Toward Curved Polycyclic Aromatic Hydrocarbons (PAHs)

A thesis submitted in partial fulfillment of the requirements for the degree of Masters of Science in Chemistry

by

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Abstract

The chemistry of polycyclic aromatic hydrocarbons (PAHs) has been studied for many years. We are interested in the synthesis of bent PAHs particular bowl-shaped PAHs, polymeric helicenes, and also saddle-shaped tetrabenzo-[8]-circulene. They are interesting not only due to their aesthetic nature, but also due to their potential application in catalysis and material chemistry.

The synthetic chemistry of curved PAHs was studied. New PAHs were synthesized using Heck reaction followed by Scholl oxidation. The synthesis and an attempted Scholl oxidation of a new ruthenecene are described here. Computational studies for the Scholl oxidation of 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene are also reported.

The synthesis of monomers required for the synthesis of polymeric azahelicenes is described. The synthesis of polymeric carbohelicene precursor, trans, trans-1,5-dibromo-2,4-dipropenyl-benzene, by Grignard reaction followed by dehydration, is discussed.

The attempted synthesis of tetrabenzo-[8]-circulene precursor by dimerization of 2,3-dibromo-1,4-dimethyl-naphthalene is described.
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Chapter 1

1.1 Introduction and background

The discovery of Buckminsterfullerene \((C_{60})\) by Smalley and Kroto\(^1\) has sparked interest to model its curvature by synthesizing new polycyclic aromatic hydrocarbons (PAHs). The curvature is best exhibited by Corannulene\(^2\) shown in Figure 1.1. PAHs consist a graphite-like carbon network, which is made up of fused aromatic rings. King and Ormsby\(^3,4\) have computationally studied the electronic properties of curved carbon nanotubes (CNTs).

![Buckyministerfullerene (C\(_{60}\))](image1)

![Corannulene](image2)

**Figure 1.1.** Structures of buckminsterfullerene and corannulene.

PAHs are not only captivating due to their beauty, but also due their potential use in catalysis and in materials chemistry. Their unique properties such as photoabsorbtion, electroconductivity, and fluorescence make them suitable for material application such as computer screens, solar panels, and semiconductors.\(^5\)

This thesis will discuss some useful synthetic transformation to produce PAHs. These include the Heck reaction, Scholl oxidation, ring closing metathesis (RCM),
cyclization reactions and metal halogen exchange reactions.

The goal of this work was to synthesize three types of bent PAHs: (1) metal ligated bowl-shaped PAHs, (2) polymeric helicenes (azahelicene and carbohelicenes), and (3) saddlenes shown in Figure 1.2.

![Metal-embedded bowl-shaped PAH](image1)

![Carbohelicene](image2)

![Azahelicene](image3)

![Saddlene](image4)

**Figure 1.2.** Target molecules.
The generation of PAHs with a particular geometry requires functionalization of the starting material. For example, electron withdrawing or electron donating substituents influence the outcome of the Scholl oxidation reaction. The methoxy substituents can be used as para or ortho directors, as shown in Scheme 2.3. Butyl groups, on the other hand, can suppress the dimerization and enhance solubility. Although examples of Scholl oxidation on PAHs ligands have been reported in the literature, no reports were found on Scholl oxidation on metal coordinated PAHs.

The synthesis of polymeric carbohelicenes requires functionalization of the polymerization precursor 5 with vinyl substituents, which would form an arene after ring closing metathesis as shown in section 3.1.1. These vinyl substituents are strategically positioned to form aromatic ring upon RCM on the tetrabenzo-[8]-circulene precursor 5 in section 4.1. Functionalized arenes can be polymerized followed by ring formation to generate rigid PAH as described in section 3.1.

1.2 Scope and Organization

This thesis is organized into five chapters. Compounds, figures, schemes and tables are independently numbered for each chapter. The spectral data for new compounds are reported on the appendix while the spectral data for the known compounds are compared with the literature values. The references are listed at the end of each chapter. The level of theory used in computation studies to generate three-dimension structures is indicated on the captions.

Chapter 2 focuses on the chemistry toward the synthesis of bowl-shaped PAHs. The synthesis of bulky cyclopentadienyl ligands is discussed. Two different routes
toward transition metal ligated PAHs are reported here. Computational studies of C-C bond formation using Scholl oxidation are also described.

The preparation of monomers required for the syntheses of carbohelicenes and azahelicenes are described in chapter 3. This includes the synthesis of acetal protected 4,6-dibromobenzene-1,3-dicarbaldehyde, trans, trans-1,5-dibromo-2,4-dipropenyl-benzene, [5-tert-butoxycarbonylamino-2,4-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-carbamic acid tert-butyl ester.

The synthetic progress toward tetrabenzo-[8]-circulene precursors is discussed in Chapter 4, while chapter 5 holds the general conclusions of this thesis.

1.3 References


Chapter 2

The Chemistry of Graphene: Metal-Ligated Cyclopentadienide

2.1 Introduction and Background

For years, the chemistry of the cyclopentadienyl (Cp) ligand and its bulky derivatives have received much attention due to their role in the development of organometallic chemistry catalysis,\textsuperscript{1,2} and material chemistry.\textsuperscript{3} Their steric and electronic properties confer a unique stability to metal complexes.\textsuperscript{4-6} While the coordination of bulky Cp\textsuperscript{*} has been widely studied,\textsuperscript{4,5,7-11} the coordination of polycyclic aromatic hydrocarbons (PAHs) to transition metals has received less attention. There are reports of metal coordination to aromatic ligands such as indenide,\textsuperscript{12} naphthalene, and more recently, flourene.\textsuperscript{13} Nakamura and coworkers\textsuperscript{14-16} have popularized the coordination of fullerene\textsuperscript{17} to transition metals.

Our goal is to synthesize the novel bowl-shaped PAH, 1, as shown in Figure 2.1. The key feature of our PAHs is that they possess an odd number of carbon atoms. This offers a site for acidic hydrogen that can be deprotonated to provide new Cp-type anion, 2. Most of the literature\textsuperscript{18-21} precedents regarding bowl-shaped PAHs have even number of carbon atoms, which do not provide access to metal coordination.
Our attempt to synthesize bowl-shaped PAHs is reported herein. Two synthetic strategies are employed, as shown in Scheme 2.1. The initial strategy involved the synthesis of the bulky 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene (Cp**) ligand, 7, using the Heck reaction,\textsuperscript{22} which is the palladium catalyzed coupling of an aryl halide with an alkene. The ligand precursor will then be subjected to a Scholl reaction to form five new C-C bonds to afford 8. The synthesized bowl-shaped PAH 8 will be coordinated to a transition metal, 3. The second strategy involves the Heck reaction, followed by transition metal coordination. The metal complex is then subjected to Scholl reaction to form a metal coordinated PAH.
Scheme 2.1. Synthetic strategy for bowl-shaped PAHs.
The Scholl reaction is a powerful transformation that generates new aryl-aryl bonds between vertices of an arene. It is an acid catalyzed reaction that requires no functionality on the arene. Müllen and coworkers have widely used this reaction to prepare hexa-peri-hexabenzocoronene (HBC) and its derivatives, as well as other large planar PAHs. An acid, often as a Lewis acidic transition metal salt, is required for Scholl oxidation. A wide range of conditions have been reported that promote cyclodehydrogenation of arenes. Kovacics conditions, which exploit FeCl$_3$, AlCl$_3$, and CF$_3$(COO)$_2$I$_3$C$_6$H$_5$ (PIFA), with BF$_3$.Et$_2$O and MoCl$_5$ in CH$_2$Cl$_2$, have been the most popular oxidation conditions for preparation of PAHs.

