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Practical Synthesis of [*n*]Cycloparaphenylenes (*n* = 5, 7–12) by H_2SnCl_4-Mediated Aromatization of 1,4-Dihydroxycyclo-2,5-diene Precursors

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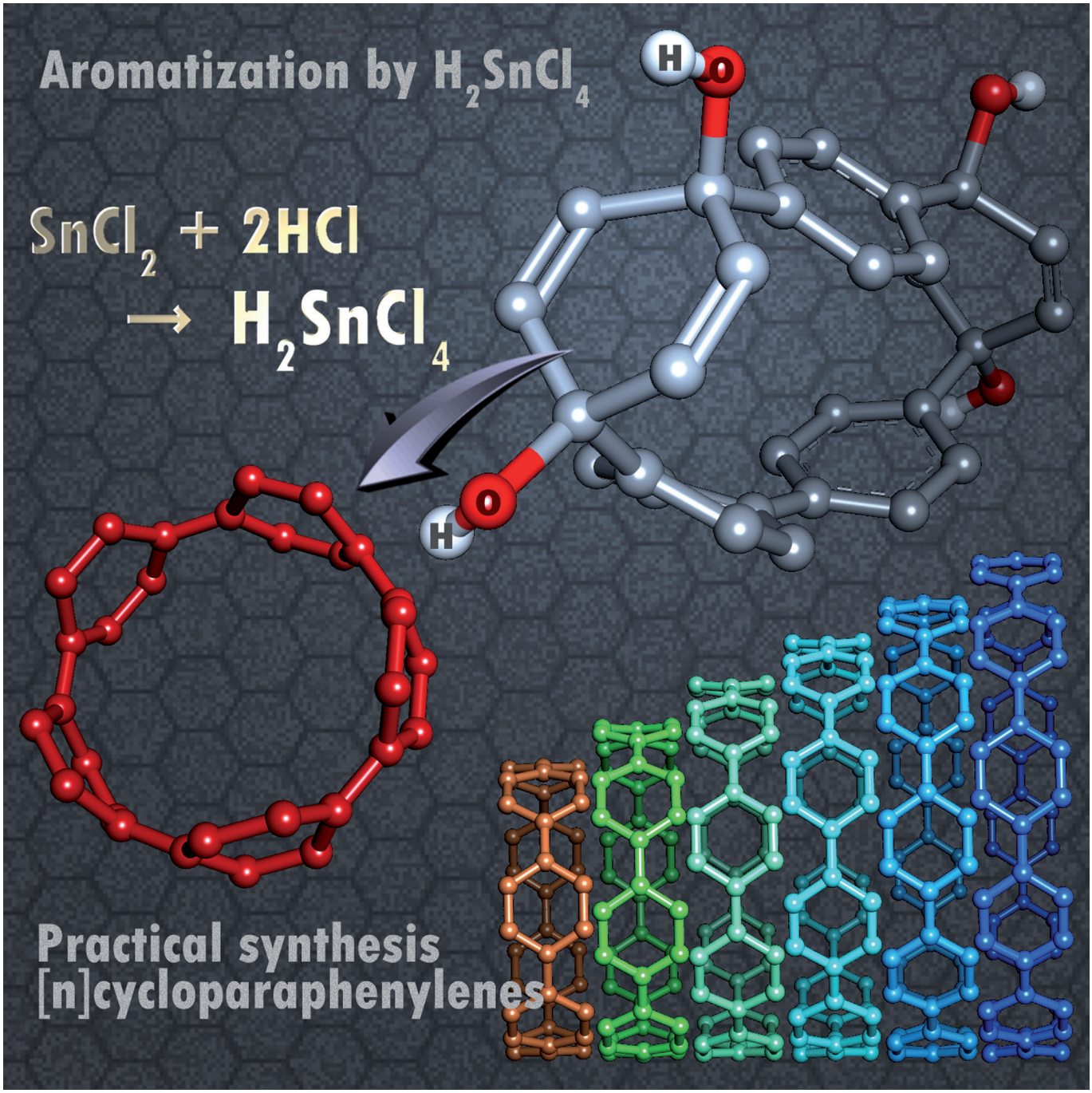

Abstract: Cyclic precursors of cycloparaphenylenes (CPPs) containing 1,4-dihydroxy-2,5-cyclohexadien-1,4-diyl units are prepared by modifying a synthetic method developed by Jasti and co-workers for the synthesis of corresponding 1,4-dimethoxy derivatives. Reductive aromatization of the diyl moieties by $SnCl_2$/2 HCl takes place under mild conditions and affords the CPPs in good yields, incorporating 5 or 7–12 phenylene units. Highly strained [5]CPP is synthesized in greater than 0.3 g scale. ^{119}Sn NMR spectroscopy clarifies the in situ formation of an ate complex, H_2SnCl_4, upon mixing a 2:1 ratio of HCl and $SnCl_2$, which serves as a highly active reducing agent under nearly neutral conditions. When more than 2 equivalents of HCl, in relation to $SnCl_2$, are used, acid-catalyzed decomposition of the CPP precursors takes place. The stoichiometry of HCl and $SnCl_2$ is critical in achieving the desired aromatization reaction of highly strained CPP precursors.

