Synthesis and Reactions of Carbon Nanohoop

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Abstract: Despite their intriguing structure and potential applications, the synthesis of structurally uniform carbon nanohoops has been a significant challenge until recently. The first synthesis of cycloparaphenylene (CPPs), which are representative carbon nanohoops, nearly a decade ago considerably enhanced the availability of various carbon nanohoops, but the final products are usually only prepared on a mg scale. This review describes our endeavors to increase the availability of CPPs and their derivatives in large quantities. The three key reactions are 1) the one-pot, stereoselective two-fold addition of aryllithium to 1,4-benzoquinones to give U-shaped cyclization precursors, 2) subsequent nickel- or platinum-mediated selective cyclization, and 3) H$_2$SnCl$_4$-mediated reductive aromatization. This straightforward and high-yielding synthetic route provides gram quantities of various CPPs and their derivatives. Preliminary results on the applications of CPPs in electronic devices and the elucidation of CPP reactivity are also discussed.

1. Introduction

π-Conjugated molecules have attracted significant attention due to their rich functionality as exemplified by their light absorption/emission and charge transportation properties. Therefore, they are key molecules in functional materials, particularly as active components of organic electronic and photoelectronic materials and sensors. To improve the properties of these materials and to access new functions, a variety of new π-conjugated molecules from small molecules to polymers have been designed and synthesized. Due to the planarity of sp$^2$-carbon centers, which form π-orbitals, π-conjugated molecules are predominantly linear and planar structures. While π-conjugated molecules having hoop structures, i.e., picotubes and cycloparaphenylecynes (Figure 1), have been synthesized, their impact on materials science has been limited due to the lack of synthetic generality and their low stability.

The discovery and mass production of fullerenes and carbon nanotubes (CNTs) at the end of the last century significantly increased the availability of carbon nanohoops, but their applications in consumer products lag far behind initial expectations. This is because carbon nanohoops are produced as a mixture of various structures, and the purification of structurally uniform compounds requires tedious separations. Indeed, C$_{60}$ is the only fullerene or CNT available in large quantities in its pure form. In addition, the flexibility for synthesizing different carbon skeletons is severely limited. These limitations are derived from the synthetic methods; these carbon nanohoops are prepared by physical means, i.e., arc discharge and laser vaporization of graphite and combustion of hydrocarbons. A bottom-up organic synthesis would be an attractive alternative for providing various hoop-shaped π-conjugated molecules in pure form and hopefully in large quantities. A suitable large-scale synthesis is particularly important when molecules are to be used in materials science. Note that the total synthesis of C$_{60}$ using flash vacuum pyrolysis as the key step was reported by Scott, but the low overall yield and lack of generality for synthesizing different structures limited its applications.

Cycloparaphenylene is a typical π-conjugated polymer consisting solely of benzene rings connected at the para-position. Cycloparaphenylene (CPP) is the cyclic analogue of paraphenylene with its ends intramolecularly connected at the para-position. The same structure is found in armchair CNTs as their simplest cyclic structural unit and in fullerenes (Figure 1). Due to its simple structure, the first report on its synthetic study was published in 1934. However, it was not synthesized until 2008, when Jasti and Bertozzi reported the first synthesis of [9], [12], and [18]CPPs (the number in the brackets represents the number of paraphenylene units in the CPP). The key synthetic strategy is to utilize tricycle 1 with a cis-substituted 1,4-bisaryl-substituted cyclohexa-2,5-diene-1,4-diol unit, which was cyclooligomerized to form cyclic precursor 2, which was reductively aromatized to give the CPPs (Scheme 1a). Itami subsequently reported the selective synthesis of [12]CPP using 3 with a 1,4-bisaryl cyclohexa-1,4-dion unit. After the stepwise coupling reaction, cyclic precursor 4 was converted to

Figure 1. Structures of representative carbon nanohoops having π-conjugated cyclic structures. The CPP structure in an armchair CNT and a fullerene (C$_{60}$) is highlighted with bold bonds.
[12]CPP by an oxidative dehydration reaction (Scheme 1b). Our group reported the selective synthesis of [8]CPP starting from 4,4'-bisstannated biphenyl precursor 5, which formed cyclic tetramer [8]CPP through tetranuclear platinum complex 6 (Scheme 1c). These pioneering works ignited research into the chemistry of hooped π-konjugated molecules, and various CPPs of different sizes, CPP derivatives, and their congeners were synthesized (Figure 2). Furthermore, these works also disclosed the unique physical properties of CPPs, such as their size-dependent redox and photophysical properties (Figure 3) and size-complementary host-guest chemistry.