King and coworkers have extensively examined the scope of the Scholl oxidation. They have established that substituents on arenes can control this often unpredictable reaction. Activating ortho, para-directing groups, for example, methoxy substituents can be used to direct the formation of bonds. Bulky substituents (e.g. tert-butyl) can effectively block dimerization or oligomerization. t-Butyl group can promote the solubility of PAHs.

Flash vacuum pyrolysis (FVP) is an established method to generate bowl-shaped PAHs. During FVP, a molecule is briefly exposed to high temperatures and low pressures. Drawbacks of using FVP include decomposition, low yields, low functional group tolerance, and often mixture products. Scott and coworkers have extensively employed this route to prepare corranulene, C$_{60}$, and other curved PAHs shown in Figure 2.2.
Figure 2.2. C<sub>60</sub> fragments synthesized using FVP method.

Dyker and Muth attempted a flash vacuum pyrolysis (FVP) route to 12, an analog of 1, as shown in Scheme 2.2. Only the fragmented products 14 and 15 were observed by mass spectrometry.  

Figure 2.2. Attempted FVP on 2-chlorophenyl-substituted cyclopentadienes.
2.2 Results and Discussions

2.2.1 Synthesis of 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene (Cp**)

The attempt to synthesize 1,2,3,4,5-penta(3,5-methoxy)phenyl-1,3-cyclopentadiene via one pot synthesis using the Lewis acid (BF$_3$.Et$_2$O or AlCl$_3$) mediated reaction of zirconacyclopentadiene with an aldehyde was ineffective (Scheme 2.3). Treatment of two equivalents of tetramethoxy tolan (provided by Gunst and Smith of Humbolt State University) with a toluene solution of Negishi reagent, generated in situ from [Cp$_2$ZrCl$_2$] and n-BuLi in toluene, afforded zirconacyclopentadiene, 17. The zirconacyclopentadiene generated was then trapped with a mixture of 3,5-dimethoxybenzaldehyde and Lewis acid. The Lewis acid of choice was BF$_3$.Et$_2$O because it was easier to handle than a highly hygroscopic AlCl$_3$, which must be freshly sublimed before use. Hydrolysis using HCl followed by a normal workup, followed by column chromatography, afforded a mixture of the target compound 18 and compound 19 as an impurity.

The mixture of 18 and 19 were difficult to separate by chromatography. Analysis using MALDI-MS and X-ray crystallography revealed the identity of the impurity as 1,2,3,4-tetrakis (3,5-dimethoxy)phenyl-buta-1,2-diene, 19. Even with rigorous exclusion of air and moisture, compound 19 was still produced. Separation methods other than column chromatography need to be investigated in order to purify the target compound prepared in this reaction.
Scheme 2.3 Tolan cyclization.

Figure 2.3 X-ray structure of 19
Another approach for preparation of pentaphenylcyclopentadiene is through the tetracyclone route, shown in Scheme 2.4. This method was developed by Ziegler and Schnell, and it is a tedious, multi-step synthesis. The reaction involves double aldol condensation of 1,2-diphenyl-ethane-1,2-dione and 1,3-diphenyl-propan-2-one to produce 2,3,4,5-tetraphenyl-cyclopenta-2,4-dienone. Compound 22 was subjected to Grignard reaction, and subsequently converted to the desired 1,2,3,4,5-pentaphenylcyclopentadiene, 23.

Scheme 2.4. The Ziegler and Schnell synthetic route for the preparation of pentaphenylcyclopentadiene.
An efficient route to functionalized cyclopentadienes was developed by Miura and Dyker, as shown in Scheme 2.5.\textsuperscript{42-44} This method allows rapid access to sterically the encumbered pentaphenylated cycloclopentadiene through one-pot, palladium-catalyzed coupling of an aryl bromide with cyclopentadiene. Reaction of zirconocene dichloride with a catalytic amount of $\text{Pd(OAc)}_2$, $\text{Cs}_2\text{CO}_3$, $\text{P-}t$-$\text{Bu}_3$, and $4-t$-butylbromobenzene in DMF at 130 °C for 3 h gave 6 in 88% yield after flash chromatography.

![Scheme 2.5. Heck reaction.](image)

2.2.2. Synthesis of 1-bromo-1,2,3,4,5-penta($4$-\textit{tert}-butyl)phenyl cyclopentadiene

To prepare 1-bromo-1,2,3,4,5-penta($4$-\textit{tert}-butyl)phenyl cyclopentadiene, 5, Gustuffson methodology was employed (Scheme 2.6).\textsuperscript{49} The 1,2,3,4,5-pentaphenyl-$1,3$-cyclopentadiene was treated with one equivalent of NBS and dibenzoyl peroxide as the radical initiator and refluxed for 1 h. After cooling, the succinimide was filtered off and washed with 1 mL portions of carbon tetrachloride. The solvent was evaporated to afford 5 in 98% yield. It is worth noting that this compound easily hydroxylated in presence of
moisture and attempt to purify it using column chromatograph afforded a 1-hydroxyl-1,2,3,4,5-penta(4-tert-butyl)phenyl cyclopentadiene.

\[
\text{H} \quad \text{NBS, dibenzoyl peroxide} \quad \text{CCl}_4, \quad 1\ h, \text{reflux} \quad 98\%
\]

\[
\text{Br}
\]

Scheme 2.6. Bromination using NBS.

2.2.3 Scholl Oxidation of 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene

Various Scholl conditions were investigated. The most promising condition used FeCl\(_3\) as the transition metal Lewis acid. Using Müllen’s methodology,\(^5\) a solution of excess FeCl\(_3\) in NO\(_2\)Me was added dropwise to a stirring solution of 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene in CH\(_2\)Cl\(_2\). The reaction mixture instantly turned deep blue and it was further stirred for 30 minutes. The solvent was evaporated and the residue was subjected to chromatographic purification to afford a new and unexpected Cp-type PAH, 22, in 77% yield (Scheme 2.7), a compound with two new aryl-aryl bonds.
Scheme 2.7. Scholl Oxidation of 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene.

The calculated 3D image of compound 22 using PM3 level of theory is shown in Figure 2.4.

Figure 2.4. The calculated 3D view of 13-(4-tert-butylphenyl)-13H-tetrakis-3,6,11,14-(4-tert-butyl)-[a,c,g,i]fluorene

Our goal was to make a bowl shaped PAH by formation of five C-C bonds on the vertices the phenyl groups on the 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene. Instead,
only 2 C-C bonds were formed. The oxidation of compound 22 under the same condition did not furnish the bowl-shaped PAHs; only the starting material was recovered.