Introduction

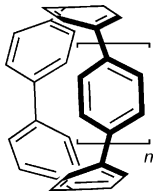

Figure 1. Structure of [*n*+4]CPPs.

Curved π-conjugated molecules have been a subject of considerable interest, not only for their aesthetic structures but also their unique physical properties derived from distorted π-orbitals.[1] Cycloparaphenylenes (CPPs; Figure 1), which consist of *para*-connected benzene rings in a cyclic arrangement and are the smallest structural unit of the sidewall of armchair carbon nanotubes,[1e,2] are representative of such molecules.[3] Although synthetic studies of CPPs date back to more than a half century ago,[3a] the first synthesis was achieved as recently as 2008 by Jasti, Bertozzi, and co-workers,[4] who utilized a *cis*-1,4-dimethoxy-2,5-cyclohexadiene-1,4-diyl moiety as a masked paraphenylene unit for the construction of the cyclic structure. After cyclo-oligomerization of a diyl-containing precursor, reductive aromatization of the masked unit gave CPPs. Shortly after this work, two independent routes for the syntheses of CPPs were reported by Itami's group[5] and by our group.[6] Itami and co-workers used a *cis*-1,4-dimethoxymethylcyclohexane-1,4-diyl as a masked paraphenylene unit, which was aromatized at the final step, whereas our group's synthesis relied on the assembly of linear π-units by a platinum complex and subsequent reductive elimination of platinum to afford the CPPs. In light of these seminal works, CPPs of different sizes (5–16, 18 phenylene units)[4,7,5,8,6,9] and various CPP derivatives[10] have been synthesized to date, and unique physical properties of CPPs, such as size-dependent photophysical[11] and redox properties[9a,12] and size-complementary host–guest complex formation,[13] have been elucidated.

Despite these developments, however, effective methods for the mass production of CPPs are still limited. In the case of Jasti and Bertozzi's method, the final step (i.e., reductive aromatization of 1,4-dimethoxy-2,5-cyclohexadiene moiety) required a strong reducing agent and low temperature and is unsuitable for large-scale preparation. Furthermore, the aromatization reaction required two steps in the synthesis of [5]CPP.[7e] For Itami's method, aromatization of 1,4-dimethoxymethylcyclohexane required strong acidic conditions and high temperature, resulting in low yields of CPPs. Furthermore, this condition has never been tested for the synthesis of small, highly strained CPPs, such as [6]- and [5]CPPs. Our group's method required stoichiometric amounts of platinum complex, although all reactions proceeded under neutral conditions. Therefore, the development of a new synthetic route that can be applicable for large-scale synthesis is desired.

During our synthesis of [5]CPP, utilizing a hybrid of Jasti's synthetic method and that from our own group,[9d] 1,4-dihydroxy-2,5-cyclohexadiene was found to serve as an excellent precursor of a masked benzene ring and could be aromatized under mild conditions by using $SnCl_2$ as a reducing agent at 60 °C. However, this condition was less reproducible and sometimes resulted in low yields of [5]CPP when the scaled-up synthesis was attempted. To overcome this problem, we optimized the reductive aromatization conditions and found that addition of two equivalent of HCl effectively activated $SnCl_2$, so that the thus-generated species facilitated reproducible results along with improved yields of [5]CPP. In addition, we identified the formation of an ate complex, H_2SnCl_4, for the first time by the reaction of $SnCl_2$ and 2 equivalents of HCl, which served as a reactive intermediate.[14] Furthermore, this method was extended to the synthesis of [7]–[12]CPPs by improving the synthetic route of CPP precursors with 1,4-dihydroxy-2,5-cyclohexadien-1,4-yl units and subsequent high-yield reductive aromatization reaction of the diyl units by H_2SnCl_4. Although these CPPs are already known species, the current method significantly improves the availability of these compounds.

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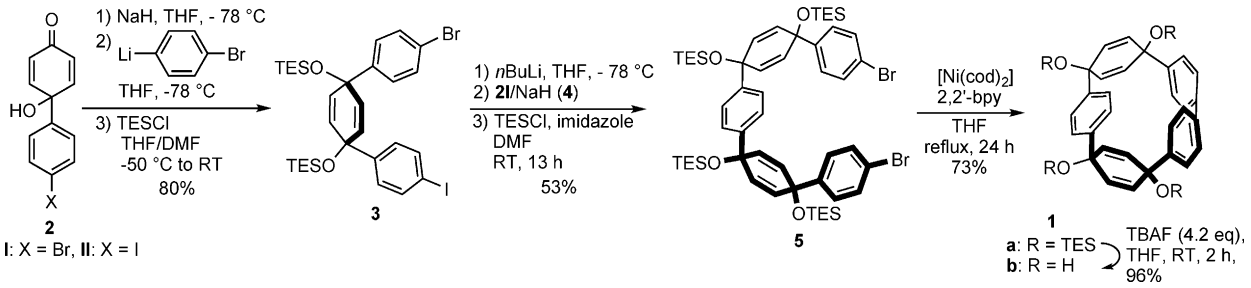


Scheme 1. Synthesis of [5]CPP precursor **1b**.