Despite these developments, however, the quantities of hooped molecules synthesized were usually limited to the mg scale. While Jasti reported the gram synthesis of [10] and [8]CPPs based on their synthetic strategy (shown in Scheme 1a), its generality was unclear and the overall yields were rather low (7.4 and 3.1%, respectively). In particular, the synthesis requires a low temperature for the reductive aromatization step, and such conditions are undesirable, especially for large-scale syntheses. Therefore, we refocused our program toward synthesizing CPPs of various sizes in large quantities, and the results of this research program are described in this review article. The large-scale synthesis also enabled us to elucidate the reactivities of CPPs, which further led to the synthesis of CPP derivatives by late-stage functionalizations, and these results are also described. There are several review articles and book chapters already published on the chemistry of CPPs and carbon nanohoops, and here we focused on our works on CPPs.

Figure 2. Representative hoop-shaped π-konjugated molecules synthesized by platinum-mediated method.
the large-scale synthesis of CPPs.

2. Practical Synthesis of CPPs

2.1 Large Scale Synthesis of [5]CPP

We became interested in synthesizing small CPPs after the successful synthesis of [8]–[13]CPPs based on the platinum-mediated synthetic route as shown in Scheme 1c. This is because we theoretically predicted the unique orbital properties of CPPs; the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of CPPs become higher and lower in energy, respectively, as the number of paraphenylene units decrease. The results are in sharp contrast to linear \( \pi \)-conjugated molecules, such as polyparaphenylene, in which the HOMO and LUMO energies become lower and higher, respectively, as the number of monomer units decrease due to the decrease in the effective conjugation. Furthermore, the prediction was experimentally proven by the electrochemical analyses of [5]–[13]CPPs and their photochemical properties, especially their size-dependent oxidation potentials, which decrease as the CPP size decreases (Figure 3a). The HOMO–LUMO gap of [5]CPP calculated at the B3LYP/6–31G* is 2.71 eV, which is very similar to that of \( C_{60} \) determined experimentally (2.88 eV), suggesting that [5]CPP should be an interesting lead molecule in materials applications. Additionally, [5]CPP is a structural constituent of \( C_{60} \) and its diameter is identical to that of \( C_{60} \). In this respect, [5]CPP is an important model system and an excellent synthetic target.

An apparent challenge in synthesizing [5]CPP is its high strain energy of 490 kJ mol\(^{-1}\), which is significantly larger than those of [8]CPP (307 kJ mol\(^{-1}\)) and [12]CPP (205 kJ mol\(^{-1}\)). However, we now know from our previous works that reductive elimination is well suited to synthesizing strained molecules. Therefore, we devised a new synthetic method using a metal-mediated reductive cyclization reaction as a key step. Pentacycle 7a (\( R = \text{Me} \)) was used by Jasti for the synthesis of [6]CPP. We thought that 7 would directly cyclize to 8 by a metal-mediated intramolecular reductive elimination (Scheme 2). Indeed, the desired transformation was easily achieved in three steps through the transmetallation of the bromine of 7a to a trimethylstanane group followed by treatment with Pt(cod)Cl\(_2\) (cod: 1,5-\( \pi \)-cyclooctadiene) and subsequent reductive elimination with excess PPh\(_3\). The same transformation was also performed in one step with a higher yield by a Yamamoto coupling using stoichiometric Ni(cod)\(_2\) and 2,2′-\( \pi \)-bipyridyl. However, the reductive aromatization of 8a was unsuccessful in our hands when employing various reducing agents. The deprotection of the methyl group in 8a was examined because the hydroxyl group could be used as a directing group for the reductive aromatization. However, several attempts to deprotect 8a with various Lewis acidic metals were unsuccessful because of the competing acid-catalyzed skeletal rearrangement of 8a.

Finally, triethylsilyl (TES)-protected substrate was employed. After converting 7b to 8b, quantitative deprotection of the TES group by TBAF and subsequent reductive aromatization of 8c (\( R = \text{H} \)) using excess SnCl\(_2\) afforded [5]CPP in a 20% overall yield (8 steps). While only 11 mg of pure [5]CPP was isolated, the absorption spectrum and redox potentials measurements clearly confirmed the narrow HOMO–LUMO gap of [5]CPP (1.91 eV by the absorption spectrum and 1.69 eV by the redox potentials).

Justi independently reported the synthesis of [5]CPP using a similar synthetic route starting from methyl-protected precursor 7a. Transmetallation of the bromine of 7a to a pinacolborane and subsequent palladium-catalyzed oxidative cyclization afforded 8a. Then, a two-step reductive aromatization of 8a by treatment with sodium naphthalenide yielded the mono-methoxy reduction product, and subsequent treatment with lithium disopropylamide afforded [5]CPP. The synthesis required 11 steps and had a 7% overall yield.

Our synthetic route has advantages, especially for the
reductive aromatization of 8, which could be carried out in one step at ambient temperature. Therefore, the scaled-up synthesis was attempted, but the reproducibility of the reductive aromatization using SnCl₂ on a large scale was very poor. After several attempts, we found that the addition of two equivalents of aqueous HCl was highly effective, and under these conditions, the aromatization proceeded in >90% yield with high reproducibility even on the gram scale. Further addition of HCl caused the acid-catalyzed rearrangement of 8; thus, two equivalents of HCl are optimal for this reaction. The additional advantages of these conditions are the necessity of only stoichiometric SnCl₂ (1.1 equiv. to each cyclohexadiene–diol unit) and the mild reaction conditions (room temperature).