An analogous compound, 3,6,11,14-tetramethyl-17-(p-tolyl)-17H-cyclopenta-[1,2-/3,4-']-diphenanthrene, 24 was previously synthesized by Dyker and Muth as shown in Scheme 2.8.\textsuperscript{45} They treated a solution of 1,2,3,4,5-pentakis-(4-methylphenyl)-cyclopenta-1,3-diene, 23, in CS\textsubscript{2} with 2 equivalents of AlCl\textsubscript{3} and 2 equivalents of CuCl\textsubscript{2} under argon. After stirring the mixture for 5 min followed by normal workup and chromatographic isolation, they obtained 24 in 26% yield.

\[
\text{AlCl}_3, \text{CuCl}_2 \quad \text{CS}_2, \, 5 \text{ min, R.T} \rightarrow ~ 26\%
\]

\textbf{Scheme 2.8.} Synthesis 3,6,11,14-tetramethyl-17-(p-tolyl)-17H-cyclopenta-[1,2-/3,4-']-diphenanthrene by Muth.\textsuperscript{45}

With careful control of the stoichiometric amount of the Lewis acid, as well as the reaction time, it is possible to generate only one C-C bond as shown in Scheme 2.9.
Scheme 2.9. Synthesis of 6,9-di-tert-butyl-1,2,3-tris-(4-tert-butyl-phenyl)-1H-cyclopenta[l]phenanthrene

Other Scholl reaction conditions used were MoCl$_3$ in dichloromethane, and PIFA and BF$_3$Et$_2$O in dichloromethane. Neither of these conditions generated the expected bowl-shaped PAH.

These results can be rationalized if one assumes that bonds are only formed to make six $\pi$ electron cycles. This is a likely explanation why the reaction stopped after two bonds were formed. This hypothesis is supported by calculations which, relative energies calculated using PM3 level of theory showed that isomers with bonds formed to make a six $\pi$ electron cycle were lower in energy compared to other isomers (Figure 2.4).

2.2.4. Computational Studies

To better understand this result, we turned to computational examination (PM3 level of theory) of the relative energies for all possible isomers of the C-C bond formation as shown in Figure 2.5. The calculations gave an insight on the position of C-C bond formation, which is dictated by formation of an energetically favored aromatic
Figure 2.5. Relative energy calculations of isomers using PM3 level of theory
Motivated by these findings, we then adopted a strategy to ensure all cycles could form with six \( n \) electrons. Our new synthetic strategy involved an initial coordination of a transition metal to 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene ligand, followed by Scholl oxidation. Ruthenocene or ferocene fragments on the bulky Cp ligand were desirable because of their reversible redox activity. Fullerene ferocene and ruthenocene derivatives synthesized by Nakamura and coworkers demonstrated a reversible redox activity.

**2.2.5. Transition metal embedded bulky cyclopentadienyls**

Coordination of transition metals to these bulky cyclopentadienyl ligands proved difficult using traditional synthetic procedures. Our original approach started by attempts to prepare, sodium, potassium or thalium cyclopentadienides under basic conditions, and then incorporate a metal fragment, e.g., FeCp, Mo(CO)\(_3\), Fe(CO)\(_3\), or Ru(CO)\(_2\)Cl. Attempts using a variety of conditions showed no evidence of coordination by \(^1\text{H} \) NMR and also by IR spectroscopy. This is probably due to steric hindrance by the bulky 4-tert-butylphenyl substitution of hydrogens on the cyclopentadiene. Only starting material was recovered. These reactions are summarized in Table 2.1.
The successful preparation of the pure piano stool (Cp** = 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene) compound Cp**Ru(CO)₂Br, 5, was realized using Manner’s methodology, which involved the oxidative insertion of Ru to the C-Br bond of compound 6 (Scheme 2.10). A solution of 6 (3 equivalents) in toluene was treated with Ru₃(CO)₁₀ and was allowed to reflux for 2 h. The reaction was monitored by a characteristic rapid color change from yellow to deep green color, and finally a cherry red. The high polarity of Cp**Ru(CO)₂Br permitted easy isolation by flash chromatography (20% dichloromethane in hexane Rᵣ = 0.17) to afford the target complex in 47% yield. The starting material, 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene, was always recovered in this reaction.
The Scholl oxidation precursor, 4, was synthesized by ligand exchange of bromine with a cyclopentadienyl ligand, as shown in Scheme 2.10. Compound 5 was first treated with sodium cyclopentadiene in THF and then stirred at room temperature for 18 h. The solvent was evaporated in vacuo and the intermediate then was thermolyzed at 180 °C under 30 mTorr vacuum for 6 h to displace the two CO ligands. The resulting tan solid was subjected to chromatographic separation to afford 3 in 81% yield. This procedure is a modification of an original synthesis by Macvey and Paulson. 47 The compound was obtained as a yellow, air stable complex after column chromatography.
The IR spectrum revealed carbonyl stretches, possibly from unreacted starting material or other byproducts.

The deprotonated complex 4 possesses delocalized $6\pi$ electrons in the central core. This should permit the Scholl reaction to proceed to completion, as the central electrons are not localized. The attempted Scholl oxidation of compound 3 using FeCl$_3$ in dichloromethane and CF$_3$(COO)$_2$C$_6$H$_5$ (PIFA), with BF$_3$.Et$_2$O in dichloromethane did not, however, generate the expected metal-coordinated bowl-shaped PAH (Scheme 2.11). Instead, dimerization products and starting material were observed on MALDI-MS spectrum shown in Figure 2.9. We hypothesized that dimerization could be suppressed by the replacement of cyclopentadiene ligand with pentamethylcyclopentadiene.

![Diagram of complex 4](image)

4 a. (i) FeCl$_3$, NO$_2$Me, CH$_2$Cl$_2$, 30 min
   (ii) PIFA, BF$_3$.Et$_2$O, CH$_2$Cl$_2$, 3 h

Scheme 2.11. Attempted synthesis of metal-coordinated bowl-shaped PAH ($t$-butyl omitted for clarity).

2.3 Conclusion

The synthesis of 19 failed because it could not be isolated from 18 using chromatography. Other separation methods have to be considered. However, the
synthesis of 6 was achieved by a single step Heck reaction. Scholl reaction of compound 16 did not generate the fully-fused compound 1, but two new PAHs, but rather the partially-fused fragment, 22, and 25. The necessity to form a 6 π electron ring could explain why the oxidation stopped at two bonds. Computational studies showed that isomers with bond formation to generate 6 π electron ring were lower in energy, an observation that was consistent with the experimental data.

A new strategy employed to ensure the formation of 6 π electron ring was by metal coordination of 6. Direct metal coordination to 6 proved difficult. An improved strategy involved bromination of 6 followed by coordination to ruthenium was successful. Metal ligand exchange with sodium cyclopentadiene afforded a new ruthenocene 3. Scholl oxidation of 3 was not successful. Instead, dimerization products were observed by MALDI-MS as shown in Figure 2.6. It may be possible to suppress dimerization by replacing the cyclopentadiene ligand with pentamethylcyclopentadiene ligand.