Results and Discussion

Synthesis of CPP precursors having 1,4-dihydroxy-2,5-cyclohexadien-1,4-yl unit

In our previous report on the synthesis of [5]CPP, cyclic tetraol **1b**, a precursor of [5]CPP, was prepared based on the Jasti's synthesis for the corresponding dimethoxy derivative, starting from 4-bromophenyl-4-hydroxycyclohexadienone (**2I**). However, the method was lengthy, requiring 9 steps and 8 pots, and gave **1b** in 29% overall yields. We have succeeded in reducing the number of synthetic steps and have prepared **1b** in 7 steps and 5 pots from 4-iodophenyl-4-hydroxycyclohexadienone (**2II**) in 30% overall yield (Scheme 1). Thus, treatment of **2II** with NaH (1.3 equiv) followed by addition of 4-bromophenyllithium prepared from 1,4-dibromebenzene (2.0 equiv) and *n*-butyllithium (*n*BuLi, 2.2 equiv) and subsequent treatment with triethylsilyl (TES) chloride (3.0 equiv) gave TES-protected tri-ring unit **3**, having different functional groups (bromo and iodo), in 80% yield. Selective lithiation of the iodide group of **3** by treatment with *n*BuLi and addition to deprotonated **2I** (**4**), followed by protection with TES chloride gave **5** in 53% yield. Ni^0-mediated Yamamoto coupling of **5** and subsequent treatment of the cyclized product **1a** with tetrabutylammonium fluoride (TBAF) afforded **1b** in 70% yield (2 steps). Since all steps could be carried out on large scale, 10 g of **5** and 2 g of **1b** were easily prepared.

Cyclic precursors of [7]–[12]CPPs **6**–**11** were also prepared by modifying the synthetic method developed by Jasti and coworkers.[7b] For example, [7]CPP precursor **6b** was synthesized in 6 steps and 4 pots starting from **2I**. After transformation into the bis-TES protected dibromo precursor **12**, the bromo groups were lithiated; treatment with two equivalents of **4** followed by TES protection afforded hexa-TES protected **13**. Ni^0-mediated cyclization of **13** followed by deprotection of TES group of **6a** afforded **6b** (Scheme 2a). Bromine–borane exchange reaction of dibromide **12** afforded **14**, which underwent Suzuki–Miyaura coupling with **5** to provide **7a**. A mixture consisting of [PdCl($C_6H_4CH_2NH_2$)(SPhos)] (SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl) catalyst (20 mol%)[15] in the presence of K_3PO_4 (8 equiv) in toluene/H_2O (10:1) was most efficient for the above coupling reaction among the conditions we examined. The TES groups of **7a** were removed by TBAF, giving [8]CPP precursor **7b** (Scheme 2b). **15** was synthesized from **3** through iodine–borane exchange reaction by treatment of *n*BuLi followed by quenching with isopropylpinacolylborane. Subsequent coupling of **15** and **3**, to give **16**, and further coupling of **16** with **14** afforded the cyclic product **8a**, which was deprotected to give [9]CPP precursor **8b** (Scheme 2c). Twofold bromine–borane exchange reaction of **5** afforded bispinacolate **17**. Twofold Suzuki–Miyaura coupling of **17** and **5** gave cyclic product **9a**, which was deprotected to give [10]CPP precursor **9b** (Scheme 2d). Twofold Suzuki–Miyaura coupling of **16** with **17** and twofold Ni^0-mediated homocoupling reaction of **16** gave cyclic products **10a** and **11a**, respectively, and subsequent removal of TES groups gave [11]- and [12]CPP precursors **10b** and **11b**, respectively (Scheme 2e and 2f). Since we did not optimize all of the reaction conditions extensively, several steps were low yielding. However, short reaction steps with high pot economy[16] should be attractive for large-scale synthesis.

