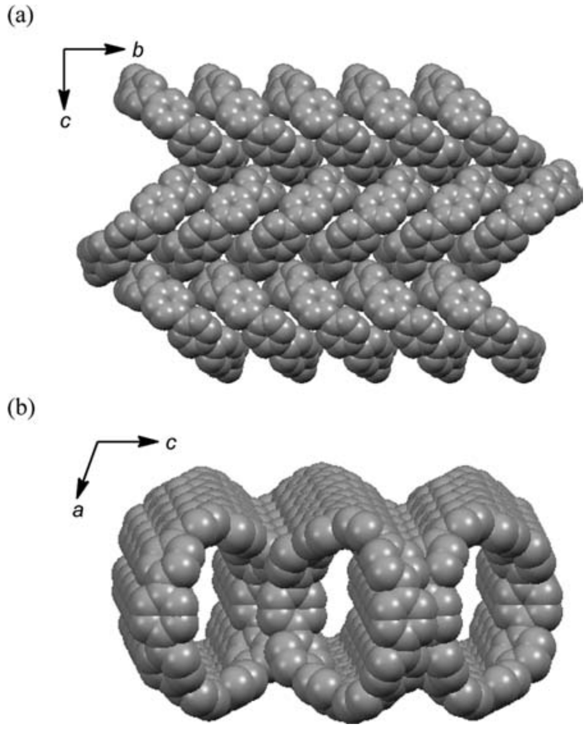


Figure 3. Packing structure of [10]CPP. Solvent molecules and hydrogen atoms are omitted for clarity.

[10]CPP molecules pack in a herringbone manner along the *a* axis (Figure 3a), and there are no significant $\pi-\pi$ interactions among [10]CPP molecules. A tilted tubular channel structure was observed along the *b* axis (Figure 3b). The crystal packing is similar to [9]-[19] and [12]CPPs but different from [6]CPP.[14] The size of the CPP may be important for determining the packing arrangement.

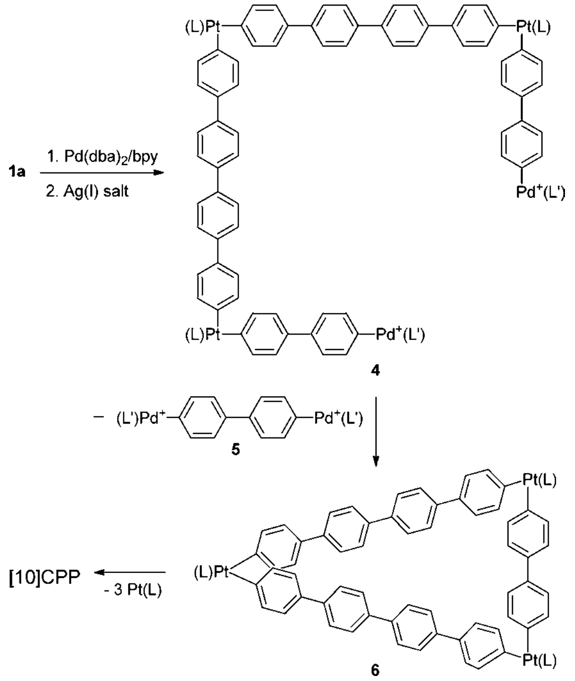
Table 1. Average C−C bond lengths (Å) of [10]CPP in the Solid State and Gas Phase from Calculations

	X-ray	calculation[a]
$C_{ipso}-C_{ipso}$	1.484	1.485
$C_{ipso}-C_{ortho}$	1.399	1.407
$C_{ortho}-C_{ortho}$	1.385	1.391

[a] B3LYP/6-31G* level of theory.[8]

A plausible mechanism for the formation of [10]CPP from **1a** is illustrated in Scheme 3.[26] Oxidative addition of **1a** to a $Pd(dba)_2$/bpy species affords the corresponding aryl-Pd(II) complex **1b** (Scheme 1; L, L′ may be cod or bpy). The cationic Pd complex generated from **1b** upon treatment with a silver salt induces an aryl-coupling reaction to give cationic Pd/Pt hybrid complex **4**,[25] from which elimination of 4,4′-bispalladiumbiphenyl **5** occurs to give triangular trinuclear platinum complex **6**. Aryl group migration between the Pt and Pd ions has already been reported by Osakada.[26,28] While cyclopropanes are strained molecules due mainly to the bond angle distortion from 110° to around 60°,[29] triangular complex **6** may not induce that much strain, because the bond angle in *cis*-coordinated Pt compounds is around 90°. Indeed, structurally related triangular tris(4,4′-bipyridyl)tripalladium complexes sometimes selectively form over the corresponding square-shaped tetrapalladium complexes.[30,31] Therefore,

Scheme 3. Plausible Mechanism for the Formation of [10]CPP from **1a**



the formation of **6** presumably occurs without inducing high strain. Reductive elimination of platinum from **6** selectively gives [10]CPP. Although the addition of Br_2 was needed to increase the efficiency of the reductive elimination in our previous work,[8,23] no such additive was needed under the current conditions. While further studies are needed to clarify the detailed mechanism, this synthetic route is attractive because it selectively gives [10]CPP, which acts as a selective host for C_{60}.

In summary, a new, short, and selective synthetic route for [10]CPP was developed. The overall yield of [10]CPP from the commercially available starting material **3c** was reasonably high (13%), considering the highly strained nature of [10]CPP. A trinuclear triangle-shaped platinum intermediate is proposed to account for the formation of [10]CPP. For the first time, single-crystal X-ray analysis of [10]CPP was performed.

Acknowledgment. This work was partly supported by the Core Research for Evolution Science and Technology (CREST), Japan Science and Technology Agency. This study was also carried out with the NMR spectrometer in the JURC at the Institute for Chemical Research, Kyoto University. We thank Prof. Takahiro Sasamori and Prof. Norihiro Tokitoh of Kyoto University for valuable discussions and suggestions for single-crystal X-ray analysis.

Supporting Information Available. Experimental procedures and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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