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Cyclophanes

Synthesis of [8]Cycloparaphenylene from a Square-Shaped Tetranuclear Platinum Complex**

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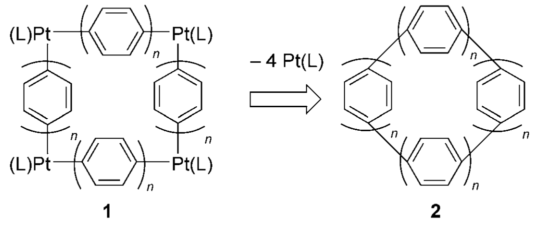
Hoop-shaped π-conjugated molecules have attracted the attention of theoretical, synthetic, and supramolecular chemists for more than a half century because of their unique structures which have a distorted π system.[1,2] Among these types of compounds, cycloparaphenylenes have gained much interest recently because of their potential applications in material science; they are the simplest structural unit of armchair carbon nanotubes. Although they have a simple structure, their synthesis has been a significant challenge.[3] Whereas the parent paraphenylenes adopt an extended linear structure, the induced strain resulting from the cyclic and curved structure of cycloparaphenylenes is the major synthetic drawback. Recently, Bertozzi and co-workers have reported the first, and elegant, synthesis of [9]-, [12]-, and [18]cycloparaphenylenes.[4] More recently, Itami and co-workers have reported a selective synthesis of [12]cycloparaphenylene.[5] Both groups utilize the sp^3-hybridized carbon atom in either cyclohexa-2,5-diene-1,4-diol or cyclohexane-1,4-diol derivatives to induce the curvature, and the diol units are aromatized in the final step. We report herein the synthesis of [8]cycloparaphenylene, which is the smallest cycloparaphenylene synthesized thus far, based on a new synthetic strategy.[6]

We envisioned that *cis*-coordinated, square-shaped tetra(*para*-substituted oligoaryl)platinum complex **1** could be used as a universal precursor for [4*n*]cycloparaphenylenes **2** (Scheme 1). Since the bond angles of the *cis* substituents in platinum complexes are about 90°, formation of **1** should not induce significant strain. Indeed, structurally related coordination complexes of palladium and platinum macrocycles containing a 4,4′-bipyridyl unit have been already reported,[7] and their analogues have been widely used in supramolecular chemistry.[8] However, to the best of our knowledge, there is no report involving the synthesis of **1** with only covalent platinum–carbon bonds.[9] If multiple reductive eliminations of platinum from **1** occur, **2** could be formed despite of the increase of molecular strain. We report herein the synthesis of [8]cycloparaphenylene ($n = 2$) from the corresponding precursor as a proof of principle for this strategy.[10]

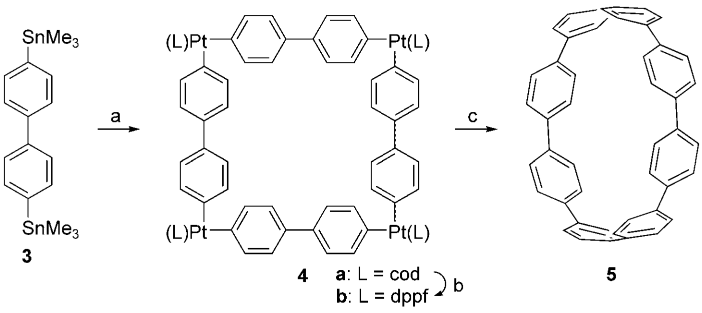


Scheme 1. Synthetic strategy for [4*n*]cycloparaphenylene.

We calculated the strain energies of several cycloparaphenylenes before attempting the synthesis. On the basis of density functional theory calculations at the B3LYP/6-31G* level of theory, the strain energy of [8]cycloparaphenylene was 74 kcal mol^{-1}, whereas those of [9]-, [12]-, and [18]cycloparaphenylenes were 69, 50, and 33 kcal mol^{-1}, respectively.[11]

To synthesize [8]cycloparaphenylene (**5**), 4,4′-bis(trimethylstannyl)biphenyl **3**[12] was first treated with one equivalent of [PtCl$_2$(cod)] (cod = 1,5-cyclooctadiene) in refluxing THF for 35 hours (Scheme 2).[13] The reaction gave the square-shaped platinum complex **4a** in 57 % yield, which was treated with 1,1′-bis(diphenylphosphino)ferrocene (dppf) to give **4b** in 91 % yield. Bromine-induced reductive elimination[14] from **4b** at 95 °C for 17 hours in toluene afforded **5** in 49 % yield upon isolation. Addition of iodine[15] or triphenylphosphine,[16] instead of bromide, did not improve the efficiency of the reductive elimination.

In the ^{1}H NMR spectrum of **5**, a single peak was observed at $\delta = 7.48$ ppm, and in the ^{13}C NMR spectrum, peaks were observed at $\delta = 137.8$ and 127.6 ppm. These spectra are



Scheme 2. Synthesis of **5**. Reaction conditions and reagents: a) [PtCl$_2$(cod)] (1 equiv), THF, reflux, 35 h, 57%. b) dppf (4.0 equiv), CH$_2$Cl$_2$, RT, 20 h, 91%. c) Br$_2$ (7 equiv), toluene, 95 °C, 17 h, 49%.