The generation of a new species, H₂SnCl₄, was suggested by ¹¹⁹Sn NMR by mixing SnCl₂ and two equivalents of HCl (Figure 4). Further addition of HCl did not affect the stannane, and the results are consistent with the experimental results. The reductive aromatization of cyclohexa-2,5-diene-1,5-diol derivatives by SnCl₂ in the presence of excess aqueous HCl is widely used, and our results suggest that only two equivalents of HCl are essential to increase the reactivity of the SnCl₂ and that the conditions would be suitable for substrates having acid-sensitive functional groups.

2.2 Large Scale Synthesis of [7]–[12]CPPs Using Modified Justi’s Precursors

The reductive aromatization using H₂SnCl₄ was successfully applied to the synthesis of [7]–[12]CPPs (Scheme 3) using cyclic precursors with multiple cyclohexadiene–diol units prepared by modifying the method developed by Justi. The reaction conditions were not fully optimized, but the yields of the aromatization were high (56–87%) in all cases considering the presence of at least four cyclohexadiene–diol units. Indeed, the net yield of each unit are excellent (86–95%). These conditions have already been used by other research groups for synthesizing various carbon nanohoops, including CPP derivatives.

2.3 Large Scale Synthesis of [6] and [10]CPPs by Pt-mediated Cyclization

We were also interested in the large-scale synthesis of [6]CPP because it shows unique crystal packing in the solid state and a considerably narrow HOMO–LUMO gap, similar to that of [5]CPP. Although [6]CPP was already synthesized by Justi and us, the overall yields were low (0.7 and 8.7% yields, respectively) and the synthetic routes were unsuitable for large-scale synthesis. We thought the dimerization of

![Figure 4](image_url)

**Figure 4.** Determination of the Sn species by ¹¹⁹Sn NMR spectroscopy in THF–d₈ at room temperature.

![Scheme 3](image_url)

**Scheme 3.** Selective synthesis of [7]–[12]CPPs by a H₂SnCl₄-mediated reductive aromatization.

*Net yields of one cyclohexadienedioli unit*
tricycle 9 and subsequent reductive aromatization of cyclic product 10 would be an excellent practical synthetic route to [6]CPP.\(^\text{12i}\)

When 9d (X=Br) was subjected Yamamoto coupling conditions, a mixture of cyclic trimer and tetramer was obtained as the major products (31 and 16% yields, respectively), and desired dimer 10 was obtained in only 11% yield. In this case, the platinum-mediated method was highly efficient (Scheme 4). Thus, 9d was transformed to trimethyl derivative 9e, and subsequent treatment of 9e with Pt(cod)Cl$_2$ selectively gave cyclic dimer 10 in 78% yield. The advantage of the platinum-mediated assembly is the low reactivity of bisaryl platinum species towards the reductive elimination reaction, which provides sufficient time for the formation of the desired cyclic structure, as already observed in our previous synthesis of [8]CPP.\(^\text{7}\) The reductive elimination of platinum from 10, deprotection of the TES group, and reductive aromatization using H$_2$SnCl$_4$ afforded >1 g of [6]CPP in 23% overall yield (7 steps).

**Scheme 4.** Selective, gram–scale synthesis of [6]CPP.

![Scheme 4. Selective, gram–scale synthesis of [6]CPP.](image)

Tricycle 9 does not have to be an organostannane, and borane–derivative 9f and organosilicon compound 9g were also effective for synthesizing 10. However, the yield using organostannane 9e was highest (78%), followed by 9f (59%) and then 9g (51%).

The same synthetic protocol was extended to the selective, gram–scale synthesis of [10]CPP and its tetraalkoxy derivatives (Scheme 5).\(^\text{12k}\) For the synthesis of parent [10]CPP, requisite pentacycle 12h (R$^\text{II}$=H) was synthesized by the two–fold addition of 4-bromo–4’–liithiobiphenyl, prepared by mixing 4-bromo–4’–iodobiphenyl and butyl lithium, to 1,4-benzoquinone (11h) to give cis–12h in 42% yield. While the yield was moderate, selective formation of the cis isomer was observed with >95% selectivity. Once cis–12h was obtained, the same synthetic protocol was used for the synthesis of [6]CPP afforded [10]CPP. Though [10]CPP had already been synthesized on a gram scale, that synthesis required 10 steps and provided a 7% overall yield. In contrast, the current synthesis only requires 7 steps and gives a 17% overall yield.