Figure 2.6. MALDI-MS spectrum for the attempted Scholl oxidation of 3
2.4 Experimental

General Methods

All reactions were carried out under an atmosphere of dry nitrogen in oven dried glassware with standard Schlenk or vacuum-line techniques. Reactions were monitored by TLC, GC/MS, and NMR. GC/MS was performed on a Varian CP-3800 GC with a Saturn 2200 MS system. Compounds were separated by column chromatography using 60 mesh silica gel. $^1$H and $^{13}$C NMR spectra were recorded on General Electric QE-300 MHz, Varian 400MHz spectrometer, or Varian 500 MHz spectrometer. IR was recorded on Perkin Elmer Spectrum 2000.

Cp**RuCp (3)

A solution of 22 (351mg, 0.0323 mmol), NaCp (0.265 mL, 2.21 M in THF) in THF (10 mL) was stirred for 18h at room temperature. The solvent was removed in vacuo, resulting to a brown solid and then heated at 200 °C under vacuum (60 mTorr) for 6 h. After cooling, the residue was extracted with hot benzene to produce a dark purple solution. The product was isolated by chromatography using 20% dichloromethane in hexane ($R_f = 0.42$) as the eluent to afford 262 mg 81% yield of the title compound. $^1$H NMR (500MHz, CDCl$_3$): $\delta$ 1.24 (s, 45H), 6.93(d, 10 H), 7.06(d, 10 H. $^{13}$C NMR (125 MHz, CDCl$_3$): 31.6, 34.5, 76.2, 93.9, 123.7, 132.4, 133.0, 148.6 ppm. IR (NaCl thin film) 2962.99, 2866.52, 1519.98, 1494.67, 1463.71, 1393.39, 1362.38, 1268.27, 836.94 cm$^{-1}$. MALDI-TOF ($m$/$e$) 892.38. Anal calcd for C$_{60}$H$_{70}$Ru mol. Found C, 80.47, H, 7.90.
**Cp**\(\text{Ru(CO)}_2\text{Br} \ (5)\)

A mixture of \(17\) (58 mg, 0.072 mmol) and \(\text{Ru}_3(\text{CO})_{10}\) (15 mg, 0.024 mmol) in toluene (15 mL) were refluxed for 2 h under \(\text{N}_2\) atmosphere. The reaction turns from yellow to deep green and finally to cherry red as an indication that reaction went to completion. The solvent was removed followed by chromatographic purification (20% dichloromethane in hexane, \(R_f = 0.17\)) to give \(\text{Cp}**\text{rutheniumdicarbonylbromide}\) in 67% (44 mg) yield. \(\text{H NMR (400 MHz, CDCl}_3\text{):} \delta 1.24 \ (s, 45 \text{ H}), 6.92 \ (d, 8.2 \text{ Hz, 10 H}), 7.06 \ (d, 8.6 \text{ Hz, 10 H}).\)

\(\text{C NMR (500 MHz, CDCl}_3\text{):} \delta 197.4, 151.9, 132.2, 127.0, 124.6, 106.5, 34.8, 31.4.\) IR (NaCl thin film): 2\(\text{CO}: 1992.26, 2040.30 \text{ cm}^{-1}.\) Anal Calcd for C\(_{57}\)H\(_{65}\)BrO\(_2\)Ru; C, 71.08, H, 6.80, Found C, 70.99, H, 6.84

**1-hydroxyl-1,2,3,4,5-penta(4-tert-butylphenyl)cyclopentadiene**

In a Schlenk flask, a mixture of 1,2,3,4,5-pentaphenyl(4-tert-butyl)-1,3-cyclopentadiene (0.40 g, 0.55 mmol), \(N\)-bromosuccinimide (102 mg, 0.58 mmol), and dibenzoyl peroxide (2 mg) in 20 mL \(\text{CCl}_4\) was refluxed for 1 h. After cooling to room temperature, succinimide was filtered off and washed with \(\text{CCl}_4\). The solvent was evaporated and run through a silica column to followed by recrystallization in ethanol hydrolyzed 23 to afford 1-hydroxyl-1,2,3,4,5-penta(4-tert-butylphenyl)cyclopentadiene as a yellow compound in 70% (295 mg). \(\text{H NMR (500MHz, CDCl}_3\text{):} \ 1.20 \ (s, 18 \text{ H}), 1.25 \ (s, 18 \text{ H}), 1.28 \ (s, 9 \text{ H}), 6.90 \ (d, 8.4 \text{ Hz, 4 H}), 6.98-7.04 \ (m, 8 \text{ H}), 7.10 \ (d, 8.4 \text{ Hz, 2 H}), 7.26 \ (d, 8.6 \text{ Hz, 2 H}), 7.56 \ (d, 8.4 \text{ Hz, 2 H}).\) \(\text{C NMR (125 MHz, CDCl}_3\text{):} \ 31.4, 31.5, 31.6, 34.6, 34.7, 90.2, 124.7, 124.8, 125.0, 125.4, 129.1, 129.7, 131.2, 133.1, 142.5, 147.0, 149.5, 149.8 \text{ ppm.}\) Anal calcd for C\(_{55}\)H\(_{66}\)O, C, 88.89; H, 8.95. Found C, 88.51; H, 8.97.
1-bromo-1,2,3,4,5-penta(4-tert-butylphenyl)cyclopentadiene (6)

In a Schlenk flask, a mixture of 1,2,3,4,5-pentaphenyl(4-tert-butyl)-1,3-
cyclopentadiene (0.40 g, 0.55 mmol), N-bromosuccinimide (102 mg, 0.58 mmol), and
dibenzoyl peroxide (2 mg) in 20 mL CCl₄ was refluxed for 1 h. After cooling to room
temperature, succinimide was filtered off and washed with CCl₄. The solvent was
evaporated to afford the title compound as a yellow compound in 70% (295 mg). ¹H
NMR (CDCl₃, 500 MHz): δ 1.21 (s, 18 H), 1.23 (s, 18 H), 1.29 (s, 9 H), 6.85-6.89 (m, 8
H), 7.01 (d, 8.4 Hz), 7.07 (d, 8.6 Hz), 7.21 (d, 8.6 Hz), 7.38 (d, 8.4 Hz). ¹³C NMR
(CDCl₃) δ 31.5, 31.5, 31.5, 34.6, 34.7, 124.3, 124.3, 124.6, 125.1, 127.31, 129.9, 130.1
131.6, 132.6, 133.9, 141.9, 147.3, 149.6, 149.6, 149.88, 150.8. IR (NaCl thin film)
2962.51, 2866.07, 1607.44, 1495.00, 1404.2, 1363.28, 1268.41, 1202.43, 1117.24,
1050.24, 1017.32, 825.66 cm⁻¹. Anal Calcd for C₅₅H₆₅Br: C, 81.96; H, 8.13; Br, 9.91.
Found: Not measured.