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similar to those of the larger cycloparaphenylenes. In the MALDI TOF mass spectrum, a molecular ion peak was observed at m/z 608.25. All of the results are consistent with the structure of **5**.

Compound **5** absorbs UV/Vis light at λ_{max} of 340 nm with an absorption coefficient $\varepsilon = 34\,200\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$. (Figure 1). The absorption wavelength is similar to [9]-, [12]-, and [18]cycloparaphenylenes,[4] and the fluorescence spectra of **5** showed a maximum emission at around 540 nm. The observed Stokes shift is approximately 200 nm, the value of which is much larger than those reported for the larger cycloparaphenylenes. The observed trend of the Stokes shifts is also consistent with the results reported by Bertozzi and co-workers,[4] but the origin of the larger shift in [8]cycloparaphenylene requires additional studies.

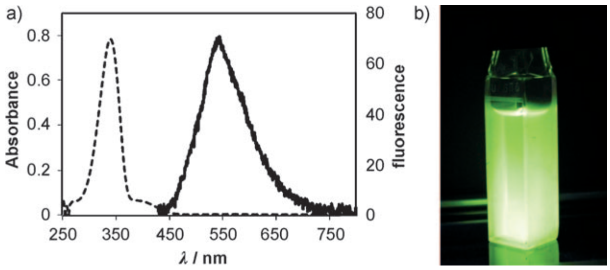

Figure 1. a) UV (dashed line) and fluorescence (solid line) spectra and b) fluorescent emission of **5** in chloroform.

In summary, for the first time, we have synthesized [8]cycloparaphenylene, which is the smallest cycloparaphenylene derivative synthesized to date, in 25% overall yield starting from **3**. The current synthetic strategy would be applicable to the syntheses of other [4*n*]cycloparaphenylenes. In addition, since all of the reaction steps proceed under mild and neutral reaction conditions, it should be possible to introduce various functional groups on the aryl rings to prepare a variety of substituted cycloparaphenylenes. We are now actively investigating these possibilities and will report our results in due course.

Experimental Section

Compound **4a**: **3** (221 mg, 0.461 mmol) and [$PtCl_2$(cod)] (172 mg, 0.461 mmol) were dissolved in THF (115 mL), and the mixture was refluxed for 35 h under a nitrogen atmosphere. An off-white precipitate was formed and subsequently collected by filtration. The solid residue was washed with hexanes and then by a small amount of CH_2Cl_2 to give **4a** (119 mg) in 57% yield as a off-white solid. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 2.52$ (bs, 32H), 5.10 (bs, 16H), 7.12 (d, $J = 6.8$ Hz, 16H), 7.19 ppm (d, $J = 8.0$ Hz, 16H); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 30.1$, 104.8, 125.6, 135.0, 136.1, 154.3 ppm. IR (KBr): $\nu =$ 3049, 3001, 2943, 2922, 2883, 2833, 1582, 1472, 1427, 1341, 1314, 1072, 1016, 997, 874, 799, 760 cm^{-1}. MS (FAB) m/z calcd for $C_{80}H_{80}Pt_4$ $[M]^+$ 1820.5, found 1820.4.

Compound **4b**: A suspension of **4a** (31.1 mg, 17.0 μmol) and 1,1′-bis(diphenylphosphino)ferrocene (39.5 mg, 71.2 μmol) in CH_2Cl_2 (10 mL) was stirred at room temperature under a nitrogen atmosphere for 6 h. The solvent was removed under reduced pressure, and the residue was washed with ethyl acetate to give **4b** (55.8 mg, 91%) as a pale orange solid. Due to the low solubility of **4b** in common deuterated solvents, a sufficient signal-to-noise ratio could not be obtained to perform ^{13}C NMR spectroscopy. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 4.20$ (bs, 16H), 4.29 (bs, 16H), 6.37 (d, $J = 7.6$ Hz, 16H), 6.69 (m, 16H), 7.21 (t, 32H), 7.31 (t, 16H), 7.48 ppm (t, 32H). ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 15.47$ ppm (s, $J_{PtP} = 1776$ Hz). IR (KBr): $\nu = 3051$, 3003, 1674, 1639, 1582, 1475, 1435, 1389, 1308, 1099, 1072, 1037, 999, 802, 746, 694, 638, 569, 516, 492, 473 cm^{-1}.

Compound **5**: Br_2 (3 μL, 49 μmol) was added to a stirred suspension of **4b** (24.2 mg, 6.71 μmol) in toluene (5 mL) which was maintained under a nitrogen atmosphere. The reaction mixture was stirred at 95 °C for 17 h, and then the insoluble materials were filtered off. Volatile materials in the filtrate were removed under reduced pressure. The residue was purified using preparative gel permeation chromatography with chloroform as the eluent, and subsequent column chromatography on silica gel using chloroform/hexanes mixtures with ratios (v/v) ranging from from 1:4 to 1:1 as the eluent to give **5** (2.0 mg, 49%) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.48$ ppm (s, 32H); ^{13}C NMR (100 MHz): $\delta = 127.6$, 137.8. IR (KBr): $\nu = 2922$, 2853, 1458, 820 cm^{-1}. MS (MALDI-TOF) m/z calcd for $C_{48}H_{32}$ $[M]^+$ 608.2505, found 608.2504.[17]

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