The method was also extended to the synthesis of tetraalkoxy [10]CPPs starting from 2,5–dihydroxy–1,4–benzoquinone (11i, R$^\text{II}$ = OH); 11i was converted to several dialkoxyl–substituted benzoquinones 11j by BF$_3$·OEt$_2$–mediated alcohol exchange using n–butanol (R$^\text{III}$=Bu), n–octanol (R$^\text{III}$=Oct), and 2–ethylhexan–1–ol (R$^\text{III}$=EthHex). The resulting dialkoxyl–1,4–benzoquinones were also transformed to corresponding tetraalkoxy cis–12 by treatment with 4–lithio–4’–bromobiphenyl in high yields (68–88%) with >95% cis–selectivity in all cases.

**Scheme 5.** Large scale synthesis of [10]CPP and tetraalkoxy [10]CPPs.

![Scheme 5. Large scale synthesis of [10]CPP and tetraalkoxy [10]CPPs.](image)

Then, cis–12j were transformed to the corresponding tetraalkoxy [10]CPPs by applying the same synthetic procedure. The overall yields from 11i were high in all cases (4–19%), and several compounds were synthesized on the gram scale. A significant advantage of the introduction of alkoxyl groups on [10]CPP is the increase in the solubility of these compounds in common organic solvents (Table 1). The solubility of the parent [10]CPP in CHCl$_3$, at 25°C is 0.38 mmol L$^{-1}$, and the synthesized tetraalkoxy [10]CPPs are 10–70 times more soluble than [10]CPP.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>R$^\text{III}$</th>
<th>Overall yield (%)</th>
<th>Relative solubility (%)$^*$</th>
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<tbody>
<tr>
<td></td>
<td>H</td>
<td>17</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Bu</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Oct</td>
<td>14</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>EthHex</td>
<td>4</td>
<td>70</td>
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</table>

$^*$In CDCl$_3$ at 25°C.

The origin of the cis–selectivity for the formation of 12 is currently unclear. The cis–selective bis–addition of several organolithium species to 1,4–benzoquinone has already been reported, and the results were attributed to the electronic repulsion between the lithium alkoxide formed by the first addition reaction and the incoming organolithium species.\(^\text{13}\) However, there are many examples of trans–selective additions of organometallic species to higher acene diones.\(^\text{13}\) Therefore, further studies are needed to clarify the observed cis–selectivity.

The high solubility of tetraalkoxy [10]CPPs enabled the fabrication of CPP–based devices using wet processes; neat thin amorphous films of tetraalkoxy [10]CPPs were prepared by spin–coating on quartz or indium tin oxide (IOT) coated glass substrates (Figure 5a), and several important physical properties of CPPs in solid state were successfully obtained. For example, the ionization potentials (IPs) were determined to be ca. 6.0 eV regardless of the R$^\text{III}$ substituent (hydrogen and
by an atmospheric photoelectron spectrophotometer for the first time. With the IP data combined with the HOMO/LUMO energies estimated from the absorption spectra of the thin films, the electron affinities (EAs) were estimated to be ca. 3.3 eV. Both the IPs and EAs were similar to those of phenyl_C61_C61_C18 butyric acid methyl ester (PCBM) film (IP 6.1 eV, EA 3.9 eV), which is widely used as an acceptor in bulk heterojunction photovoltaics. Due to the highly tunable electronic properties of CPPs by structural modifications and their high availability, CPP derivatives would be excellent candidates as alternatives to PCBM.

The potential of CPPs as electron transport materials was clarified by fabricating an electron only device by spin-coating (BuO)4[10]CPP (Figure 5b). The current density-voltage (J-V) characteristic showed a space charge limited current (SCLC), and the electron mobility was determined to be 4.5 x 10^-6 cm^2 V^-1 s^-1 at 0.7 MV cm^-1 in the SCLC region (Figure 5c). Although the value is moderate, this work provides a valuable benchmark for CPP devices. Recent theoretical studies by Houk suggest that CPPs are potentially excellent charge transport materials in the solid state, and [10]CPP thin film is expected to have a mobility of >1 cm^2 V^-1 s^-1. The discrepancy between our results and the predicted value is likely due to the structural order of the CPP molecules in the solid state. Therefore, device performance can be improved by controlling the higher-order aggregation structure by appropriate crystal engineering.

The IPs and EAs obtained for the film samples in this study somewhat deviate from the results obtained from solution-phase experiments and theoretical calculations; the oxidation potentials measured in solution-phase samples and the HOMO energies estimated by theoretical calculations suggest that tetraalkoxy[10]CPPs have lower oxidation potentials and higher HOMO energies than [10]CPP due to the presence of electron-donating alkoxy groups. The origin of the discrepancy is currently unclear, and further studies are needed to clarify this point.

### 2.4 Synthesis of Large CPPs

Large CPPs have high fluorescence quantum yields and can potentially be applied as emitting layers in organic optoelectronic devices. However, the availability of CPPs larger than [13]CPP is limited, as they require a lengthy synthesis with a low overall yield. The high availability of U-shaped tri- and pentacyclic species 9 and 12 prompted us to investigate the synthesis of large CPPs. For example, [14]CPP was prepared from heptacycle cis-13, which was prepared from 1,4-benzoquinone (11b) and 4-bromo-4″-lithioperphenyl and subsequent platinum-mediated dimerization through the corresponding cyclic dimer (Scheme 6).