1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene (16) (previously reported compound⁴⁴)

In the glove box, Cp₂ZrCl₂ (114 mg, 0.393 mmol), 4-tert-butylbromobenzene
(1.00 g, 4.17 mmol), Cs₂CO₃ (1.5137 g, 4.717 mmol), Pd(OAc)₂ (22 mg, 0.0983 mmol),
P₂Bu₃ (5.00 mL, 2.00 mmol) and 15 mL DMF were combined in a Schlenk tube. The
contents were then heated to 130 °C in an oil bath for 1 h, forming a creamy brown
precipitate settled at the bottom. The Schlenk tube and its contents were then cooled to
room temperature and exposed to air. CH₂Cl₂ (150 mL) was then added, followed by p-
toluenesulfonic acid (1.811 g, 9.434 mmol). This was stirred at room temperature for 15
min, and then passed through a column of silica gel to yield a brown solution. The
column was additionally rinsed with small portions of CH₂Cl₂ until the washings were
colorless (~10 mL each). The solvent was then removed under vacuum (60 mTorr at 60 °C) to give a brown tar. The solid was dissolved in CHCl₃ (150 mL) and extracted with saturated aqueous NaHCO₃ solution (3 × 150 mL) and saturated aqueous NaCl solution (3 × 150 ml). The organic layer was dried over MgSO₄ and passed through a column of silica gel to give a brown solution. The solvent was removed under vacuum and the oily solid washed with hexanes until the washings were colorless, yielding 1a as a yellow solid (252.2 mg, 88% yield) CDCl₃: ¹³C NMR CDCl₃: δ 151.2, 150.8, 150.10, 148.2, 146.1, 139.0, 137.4, 136.6, 125.3, 124.7, 123.8, 120.9, 120.3, 120.2, 63.8, 35.3, 35.07, 33.0, 32.4, 32.0, 31.5. MALDI-TOF. MS 726.5 Calculated for C₅₅H₆₆ C, 90.85; H, 9.15. Found C, 90.83; H, 9.24

13-(4-tert-butylphenyl)-13H-tetrakis-3,6,11,14-(4-tert-butyl)-[a,c,g,i]fluorene (22)

A Schlenk flask containing a magnetic stirrer was charged with 16 and 10 mL of dry CH₂Cl₂. Under N₂ atmosphere, a solution of anhydrous FeCl₃ dissolved in CH₃NO₂ (5 mL) was added dropwise using a syringe. After 30 min, the solvent was evaporated and the crude product was chromatographed in hexane/CH₂Cl₂ in 4:1 ratio affording a yellow solid in 34% yield. ¹H NMR (500MHz, CDCl₃): δ 1.20 (s, 9H), 1.49 (s, 18H), 1.58 (s, 18H), 5.79 (s, 1H), 7.15-7.22 (m, 4H), 7.56 (dd, 1.76 Hz, 1.2 Hz, 2H), 7.74 (dd, 1.76 Hz, 8.6 Hz, 2H), 8.04 (d, 8.6 Hz), 8.72-8.78 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): 149.3, 148.3, 148.3, 144.7, 138.2, 136.4, 131.7, 130.6, 128.5, 127.9, 127.3, 126.5, 125.9, 125.1, 124.6, 123.4, 119.2, 118.9, 54.7, 35.4, 35.4, 34.6, 31.8, 31.7, 31.5 ppm. IR: 2963.23, 2905.41, 2868.77, 1514.47, 1505.52, 1478.72, 1463.95, 1362.86, 1262.38, 908.82, 822.66, 735.29, 600.50 cm⁻¹. MALDI TOF: MS 722.5 (100%). Anal calcd for C₅₅H₆₂ C, 91.36; H, 8.64 found C, 91.51; H, 8.44
6,9-di-tert-butyl-1,2,3-tris-(4-tert-butyl-phenyl)-1H-cyclopenta[l]phenanthrene (25)

A Schlenk flask containing a magnetic bar was charged with 16 and 10 mL of dry CH₂Cl₂. Under N₂ atmosphere, a solution of anhydrous FeCl₃ dissolved in CH₃NO₂ (5 mL) was added dropwise using a syringe. After 30 min, the solvent was evaporated and the crude product was recrystallized in methanol to afford white needle-like crystals. ¹H NMR (500MHz, CDCl₃): 1.20(s, 9H), 1.21(s, 9H), 1.44(s, 9H), 1.44 (s, 9H), 1.45 (s, 9H), 5.41(s, 1H), 7.00-7.04 (m, 4 H), 7.14-7.18 (m, 4 H), 7.22-7.88 (m, 8 H), 8.65 (s, 1 H), 8.71 (s, 1 H). ¹³C NMR (125 MHz, CDCl₃) 31.3, 31.5, 31.6, 31.7, 34.5, 34.5, 34.9, 35.1, 35.2, 57.5, 118.7, 118.8, 124.0, 118.3, 124.5, 124.9, 125.6, 126.1, 126.5, 126.9, 128.2, 128.8, 129.3, 129.4, 130.4, 130.3, 132.3, 132.9, 133.0, 136.3, 136.9, 138.2, 141.4, 142.5, 147.6, 148.7, 148.5, 149.0, 150.5 ppm. MALDI TOF: 724.5. Anal calcd for C₅₅H₆₄ C, 91.10; H 8.90 Found: not measured

2.5. References


(44) Miura, M.; Pivsa-Art, S.; Dyker, G.; Heiermann, J.; Satoh, T.; Nomura, M.


Chapter 3

Toward Extended Polymeric Helicenes: Monomer Synthesis

3.1 Introduction and Background

Polymeric helicenes are promising synthesis targets. Molecular dynamics calculations on spring-like polymeric helicenes have demonstrated their potential to serve as pH-driven artificial muscles. Protonation of the basic sites, which could be incorporated on the periphery of the helix, should cause a reversible expansion of 160%. Polymeric helicenes might also be used as a molecular sensors. Computer studies have also shown that nitratated arenes can be intercalated into a carbohelicene causing it to expand. These results sparked our interest in the synthesis of two types of polymeric helicenes: the aza-helicene 4 and the carbo-helicene 12. This chapter focuses on the synthesis of monomers required for the synthesis of these two types of helicenes.

Helicenes are aromatic, non-planar, chiral structures with a helical shape. They are a part of a larger family called polycyclic aromatic hydrocarbons (PAHs). The first helicene synthesized is the nitrogen containing diaza[5]helicene synthesized by Meisenheimer and Witte in 1903. Over a half century later, Newman and Lednicer obtained 6[helicene] in enantiopure form. Recent reports have demonstrated the synthesis of oligothiophenes by means of incorporation of sulfur atoms in the helicene. In 2002, Han et al synthesized a heliphene, based on a biphenylene, by the double cyclotrimerization catalyzed by cobalt. The largest helicene reported was produced by Martin and Baes in 1975, which consisted of 14 benzene units and was synthesized by photocyclization methodology. Other synthetic route such as Diel-Alder, or tandem...
radical cyclization\textsuperscript{15} have been used to produce small helicenes. Although these approaches have been effective in the synthesis of smaller helicenes, attempts have not been successful in producing larger helicenes. Due to these shortcomings, new routes are needed for the production of large polymeric helicenes.