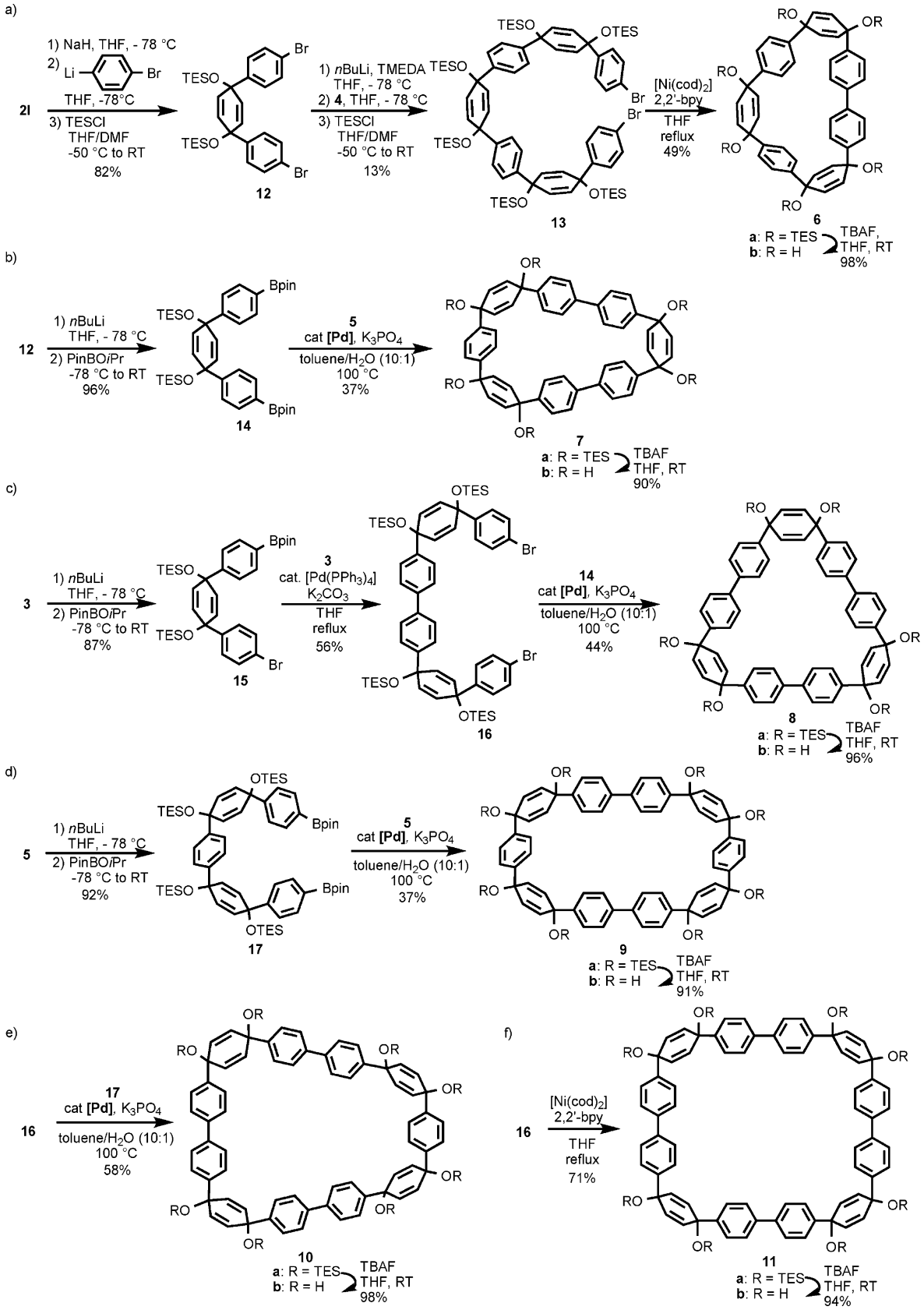
Reductive aromatization to form CPPs

In our previous synthesis of [5]CPP, tetraol **1b** was treated with excess $SnCl_2{\cdot}2H_2O$ (10 equiv) in THF at 60 °C for 3 h and the desired [5]CPP was obtained in 58% yield on 20 mg scale (Table 1, entry 1). However, attempts to scale up this reaction resulted in poor reproducibility and sometimes gave [5]CPP in low yields. After extensive investigation, we found that the addition of a limited amount of HCl was highly effective in increasing the activity of the Sn reagent and gave reproducible results. Thus, $SnCl_2{\cdot}2H_2O$ (2.2 equiv related to **1b**) was stirred with concentrated aqueous HCl (2 equiv related to $SnCl_2$) in

Table 1. Synthesis of CPPs by $SnCl_2$-mediated reductive aromatization.