While the platinum-mediated method is highly suitable for selectively obtaining the corresponding dimer, it is unsuitable for increasing structural diversity, which is particularly important during the initial screening process. Therefore, we also examined the random synthesis of large CPPs starting from 12h and 13 (Scheme 6, Table 2). The cyclooligomeration of 12h and 13 by a Yamamoto coupling using stoichiometric Ni(cod)2 and 2,2'-bipyridyl was examined, and the products were separated by preparative gel permeation chromatography (GPC). In both cases, cyclic trimers 15l and 16l were the major isomers, followed by cyclic dimers 15k and 16k. Cyclic tetramers 15m and 16m were also isolated in low yields.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
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<tbody>
<tr>
<td>12h</td>
<td>15k</td>
</tr>
<tr>
<td>12h</td>
<td>15l</td>
</tr>
<tr>
<td>12h</td>
<td>15m</td>
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<tr>
<td>13</td>
<td>16x</td>
</tr>
<tr>
<td>13</td>
<td>16i</td>
</tr>
<tr>
<td>13</td>
<td>16m</td>
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</table>

a) Yield of the cyclization step. b) Yield of the reductive aromatization step.

The conversion of 15 and 16 to CPPs was examined, and the one-step aromatization of the TES-protected derivatives was more efficient than the two-step protocol discussed above.
(TBAF desilylation and H₂SnCl₄ aromatization). For example, the reductive aromatization of the tetraol derived from 15k by SnCl₂ (4.4 equiv) and aqueous HCl (8.8 equiv) required refluxing in THF to reach a yield of 92%, but the direct aromatization of 15k with SnCl₂ (4.4 equiv) and slight excess of HCl (13.2 equiv) was achieved at room temperature and gave [10]CPP in 94% yield. This is probably because of the higher solubility of 15k compared with the desilylated tetrol in THF.

This one-step aromatization reaction was successfully applied to the synthesis of other CPPs using 15l, 15m, 16k, and 16l to afford [15], [20], [14], and [21]CPPs, respectively, in high to good yields (Table 2). [20] and [21]CPPs were synthesized for the first time, and these CPPs are the largest CPPs synthesized to date. The use of the one-step aromatization process was essential for the synthesis of these CPPs because the desired CPPs were obtained in only low yield (<5%) using the two-step procedure. [28]CPP could not be detected even with this direct aromatization method starting from 16m probably due to the low solubilities of 16m, [28]CPP, and the generated partially reduced and/or desilylated intermediates.

The physical properties of all the CPPs synthesized in Figure 6 show the same size dependence observed for other CPPs. For example, all the CPPs have an absorption maximum at approximately 336–340 nm, which are almost identical to those of other CPPs. In their fluorescence spectra, all CPPs show blue fluorescence, and their fluorescence peaks with clear vibrational structures are blueshifted as the size of the CPP increases (Figure 6a). The fluorescence quantum yields became higher with an increase in the size of the CPP, as observed for other CPPs (46, 75, 84, 93, and 92% for [10], [14], [15], [20], and [21]CPPs, respectively). The oxidation potentials increased as the size of the CPP increased and reached a plateau at approximately 0.95 V (Figure 6b). This size dependence agrees well with the trend observed in the HOMO energies of the CPPs.

2.5 Synthesis of Fluorinated CPPs

The introduction of heteroatom(s) in π-conjugated molecules is an important strategy for tuning their electronic properties. Among various heteroatoms, fluorine has been widely used to modulate the electronic properties of π-conjugated molecules without inducing notable structural changes because of its high electronegativity and similar van der Waals radii to that of hydrogen (1.47 vs. 1.20 Å, respectively). While CPP derivatives bearing boron, nitrogen, oxygen, silicon, sulfur, chlorine, bromine, and iodine have already been synthesized, no fluorine-containing CPP derivatives have been reported. We found that partially fluorinated CPPs could be synthesized based on the same synthetic route used for the practical synthesis of CPPs (Scheme 7).

Figure 6. a) UV–vis absorption (solid line) and fluorescence (dashed line) spectra of large CPPs in CHCl₃ and b) correlation between the oxidation potential obtained by electrochemical analyses and the reciprocal of the number of paraphenylenel units in the CPPs.

Key tricyclic unit 17 was synthesized from tetrafluoro-1,4-benzoquinone and 4-bromolithiobenzene and then TES protection in a good overall yield. High cis-selectivity (>90%) was also observed here. Subjecting 17 to Yamamoto coupling conditions (Route A) afforded a mixture of cyclic dimer and trimer 18 in a moderate combined yield, and the platinum-mediated cyclization (Route B) selectively gave the cyclic dimer in good yield. Both products were quantitatively deprotected to corresponding alcohol 19.