During the effort to planarize poly-$p$-phenylene (PPP), Tours and coworkers\textsuperscript{16} designed a new synthetic strategy. Their route involved the stepwise polymerization using Suzuki or Stille coupling of two monomers (Figure 3.1).

![Monomer A and Monomer B](image)

\[ M = \text{Sn(Bu)}_3 \text{ or } \text{B(OH)}_2 \]

**Figure 3.1.** Tours step polymerization monomers

In this method, monomer A, which is a boc-protected amine, was polymerized with monomer B, an acetal-protected dialdehyde, to formed a poly-$p$-phenylene. This was followed by deprotection and subsequent imine bridge formation, which formed planar conjugated PPP derivatives. We synthesized isomers of monomer A and monomer B, which would be polymerimerized followed by imine bridge formation to generate large polymeric azahelicenes (Scheme 3.1).
The use of ring-closing metathesis (RCM) to generate arenes is a new method for synthesizing new PAHs. A recent report by King and coworkers\textsuperscript{17} showed that RCM using Grubbs' 2\textsuperscript{nd} generation catalyst\textsuperscript{18,19} provides arenes. In 2006, Collins and coworkers reported the synthesis of [5]-helicenes and [6]- and [7]-helicene by RCM.\textsuperscript{20} The reversibility\textsuperscript{21} of the RCM reaction is highly desirable because it generates the thermodynamically favored PAHs.

Scheme 3.1. Synthetic strategy for azahelicenes
Our research is focused on using RCM to synthesize a large polymeric carbohelicene. The structure of poly-(2,4-dipropenyl) m-phenylene determines the structure of the helicene (Scheme 3.2). My research also involved the synthesis of a pure trans, trans-
1,5-dibromo-2,4-dipropenyl-benzene with dipropenyl functionalities for the synthesis of carbohelicenes.

3.2 Results and Discussions

3.2.1 Synthesis of \textit{trans, trans}-1,5-Dibromo-2,4-dipropenyl-benzene

The route examined in the synthesis of \textit{trans, trans}-1,5-dibromo-2,4-dipropenyl-benzene toward 5, which is needed for coupling reaction to form carbohelicenes, is delineated in Scheme 3.3 and Scheme 3.4. The first step involved electrophilic aromatic bromination of \textit{m}-xylene using Schlüter’s method which afforded 2,4-dibromo-\textit{m}-xylene 9 upon recrystallization with ethanol (Scheme 3.3).\textsuperscript{22} The procedure to synthesize compound 10 was developed by Margel Bonifacio in King Group. It involved further allylic bromination of 2,4-dibromo-\textit{m}-xylene to afforded 1,5-dibromo-2,4-bis-dibromomethyl-benzene 10 in 92\% (45g) yield. Hydrolysis of 10 to 1,5-dibromo-2,4-bis-benzaldehyde was achieved using silver nitrate in ethanol.\textsuperscript{23} The dialdehyde was further protected by treatment with ethylene glycol and \textit{p}-toluene sulfonic acid in benzene under reflux to afford 11 after normal workup. This compound was previously synthesized and characterized by David Pearson in the King Group.
Scheme 3.3. Preparation of acetal protected 1,5-dibromo-2,4-bis-benzaldehyde

Formation of 1 was qualitatively monitored by the precipitation of heavy dark-green silver bromide at the bottom of the flask. Silver bromide was filtered and evaporation of the filtrate gave a white residue. The white residue was washed with copious amounts of water until neutral pH was achieved. The white solid was recrystallized in ethanol to afford dialdehyde 3 in near quantitative yield (7 g, 94%).

An efficient route to a key intermediate to polymeric carbo-helicene was developed as shown in Scheme 3.4. The precedent for this route was developed by Padwa and coworkers\textsuperscript{25} to prepare (\textit{E})-1-(propen-1-yl)-2-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl) benzene. Using their procedure as model, previously synthesized 1,5-dibromo-2,4-bis-benzaldehyde was subjected to Grignard reaction to afford diol 12 as a mixture of stereoisomers in excellent yields. The diol was subsequently dehydrated using
a KHSO₄, P₂O₅, and 4-tert-butyl catechol (added to inhibit polymerization) heated in a sand bath at 230 °C under a pressure of 100 mm Hg. The product formed within 15 minutes and it was collected via distillation and recrystallized from ethanol afforded 5 (44 %).

![Scheme 3.4. Grignard reaction to make 12 followed dehydration to give 5 in 44%.](image)

Other elimination conditions are summarized in Table 3.1 and did not furnish the title compound and mostly starting material was recovered.

**Table 3.1** The attempted dehydration of 1-[2,4-dibromo-5-(1-hydroxy-propyl)-phenyl]-propan-1-ol.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Condition</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TsOH, toluene, 130°C</td>
<td>Recovered starting material</td>
</tr>
<tr>
<td>2</td>
<td>KHSO₄, toluene, reflux</td>
<td>Recovered starting material</td>
</tr>
<tr>
<td>3</td>
<td>KHSO₄, DMSO, reflux</td>
<td>Recovered starting material</td>
</tr>
<tr>
<td>4</td>
<td>KHSO₄, P₂O₅, <em>tert</em>-butyl-catechol, 230°C</td>
<td>44% of 5 isolated</td>
</tr>
</tbody>
</table>
3.2.2. Attempted isomerization using Grubbs’ 2nd generation catalyst

Attempts to isomerize cis and trans isomers 5, 13, and 14 using Grubbs second generation catalyst failed. Our initial idea was to utilize the thermodynamic control of this reaction to give the most stable trans-trans isomer 5. Mixtures of compounds were treated with Grubb’s second generation and octane in CH2Cl2 (Scheme 3.5). The reaction was stirred overnight at room temperature. The GC-MS chromatogram shows a mixture of products with masses of multiples of 14 amu higher or lower than the expected ion (m/z = 372 Figure 3.2).
This is due to the migration of methylene units via isomerization and cross metathesis. Wagener and coworkers\textsuperscript{28} reported that extensive olefin isomerization of both internal and terminal olefins at temperatures of 50 – 80 °C can be caused by Grubbs’ second-generation catalyst. Olefin isomerization occurs in two steps as shown in Scheme 3.6; first, the double bond moves along the alkyl chain followed by metathesis. Recent work by Grubbs and coworkers\textsuperscript{29} showed that additives can be used to prevent undesirable products.
Scheme 3.6. Proposed mechanism for the observed mixture of products from during olefin isomerization reaction.

3.2.3. Computational studies

Computational studies using B3LYP6-31g* of the relative energies of the cis-cis, cis-trans, and trans-trans isomers revealed that trans-trans isomer was the favored. The cis-cis isomer was 7.5 kcal/mol higher than the trans-trans and the cis-trans was 6.08 kcal/mol higher than tran-trans isomer. 30

3.2.4 Synthesis of (diboron) [5-tert-butoxycarbonylamino-2,4-bis-(4,4,5,5-
tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-carbamic acid tert-butyl ester

Aza-helicene requires a nitrogen containing monomer 15. A route developed to prepare 15 is shown in Scheme 3.7. The first step involved Field’s methodology 26 of electrophilic aromatic substitution by slow addition of 1:1 ratio of concentrated nitric acid and concentrated sulfuric acid to commercially available 1,3-dibromo benzene. 26 The difficulty with is reaction was overnitration of 16 to produce small amounts of 1,3-dibromo-2,4,6-trinitrobenzene. However, recrystallization using ethanol gave pure 16.