Entry	Precursor	Reducing agent (equiv)	Product	Yield [%][b]
1	**1b**	$SnCl_2{\cdot}2H_2O$ (10)	[5]CPP	58
2[a]	**1b**	$SnCl_2{\cdot}2H_2O$ (2.2)/HCl (4.4)	[5]CPP	72
3[a]	**6b**	$SnCl_2{\cdot}2H_2O$ (3.3)/HCl (6.6)	[7]CPP	87
4[a]	**7b**	$SnCl_2{\cdot}2H_2O$ (3.3)/HCl (6.6)	[8]CPP	67
5[a]	**8b**	$SnCl_2{\cdot}2H_2O$ (3.6)/HCl (7.2)	[9]CPP	63
6[a]	**9b**	$SnCl_2{\cdot}2H_2O$ (4.4)/HCl (8.8)	[10]CPP	56
7[a]	**10b**	$SnCl_2{\cdot}2H_2O$ (4.4)/HCl (8.8)	[11]CPP	78
8[a]	**11b**	$SnCl_2{\cdot}2H_2O$ (4.4)/HCl (8.8)	[12]CPP	72

[a] A solution of $SnCl_2{\cdot}2H_2O$ and concentrated aqueous HCl in THF was stirred for 10–15 min before the precursor was added and the resulting solution was stirred at room temperature (see Experimental Section for further details); [b] yield of isolated product.



Scheme 2. Synthesis of [7], [8], [9], [10], [11], and [12]CPP precursors **6**, **7**, **8**, **9**, **10**, and **11. [Pd]** in the Scheme refers to $[PdCl(C_6H_4CH_2NH_2)(SPhos)]$.

THF for 10–15 min at room temperature, before **1 b** was added to the solution. Stirring for the next 0.5 h at room temperature followed by routine workup afforded [5]CPP in 72% yield (Table 1, entry 2). More than 300 mg of [5]CPP was synthesized

under these conditions. Notably, the aromatization proceeded at room temperature in the presence of a stoichiometric amount of $SnCl_2$, whereas previous attempts required an excess of this reagent and high temperature. The stoichiometry of HCl and the use of an aqueous solution thereof were crucial for the success of this reaction. When excess HCl was employed, acid-catalyzed decomposition of the substrate took place before the reduction. Furthermore, when anhydrous HCl in ether was used instead of aqueous HCl, no [5]CPP was formed. Other reducing agents, such as lithium or sodium naphthalenide, lithium or sodium metal, KC_8, or low-valent titanium, were ineffective for the synthesis of [5]CPP.

The $SnCl_2$/HCl reducing agent was successfully applied to the synthesis of other CPPs. For example, [7]CPP was prepared in 87% yield from **6b** by employing $SnCl_2{\cdot}2H_2O$ (3.3 equiv) and HCl (6.6 equiv) in THF at room temperature for 3 h (Table 1, entry 3). Notably, although **6b** possesses three masked aromatic units and [7]CPP is a highly strained molecule (357 kJ mol^{-1}), a net yield of the aromatization of one unit reached 95.5%. [8], [9], [10], [11], and [12]CPPs were also successfully synthesized in similar way from **7b**, **8b**, **9b**, **10b**, and **11b**, respectively, in good yields (Table 1, entries 4–8). All of these aromatization steps proceeded under much milder conditions and gave higher yields of CPPs than those previously reported by the groups of Jasti and Itami,[7b,8d,e] suggesting that these conditions are highly attractive for the large-scale synthesis of CPPs.

Analysis of the stannane intermediate

To understand the role of HCl in increasing the efficacy of the reductive aromatization step, the reaction between $SnCl_2$ and HCl was analyzed by ^{119}Sn NMR spectroscopy. Although formation of stannane ate complexes, such as H_2SnCl_4 or $HSnCl_3$, from $SnCl_2$ and HCl had been proposed,[17] no direct experimental evidence had been reported to date for the putative intermediate. When aqueous concentrated HCl (1.0 equiv) was added to $SnCl_2{\cdot}2H_2O$ (1.0 equiv) in [D_8]THF, a new singlet resonance appeared around at -610 ppm, downfield shifted from that of $SnCl_2$ by about $\delta = -224$ ppm, while the signal of $SnCl_2$ remained (Figure 2a and 2b). Addition of 1.0 equivalent of HCl to this solution further increased the signal intensity at $\delta = -610$ ppm and the signal corresponding to $SnCl_2$ completely disappeared (Figure 2c). However, further addition of HCl (1 equiv) did not induce any spectral change (Figure 2d). The large upfield shift, together with the stoichiometry between $SnCl_2$ and HCl, strongly suggested the formation of the stannane ate complex H_2SnCl_4, which is an active species in stannane-mediated reductive aromatization. The NMR experiments also suggested that, when more than 2 equivalents of HCl were added to $SnCl_2$, the excess HCl just worked as a Brønsted acid, which induced undesired acid-catalyzed decomposition of the CPP precursors. Although there are many examples of reductive aromatization of 1,4-dihydroxy-2,5-cyclohexadiene derivatives by using $SnCl_2$ in aqueous HCl solution, a large excess of HCl over $SnCl_2$ is usually employed. Our observations also suggest that this condition ($SnCl_2 + 2$ HCl) should be highly suitable for reductive aromatization of acid-sensitive substrates.