Reductive aromatization of 19 did not occur by employing H₂SnCl₄, and only the recovery of 19 was observed. The use of strong reducing agents, such as sodium naphthalenide, gave only complex mixtures. We found that the mixture of excess PBr₃ (10 equiv) and SnCl₄ (8.0 equiv) in THF reported by Schwaben was effective and induced the desired aromatization to afford the desired products in moderate yield. The conditions were highly sensitive to the solvent, and the use of acetonitrile instead of THF significantly improved the reaction, and quantitative conversion was achieved even with lower amounts of PBr₃ (4.0 equiv) and SnCl₄ (4.0 equiv). These conditions would be applicable for the aromatization of other electron-deficient substrates.

8F–[6]CPP and 12F–[9]CPP in a crystalline have alternating zigzag structures of paraphenylenel units with both C₆H₄.
and C,F, units having benzenoid character (Figure 7a, c). These structural features are essentially identical to those of the parent CPPs. In the crystal packing, 8F–[6]CPP and 12F–[9]CPP adopt herringbone and columnar–like arrangements, respectively, with a short distance between the fluorine and hydrogen atoms (Figure 7b, d), suggesting the presence of fluorne–hydrogen interactions in the solid state.19

The introduction of fluorine to CPPs significantly affects their redox properties compared to the parent CPPs. 8F–[6]CPP and 12F–[9]CPP showed one reversible and two quasi-reversible reductions, respectively, while the parent CPPs did not undergo reduction within the given solvent window. In contrast, the oxidation of the fluorinated CPPs is much more difficult than that of the parent CPPs. The results are consistent with the calculated HOMO and LUMO energies, in which the introduction of a fluorine significantly lowered the energies of these orbitals relative to those of the parent CPPs due to the withdrawing effects of the fluorine atoms.

The fluorine substituent also impacted the host–guest chemistry. We have already reported that [N]CPP selectively interacts with [N+5]CPP, giving the [N+5]CPP+[N]CPP complex,14 but the interaction between two CPPs is very weak. For example, the association constant, $K_a$, between [6]CPP and [11]CPP is $540\pm 10$ L·mol$^{-1}$ in 1,1,2,2-tetrachloroethane–$d_1$ at 25 °C. In contrast, [11]CPP encapsulates 8F–[6]CPP approximately three times more strongly than it does [6]CPP. The theoretical calculations at the wB97X-D/6-31G(d) level of theory suggest that, while the fluorine atoms have virtually no effect on the host–guest structure, the presence of F–H interactions and the increase in the polarization between the host and guest are responsible for the observed increase in these interactions.

3. Chemical Transformation of CPPs

CPPs are highly strained molecules with nonplanar paraphenylene units. Therefore, they would have unique reactivity compared to not only their linear paraphenylene analogues but also their components, i.e., benzene. The elucidation of the reactivity of CPPs will also lead to the development of new methods for the late–stage functionalization of CPPs and related conjugated hoop–shaped molecules, as the syntheses of CPP derivatives reported so far rely on early–stage functionalization starting from functionalized precursors and require tedious multistep syntheses. Therefore, the development of an efficient late–stage functionalization method would further accelerate research on carbon nanohoops.

3.1 Bromination and Subsequent Transformations

Electrophilic aromatic substitution is the most popular reaction of aromatic compounds in textbooks. Therefore, bromination was examined by mixing [5]CPP with stoichiometric bromine (Scheme 8a).24b The reaction proceeded quickly at low temperature (~15 °C) without a Lewis acid, and not the substitution reaction, but the addition reaction took place giving bis–addition adduct 20m in 46% yield. No mono–bromine addition product was observed. The addition of 2.0 equivalents of bromine gave quantitative 20n. Further addition did not occur even when a large excess of bromine was added.

The reactivity and product yield were highly dependent on the size of the CPPs; the same bis–addition reaction selectively took place with [6]CPP giving 20o but with a low efficiency (82%). [8]CPP also gave bis–addition adduct 20p, but the yield dropped to 22%. [9] and [12]CPPs were completely inert to bromine and were recovered quantitatively even upon heating at 50 °C.

The addition of bromine over an isolated benzene ring was found to be irreversible even with a large excess of bromine (Scheme 8a).[10] The reaction proceeded quickly at low temperature (~50 °C) and not the substitution reaction, but the addition reaction took place giving bis–addition adduct 20n in 46% yield. No mono–bromine addition product was observed. The addition of 2.0 equivalents of bromine gave quantitative 20o. Further addition did not occur even when a large excess of bromine was added.