CAUTION! Dinitro and trinitrobenzenes are potentially explosive and should be handled
only wet. Compound 13 was successfully reduced by addition of iron powder, and acetic acid in ethanol affording 2 in 77% (2.9 g) yield. Subsequent protection of the amine group using Boc was achieved by treatment of 2 with sodium hydride in THF followed by addition of di-tert-butyl dicarbonate and the reaction mixture was refluxed overnight. 

![Chemical structure](image)

**Scheme 3.7.** Synthesis of 17 needed for Suzuki coupling.

It was difficult to protect aryl amines with boc-group because of the reduced nucleophilicity of the aryl nitrogen atom compared to primary and secondary aliphatic amines. The reduced nucleophilicity mandated that the amine be deprotonated. This, however, resulted in double protected amine 19, as shown in Scheme 3.8.
Darnbrough and coworkers\textsuperscript{27} have previously reported similar observations. To solve this problem, they used potassium carbonate in methanol to selectively remove a single boc group, as shown in Scheme 3.8. In a simpler approach, we successfully synthesized 17 by using 2 equivalents of NaH as opposed to excess NaH used in the literature. Other attempts to protect 2 gave doubly protected products and are summarized in Table 3.2.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Condition</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>acetic anhydride, DMAP, pyridine</td>
<td>double protection</td>
</tr>
<tr>
<td>2</td>
<td>di-\textit{t}-butyldicarbonate, DMAP, THF, reflux, 24h</td>
<td>double protection</td>
</tr>
<tr>
<td>3</td>
<td>di-\textit{t}-butyldicarbonate, 10% TEA, methanol, 40-50°C</td>
<td>starting material</td>
</tr>
</tbody>
</table>

The functionalized monomer 15 was synthesized using Tour’s conditions.\textsuperscript{16} This was accomplished by tetralithiation of 14 by use of MeLi to deprotonate the amine protons
followed by metal halogen exchange using tert-butyllithium. The tetralithio species shown in Figure 3.3 was quenched with isopropyl pinacol borate to afford 9.

![Figure 3.3. Tetralithio intermediate.](image)

This compound was purified by flash chromatography containing a mixture of activated charcoal and celite as stationary phase and dichloromethane as the mobile phase. Recrystallization using in ethanol gave pure 15 in 17 % (34 mg). This provides with one of the monomers used for the step polymerization step toward aza-helicenes.

### 3.3 Conclusion

*trans, trans*-1,5-Dibromo-2,4-dipropenyl-benzene, 5, which is needed for the coupling reaction to form carbohelicenes, was successfully synthesized using Grignard reaction of 1 followed by dehydration. Olefin isomerization using Grubbs' catalys 13, 14, and 5 gave a homologous mixture of inseparable products.

The synthesis of monomer 15 proceeded in low yields. The synthesis involved a tetralithiation of 16 with subsequent quenching with isopropyl pinacol borate to afford the target compound 17. The isolation of the product needs improvement. Having successfully synthesized monomer 5 and 17 at hand, it is possible to synthesize larger polymeric helicenes.
3.4 Experimentals

General Methods

All reactions were carried out under an atmosphere of dry nitrogen in oven dried glassware with standard Schlenk or vacuum-line techniques. Reactions were monitored by TLC, GC/MS, and NMR. GC/MS was performed on a Varian CP-3800 GC with a Saturn 2200 MS system. Compounds were separated by column chromatography using 60 mesh silica gel. $^1$H and $^{13}$C NMR spectra were recorded on General Electric QE-300 MHz, Varian 400MHz spectrometer, or Varian 500 MHz spectrometer.

4,6-dibromobenzene-1,3-dicarbaldehyde (1)  (previously reported compound$^{23}$)

To a solution of 1,5-dibromo-2,4-bis(dibromomethyl)benzene (15.1g, 0.027 mol) in 95% ethanol (625 mL) was added a solution of AgNO$_3$ (19.2 g, 0.113 mol) in water (125 mL), and the mixture was stirred at reflux for 30 min. The solution was allowed to cool, green AgBr was filtered off, and the cake was washed with 95% ethanol (320 mL). The filtrate was evaporated to dryness under reduced pressure. The residue was washed with copious amounts of water until neutral and dried in vacuo to yield 4,6-dibromobenzene-1,3-dicarbaldehyde (7.21 g, 94%) as a white solid. Spectra were identical to those reported previously.$^{23}$ $^1$H NMR (CDCl$_3$): $\delta$ 10.32 (s, 2H), 8.39 (s, 1H), 8.04 (s, 1H. EI-MS: m/z 291.0.

1,5-diamine-2,4-dibromobenzene (2)  (previously reported compound$^{26}$)

To a stirred solution of 1,5-dibromo-2,4-dinitrobenzene(0.5 g 0.0015 mol) in ethanol, iron powder(1.41 g, 0.025 mol) and acetic acid (1.38 mL) were added in turn. The mixture was refluxed for 5.5 h and the formation of the product was monitored by TLC (hexane:ethyl acetate 4:1 $R_f = 0.26$). The mixture was filtered through celite and washed
with ethanol (1 L). Sodium hydroxide (25%) was added to the filtrate until a pH of 12 was achieved. The basic solution was filtered through celite and the solvent was reduced to give a brown residue. The residue was extracted with diethyl ether (3 x 200 mL) and the combined ether extract were dried over MgSO$_4$ and removed \textit{in vacuo} to give a orange product (0.31g, 75%). Spectra were identical to those reported previously.

\textit{trans, trans-1,5-dibromo-2,4-dipropenyl-benzene (5)}

A mixture of 4 (3.50 g, 9.94 mmol), KHSO$_4$ (0.414 g, 3.04 mmol), P$_2$O$_5$ (0.178 g, 1.25 mmol), and 4-\textit{tert}-butyl catechol (1.50 mg, 8.95 μmol) was heated in a sand bath at 230 °C under a pressure of 100 mm Hg with the 100 round bottom flask and short path condenser covered with aluminum foil. When no more distillate could be collected, the crude product in the receiver was extracted with diethyl ether and the condenser washed with diethyl ether. Combination of the ether solutions followed by removal of the solvent and recrystallization in ethanol affording 5 (1.39 g, 44 %) as a white solid. mp 74 – 75 °C. $^1$H NMR (CDCl$_3$): $\delta$ 7.69 (s, 1H), 7.54 (s, 1H), 6.64 (dq, $J$ = 1.57, 15.99 Hz, 2H), 6.21 (dq, $J$ = 6.85, 15.59 Hz, 2H), 1.92 (dd, $J$ = 6.65, 6.65 Hz, 6H). $^{13}$C NMR (CDCl$_3$): $\delta$ 136.93, 135.76, 129.39, 129.14, 124.365, 121.12, 18.65. IR (thin film, cm$^{-1}$): 3427.03, 3038.07, 2912.38, 1652.65, 1441.76, 1368.14, 1043.97, 1010.60, 956.63, 889.13. EI-MS: m/z 316.0. UV (acetonitrile, nm): $\lambda_{\text{max}}$ 254 (ε 48,000). Anal. Calcd. for C$_{12}$H$_{12}$Br$_2$: C, 45.61; H, 3.83. Found: C 45.43, H 3.66.