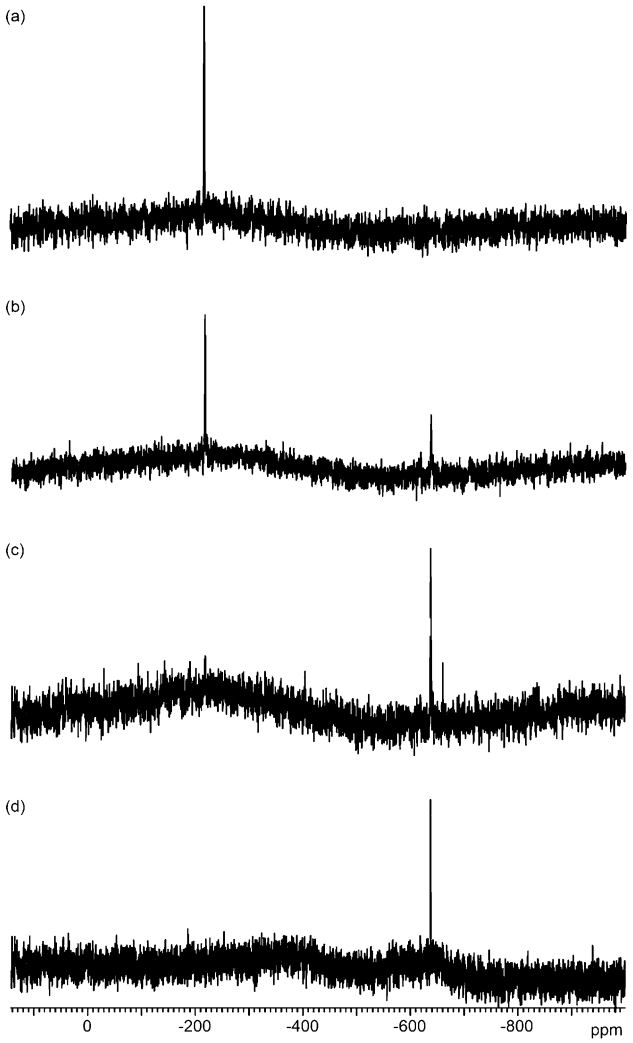


Figure 2. ^{119}Sn NMR spectra: a) $SnCl_2{\cdot}2H_2O$; b) after the addition of 1 equivalent of HCl; c) after the addition of 2 equivalents of HCl; d) after the addition of 3 equivalents of HCl to $SnCl_2{\cdot}2H_2O$ in [D_8]THF at room temperature.

Conclusions

[5] and [7]–[12]CPPs were synthesized in short reaction steps and a minimum number of reaction pots. The key reductive aromatization reaction of 1,4-dihydroxy-2,5-cyclohexadien-1,4-yl unit took place under mild conditions by employing $SnCl_2$/2 HCl and gave the desired CPPs in good yields. The reported high efficiency and mild conditions should be useful for large-scale synthesis of various CPPs including highly strained [5]CPP. In addition to the practical synthetic method of CPPs, we also identified a highly reactive but putative stannane intermediate formed by mixing $SnCl_2$ and HCl as an ate complex, H_2SnCl_4. Since reductive aromatization by using $SnCl_2$ in aqueous HCl solution has been widely used for the synthesis of various π-conjugated molecules, the result offers rational design of functionalized novel π-conjugated molecules by the reductive aromatization reaction.

Experimental Section

General: All reactions dealing with air- and moisture sensitive compounds were carried out in a dry reaction vessel under nitrogen atmosphere. ^{1}H (400 or 600 MHz) and ^{13}C NMR (100 or 150 MHz) spectra were measured for $CDCl_3$, [D_6]acetone, or dimethyl sulfoxide ([D_6]DMSO) solutions of samples and chemical shifts (δ) are reported in parts per million relative to an internal tetramethylsilane standard or residual solvent peak. ^{119}Sn NMR spectra were measured at 149 MHz, and chemical shifts are given relative to an $SnMe_4$ external standard. Electrospray ionization time-of-flight mass (ESI-TOF MS) spectra were recorded on a spectrometer in the positive or negative mode. Samples were injected as dichloromethane/isopropanol, acetone, or DMSO solutions. Matrix-assisted laser-desorption ionization time-of-flight mass (MALDI-TOF MS) spectra were obtained on a spectrometer in the positive reflection mode and at 20 kV acceleration voltage. Samples were prepared from a THF solution by mixing the investigated species (1 mg mL^{-1}) with dithranol (1 mg mL^{-1}) in a 1:1 ratio.

Materials: Unless otherwise noted, commercially available materials were used without purification. CH_2Cl_2 was distilled successively from P_2O_5 and K_2CO_3 and stored over molecular sieves. *N*,*N*-Dimethylformamide (DMF) was distilled from P_2O_5 and stored over molecular sieves. Toluene and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) were distilled from CaH_2 and stored over molecular sieves. 4-(4-Bromophenyl)-4-hydroxy-2,5-cyclohexadien-1-one **2l**,[7d] [Pt(cod)Cl_2] (cod = 1,5- cyclooctadiene),[18] [Ni(cod)$_2$],[19] and [PdCl($C_6H_4CH_2NH_2$)(SPhos)][15] were synthesized as reported.