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The addition of bromine over an isolated benzene ring was reported for highly strained [6]paracyclophanes,30 and the driving force was believed to be the release of the strain. The DFT
calculations for the mono–bromine addition reaction to \([N]\) CPPs with \(n=5-12\) suggest that the addition reaction causes a relief in strain for all CPPs and that the relief in the strain \((\Delta E)\) becomes more significant as the size of CPP decreases. For example, the \(\Delta E\) values of \([5]\) and \([12]\) CPPs were \(-164\) and \(-48\) kJ mol\(^{-1}\), respectively. The DFT calculations also suggest that the loss of aromaticity by the addition of bromine to a paraphenylene unit costs \(78\) kJ mol\(^{-1}\) of endothermicity. Therefore, the heat of formation \((\Delta H)\) is determined by the interplay between the exo– and endothermicity resulting from the relief of strain and the loss of aromaticity, respectively. As a result, the addition reaction is highly exothermic for small CPPs, and the reaction becomes endothermic for CPPs larger than \([10]\) CPP, and the results are consistent with the observed size–dependence of the reactivity.

The addition of the second bromine to the mono–brominated \([N]\) CPPs to give \(20\) is highly exothermic, especially when the ring is small. Actually, in the case of \([5]\) CPP, the addition of the second bromine to give \(20n\) is more exothermic \((\Delta H=\) \(-108\) kJ mol\(^{-1}\)) than the first addition reaction \((\Delta H=\) \(-87\) kJ mol\(^{-1}\)). Furthermore, the formation of \(20n\) is \(117\) kJ mol\(^{-1}\) more favorable than that of its regioisomer. All these results clearly indicate that the reaction kinetics are controlled by the stability of the products.

Transformations of \(20\) to CPP derivatives were also examined using \(28\), and isomer \(21\), formed by the thermal isomerization of \(20n\), was an excellent precursor (Scheme 8b). Although the reaction of \(20\) with various bases regenerated \([5]\) CPP, treatment of \(21\) with a phosphazene superbase, \(t\)–\(BuN=P(N=P(NMe\(_2\)))\)\(^{31}\) \((t\)–\(BuP\)) afforded monobrominated \([5]\) CPP \(22\) in moderate yield. Various carbon– and heteroatom–substituted \([5]\) CPPs \(21\) were obtained from \(22\) by transmetallation to lithiated \([5]\) CPP and subsequent reaction with various electrophiles. Moreover, when \(21\) was treated with \(\text{Br}_2\) in the presence of a catalytic amount of \(\text{Fe}\) powder, further bromination occurred, giving octa–bromide \(24\) nearly quantitatively. Treatment of \(24\) with \(t\)–\(BuP\), afforded a mixture of \(\text{bis}^\text{−}, \text{tri}^\text{−}, \text{and tetra}^\text{−}\)bromo \([5]\) CPPs, \(25\), \(26\), and \(27\), respectively, in good combined yield. While the number of remaining bromine atoms could not be controlled, only a single isomer was observed in all compounds. Furthermore, further transformations of these multibrominated \([5]\) CPPs were also possible; for example, \(25\) was transformed to tetraborylated \([5]\) CPP \(25\) by a routine transmetallation reaction.

### 3.2 Multinuclear Convex–bounded Ruthenium–CPP Complexes

Transition–metal complexes of hooped (nonplanar) \(\pi\)–carbon surfaces have attracted considerable interest since the initial report on Pt and Ir complexes of C\(_{60}\) because of their unique structure and potential applications, such as in catalysis. However, hooped \(\pi\)–molecules that coordinate with metals have been limited to fullerences, corannulene, sumanene, and their derivatives.

A 1:1 Ru–[5]CPP complex, \(29\), was formed by mixing cationic ruthenium complex \([CpRu(CH_3CN)_3](PF_6)\) \((Cp=\text{cyclopentadienyl})\) \((28\ 1.0 \text{equiv})\) with \([5]\) CPP at room temperature in good yield (Scheme 9a).\(^{36}\) Treatment of \([5]\) CPP with more than two equivalents of \(28\) selectively afforded 2:1 complex \(30\) in excellent yield. While a regioisomer with respect to the position of Ru complexation could be formed, only \(30\), having a skipped Ru–paraphenylene structure, was obtained.

\([6]\) CPP selectively gave tri–coordinate complex \(31\) upon treatment with more than 3 equivalents of \(28\) (Scheme 9b). The results are in sharp contrast to the multinuclear Ru complexes of linear oligoparanaphenylenes, in which Ru atom were coordinated to all the paraphenylene units and selective coordination could not be achieved. Therefore, this method could provide a new route for the site–selective functionalization of CPPs.

### Scheme 9

Complexation of the cationic CpRu complex with a) \([5]\) CPP and b) \([6]\) CPP Crystal structure of c) \(31\). The hydrogen atoms, counter ions (PF\(_6\) ), and solvent molecules are omitted for clarity.