Synthesis of [5]CPP: Concentrated aqueous HCl (0.480 mL, 5.76 mmol) was added to a solution of $SnCl_2{\cdot}2H_2O$ (0.650 g, 2.88 mmol) in THF (100 mL) at room temperature and the resulting solution was stirred for 0.5 h under nitrogen atmosphere. **1b** (0.540 g, 1.20 mmol) was then added to the resulting mixture at room temperature, and the mixture was stirred at room temperature for 1 h. To the resulting mixture was added 10% aqueous NaOH solution, and the reaction mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layer was washed with brine (40 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was passed through a plug of silica gel using CH_2Cl_2 as eluent and concentrated under reduced pressure. The obtained solid was washed with CH_2Cl_2/hexane (1:1) giving [5]CPP (0.33 g, 72%) as a dark purple solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.85 ppm (s, 20 H, -Ar); HRMS (MALDI-TOF): *m*/*z* calcd for $C_{30}H_{20}$ [M^+]: 380.1560; found: 380.1136.[9d]

Synthesis of [7]CPP: Concentrated aqueous HCl (0.120 mL, 1.45 mmol) was added to a solution of $SnCl_2{\cdot}2H_2O$ (165 mg, 0.730 mmol) in THF (6 mL) at room temperature and the resulting solution was stirred at this temperature for 10 min under nitrogen atmosphere. **6b** (140 mg, 0.220 mmol) was then added to the resulting mixture at room temperature, and the mixture was stirred at this temperature for 3 h. To the resulting mixture was added 10% aqueous NaOH solution, and the reaction mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was passed through a plug of silica gel using CH_2Cl_2 as eluent and concentrated under reduced pressure. The obtained solid was washed with CH_2Cl_2/hexane (2:1), giving [7]CPP (101.9 mg, 87%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.48 ppm (s, 28 H, -Ar); HRMS (MALDI-TOF): *m*/*z* calcd for $C_{42}H_{28}$ [M^+]: 532.2186; found: 532.1787.[7a,8e]

Synthesis of [8]CPP: Concentrated aqueous HCl (0.170 mL, 1.98 mmol) was added to a solution of $SnCl_2{\cdot}2H_2O$ (223 mg, 0.990 mmol) in THF (30 mL) was added at room temperature and the resulting solution was stirred at this temperature for 15 min under nitrogen atmosphere. **7b** (213 mg, 0.300 mmol) was then added to the resulting mixture at room temperature, and the mixture was stirred at same temperature for 12 h. To the resulting mixture was added 10% aqueous NaOH solution, and the reaction mixture was extracted with CH_2Cl_2 (40 mL × 3). The combined organic layer was washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was passed through a plug of silica gel using CH_2Cl_2 as eluent and concentrated under reduced pressure. The obtained solid was washed with CH_2Cl_2/hexane (2:1), giving [8]CPP (122.4 mg, 67%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.48 ppm (s, 32 H, -Ar); HRMS (MALDI-TOF): *m*/*z* calcd for $C_{48}H_{32}$ [M^+]: 608.2499; found: 608.2485.[9a]

Synthesis of [9]CPP: Concentrated aqueous HCl (46 μL, 0.55 mmol) was added to a solution of $SnCl_2{\cdot}2H_2O$ (62 mg, 0.27 mmol) in THF (8 mL) at room temperature and the resulting solution was stirred at this temperature for 15 min under nitrogen atmosphere. **8b** (60 mg, 0.076 mmol) was then added to the resulting mixture at room temperature, and the mixture was stirred at this temperature for 12 h. To the resulting mixture was added 10% aqueous NaOH solution, and the reaction mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was passed through a plug of silica gel using CH_2Cl_2 as eluent and concentrated under reduced pressure. The obtained solid was washed with CH_2Cl_2/hexane (4:1), giving [9]CPP (33 mg, 63%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.52 ppm (s, 36 H, -Ar); HRMS (MALDI-TOF): *m*/*z* calcd for $C_{54}H_{36}$ [M^+]: 684.2812; found: 684.2825.[9a]

Synthesis of [10]CPP: Concentrated aqueous HCl (73 μL, 0.88 mmol) was added to a solution of $SnCl_2{\cdot}2H_2O$ (99 mg, 0.44 mmol) in THF (5 mL) at room temperature and the resulting solution was stirred at same temperature for 15 min under nitrogen atmosphere. **9b** (90 mg, 0.10 mmol) was then added to the resulting mixture at room temperature, and the mixture was stirred at same temperature for 12 h. To the resulting mixture, 10% aqueous NaOH solution was added, and extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was washed with brine (30 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was passed through a plug of silica gel using CH_2Cl_2 as eluent and concentrated under reduced pressure. The obtained solid was washed with CH_2Cl_2/hexane (4:1), giving [10]CPP (42.6 mg, 56%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.56 ppm (s, 40 H, -Ar); HRMS (MALDI-TOF): *m*/*z* calcd for $C_{60}H_{40}$ [M^+]: 760.3125; found: 760.3083.[9a]

Synthesis of [11]CPP: Concentrated aqueous HCl (154 μL, 1.85 mmol) was added to a solution of $SnCl_2{\cdot}2H_2O$ (203 mg, 0.900 mmol) in THF (40 mL) at room temperature and the resulting solution was stirred at this temperature for 15 min under nitrogen atmosphere. **10b** (200 mg, 0.210 mmol) was then added to the resulting mixture at room temperature, and the mixture was stirred at this temperature for 12 h. To the resulting mixture, 10% aqueous NaOH solution was added, and extracted with CH_2Cl_2 (50 mL × 3). The combined organic layer was washed with brine (50 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was passed through a plug of silica gel using CH_2Cl_2 as eluent and concentrated under reduced pressure, giving [11]CPP (133.5 mg, 78%) as a yellow solid. d.p. > 300 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.58 ppm (s, 44 H, -Ar); HRMS (MALDI-TOF): *m*/*z* calcd for $C_{66}H_{44}$ [M^+]: 836.3438; found: 836.3215.[9a]

Synthesis of [12]CPP: Concentrated aqueous HCl (65.0 μL, 0.770 mmol) was added to a solution of $SnCl_2{\cdot}2H_2O$ (88.0 mg, 0.390 mmol) in THF (40 mL) at room temperature and the resulting solution was stirred at this temperature for 15 min under nitrogen atmosphere. **11b** (92.0 mg, 8.80×10^{-2} mmol) was then added to the resulting mixture at room temperature, and the mixture was stirred at this temperature for 21 h. To the resulting mixture, 10% aqueous NaOH solution was added, and extracted with CH_2Cl_2 (30 mL×3). The combined organic layer was washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was passed through a plug of silica gel using CH_2Cl_2 as eluent and concentrated under reduced pressure, giving [12]CPP (57.4 mg, 72%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=7.61$ ppm (s, 48H, -Ar); HRMS (MALDI-TOF): *m/z* calcd for $C_{72}H_{48}$ [M^+]: 912.3756; found: 912.3797.[9a]

Synthetic procedures and characterization data for compounds **1**, **2II**, **3**, **5**–**17** can be found in the Supporting Information.

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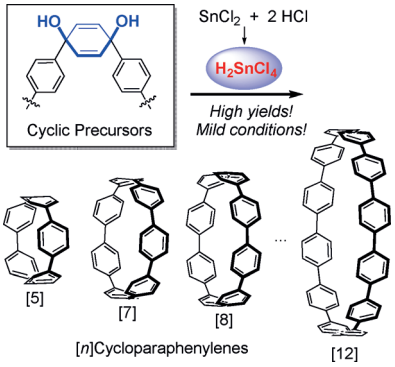
FULL PAPER

Behold the ring of rings: [*n*]Cycloparaphenylenes ($n = 5$, 7–12) have been synthesized in good yields by reductive aromatization of cyclic precursors incorporating 1,4-dihydroxycyclo-2,5-diene units, by employing H_2SnCl_4, which was prepared in situ by mixing $SnCl_2$ and 2 equivalents of concentrated aqueous HCl.

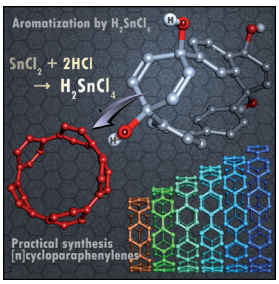


Aromatic Compounds

*V. K. Patel, E. Kayahara, S. Yamago**

■■ – ■■

Practical Synthesis of [*n*]Cycloparaphenylenes ($n = 5$, 7–12) by H_2SnCl_4-Mediated Aromatization of 1,4-Dihydroxycyclo-2,5-diene Precursors



Cycloparaphenylene

Practical synthesis of [*n*]cycloparaphenylenes ([*n*]CPPs, $n =$ 5, 7–12) is reported by S. Yamago and co-workers in their Full paper on page ■■ ff. Reductive aromatization of 1,4-dihydroxy-2,5-cyclohexadien-1,4-diyl units by $SnCl_2$/2 HCl underwent under mild conditions and afforded CPPs in good to high yields. ^{119}Sn NMR study clarified the in situ formation of an ate complex, H_2SnCl_4, upon mixing two equivalents of HCl and $SnCl_2$ which served as a highly reactive reducing agent under nearly neutral condition.