The high regioselectivity in the formation of multinuclear Ru complexes is due to thermodynamic control, as clarified by the DFT calculations. For example, \(30\) is \(32\) kJ mol\(^{-1}\) more stable than its possible regioisomer. Fully alternated complex \(31\) is also thermodynamically more stable than its two isomers by \(32\) and \(90\) kJ mol\(^{-1}\). Mulliken population analysis indicated that the ipso carbon of the Ru–coordinated paraphenylene becomes more electropositive than the same position of the parent paraphenylene, suggesting that the Ru–coordinated paraphenylene serves as an electron withdrawing group to the adjacent paraphenylene unit. Because the CpRu\(^{′}\) fragment is a \(\pi\)–acid, the coordination of an additional CpRu\(^{′}\) moiety to the adjacent paraphenylene should be electronically unfavorable. Therefore, the electronic effects dictate the stability of multi–Ru complexes.

Single crystal X–ray analyses revealed that the CpRu\(^{′}\) fragments coordinated to the convex surface of CPP with \(\eta^5\) hapticity (Scheme 9c). The crystal structure also suggested that the paraphenylene ring complexed with CpRu\(^{′}\) flattens out upon complexation, as reported in a Ru–corannulene complex.\(^{33}\) This in turn leads to greater bending in the remaining uncomplexed paraphenylene rings and induces a pyramidalization of the ipso carbons. The energy decomposition analysis indicates that this deformation induces \(20\) and \(31\) kJ mol\(^{-1}\) of destabilization to the CPP structure upon complexation to form \(30\) and its regioisomer, respectively. However, the energy differences in the deformations are rather small and thus cannot be the main reason for the selective formation of \(30\) and its regioisomer. However, the energy differences in the deformations are rather small and thus cannot be the main reason for the selective formation of \(30\) and its regioisomer. Therefore, the electronic effects dictate the stability of multi–Ru complexes.
Itami also reported the formation of mono–coordinated chromium tricarbonyl complexes of [9]CPP and [12]CPP. Although the yield of the complexation was low, the complex formed with [9]CPP was transformed to various mono–substituted [9]CPPs based on the lithiation of the Cr–complexed paraphenylene unit.

### 3.3 Carbon–carbon (C–C) Bond Activations of CPPs by a Platinum Complex

Of the possible reactions between CPP and metal complexes, i.e., π–complexation as discussed above, carbon–hydrogen insertion, and C–C insertion, the C–C insertion is among the most interesting because it significantly alters the electronic structure of the CPP and can allow the synthesis of new, cyclic π–conjugated molecules. Strain–induced C–C bond activation is well established; for example, cyclopropane reacts with platinum and rhodium complexes to form metallacyclobutanes.

The strain energy of [5]CPP is 492 kJ mol\(^{-1}\), and this value is significantly higher than that of cyclopropane (118 kJ mol\(^{-1}\)). Therefore, we investigated the activation of a C–C π bond of CPPs.

[5]CPP was reacted with one equivalent of Pt(PPh\(_3\))\(_4\) at 80 °C, and cyclic dinuclear complex \(32q\) was obtained in 47% yield, and 40% of [5]CPP was recovered (Scheme 10). The reaction should take place through mononuclear complex \(33q\), but no such product was observed. When 2.2 equivalents of Pt(PPh\(_3\))\(_4\) was used, nearly quantitative formation of \(32q\) was observed. No further C–C bond activation occurred, even when 3.0 equivalents of Pt(PPh\(_3\))\(_4\) was used. [6]CPP also participated in the same reaction at elevated temperature (100 °C), selectively giving dinuclear complex \(32r\) upon treatment with 2.2 equivalents of Pt(PPh\(_3\))\(_4\). On the other hand, CPPs larger than [6]CPP, such as [7] and [8]CPPs, were inert, even when heated above 120 °C.

The transformation of \(32\) into cyclic molecules was examined using \(32r\) as a substrate (Scheme 10). When \(32r\) was exposed to CO (1 atm) at room temperature, one phosphine ligand on each platinum center was quantitatively substituted by CO, as judged by \(^{31}\)P NMR analysis. Subsequent heating at 60 °C for 5 h followed by the addition of PhICl\(_2\) (2.2 equiv.) at 150 °C for 18 h gave cyclic diketone \(34\) in 75% yield. \(34\) is still highly strained with a calculated strain energy of 230 kJ mol\(^{-1}\), but this value is much lower than that of [6]CPP (393 kJ mol\(^{-1}\)). Various unsaturated molecules can potentially be inserted into \(32\), and such reactions would provide new synthetic routes to a variety of cyclic compounds, including new carbon nano–hoops.

### Summary and Perspectives

CPPs were theoretical molecules until a decade ago but have become available in gram quantities through the development of innovative bottom–up organic synthesis strategies. [5]–[12]CPPs are commercially available from Tokyo Chemical Industry, Inc. The increase in availability surely enhances the status of CPPs and related carbon nanohoops from the research objects of physical organic chemistry to practical components in materials science. We are very happy to have contributed to this transition. The synthesis of carbon nanohoops has been extended from CPPs to more complex structures, such as belts by Itami, Isobe, Möbius and more twisted hoops by Stepień and Tanaka, and...
catenanes by Müllen and Itami, but these species are usually available on the mg scale. Additionally, the quantities of catenanes by Müllen

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