\textit{4,6-dibromo-m-xylene (9) (previously reported compound$^{31}$)}

In a 250 mL round bottom flask, bromine (154.3 g, 0.965 mol) as added dropwise over a period of 30 min to a stirred iced-cold solution of m-xylene(50.0 g, 0.491 mol) and iodine (0.596 g, 0.00235 mol) under rigorous exclusion of light. After stirring for 1 d at room
temperature, 20% of KOH solution (400 mL) was added until the color disappeared. The aqueous solution was decanted and the white solid was washed twice with distilled water. The residue was recrystallized from ethanol to afford white crystals (39.6 g, 32%). Spectra were similar to those reported previously.\(^{31}\) H NMR (CDCl$_3$): $\delta$ 7.68 (s, 1H), 7.10 (s, 1H), 2.31 (s, 6H)

**1,5-dibromo-2,4-bis(dibromomethyl)benzene (10) (previously reported compound\(^{23}\))**

To a 1 L, three-neck round bottom flask charged with a magnetic stirrer, 22.5 g, 0.852 mol of 4,6-dibromo-$m$-xylene, CH$_2$Cl$_2$ (520 mL), bromine (54.5 g, 0.341 mol) were added and the reaction mixture was radiated with 500 W lamp. The reaction was stirred for 5 h and two more equivalents of bromine (27.2 g, 0.170 mol) were added and stirring continued for 1 d. The solvent was evaporated and the resultant solid was recrystallized with hexane to afford a tan solid (49.3 g, 92%). Spectra were identical to those reported previously.\(^{23}\) H NMR (CDCl$_3$): $\delta$ 8.66 (s, 1H), 7.71 (s, 1H), 6.97 (s, 2H). EI-MS: $m/z$ 499.0

**Acetal protected 4,6-dibromobenzene-1,3-dicarbaldehyde (11) (previously reported compound\(^{32}\))**

To a solution of 4,6-dibromobenzene-1,3-dicarbaldehyde in benzene (10 mL), ethylene glycol (0.286 g, 5.13 mmol), $p$-toluenesulfonic acid monohydrate (0.038 g, 0.342 mmol) were added to the mixture and refluxed for 4 h. Solvent was removed under vacuum and the residue was treated with water (50 mL). The organic layer was extracted in ether (3 $\times$ 30 mL) and dried over MgSO$_4$ to afford the target compound **11** as a white solid (0.599 g, 92%) Spectra were identical to those reported previously.\(^{32}\) H NMR (C$_6$D$_6$) $\delta$: 8.18 (s, 1H), 7.56(s, 1H), 6.00(s, 2H), 3.34-3.52 (m, 8H); $^{13}$C NMR (C$_6$D$_6$) $\delta$:
137.40, 137.19, 127.89, 124.79, 102.71, 65.61; EI-MS (m/z): 379, 73; UV(methanol, nm) 
n: 207(ε 39000) 220(ε 20000); Anal Calcd for C_{12}H_{12}Br_{2}O_{4}: C, 37.93 H, 3.18. Found. Not measured. EI-MS: m/z 379.0.\textsuperscript{32}

1-{2,4-dibromo-5-(1-hydroxy-propyl)-phenyl}-propan-1-ol (12)

Ethyl magnesium bromide (22.3 mL, 67.0 mmol) was added dropwise to a solution of 3 (8.50 g, 29.1 mmol) in diethyl ether (300 mL) cooled in an ice bath. The reaction mixture was stirred overnight at room temperature before quenching with saturated NH\textsubscript{4}Cl solution and then extracted with ether. The ether layer was washed three times with water and dried over MgSO\textsubscript{4}. The solvent was removed in vacuo to give 12 (9.36 g, 91\%) as a mixture of stereoisomers. mp 130 – 132 °C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): δ 7.78-7.51 (s, 2H), 4.84 (dd, J = 4.20, Hz, 2H), 4.65 (d, J = 4.22, 9.15 Hz, 2H), 4.23–3.28 (br, 2H), 1.80–1.54 (m, 4H), 0.99 (t, 6H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}): δ 143.4, 135.8, 125.9, 120.9, 74.1, 30.8, 10.3. EI-MS: m/z 277.0. UV (acetonitrile, nm): λ\textsubscript{max} 207 (ε 82,200). IR (thin film, cm\textsuperscript{-1}): 3374.84, 2965.11, 1652.22, 1549.04, 1451.12, 1369.43, 1206.80, 1109.61, 1109.61, 1038.90, 1038.90, 867.88, 733.95. Anal. Calcd. for C_{12}H_{16}Br_{2}O_{2}: C, 40.94; H, 4.58. Found: C 40.65, H 4.68.

1,5-dibromo-2,4-dinitrobenzene (16) (previously reported compound\textsuperscript{26})

To a 250 mL round bottom flask, 1,3-dibromobenzene (5.7 g, 0.024 mmol) was added slowly to a stirred mixture of 5.3 mL of conc. H\textsubscript{2}SO\textsubscript{4} and 5.3 mL of fuming HNO\textsubscript{3} cooled in an ice bath. The rate of addition was such that a temperature of 10-20 °C and the temperature was maintained between 35-40 °C for 40 min after the addition was complete. The reaction mixture was then stirred in excess crushed ice until yellow solid formed. The solid was filtered and washed with water until the filtrate was neutral. The
The product was recrystallized from ethanol:acetone (90:10) to give yellow crystalline product in (6.9 g, 77%) yield. Spectra were identical to those reported previously.

**N,N’-Bis(tert-butoxycarbonyl)-1,5-diamino-2,4-dibromobenzene (17) (previously synthesized compound)**

To a solution of sodium hydride (0.19 g, 7.74 mmol) in THF (35 mL) was added 1,5-diamino-2,4-dibromobenzene (1.00 g, 3.77 mmol). The mixture was heated at reflux for 1 h and then cooled to room temperature. Di-tert-butyl dicarbonate (0.22 g, 2.0 mL, 6.18 mmol) was added and the mixture was stirred overnight at reflux. The reaction was cooled to room temperature and carefully quenched with water. This mixture was extracted with ether (3 × 100 mL). The combined organic layers were washed with saturated ammonium chloride solution and saturated sodium bicarbonate solution. The washings were dried over sodium sulfate and the solvent was removed *in vacuo*. The crude material was purified by flash chromatography [silica gel, hexane:ether (20:1)] to afford 0.314 g (18%) of the title compound as an white solid. $^1$H NMR (C$_6$D$_6$) $\delta$: 9.678 (s, 1H), 7.251 (s, 1H), 6.896 (s, 2H), 1.356 (s); $^{13}$C NMR (C$_6$D$_6$) $\delta$: 152.12, 137.41, 134.61, 111.74, 105.50, 81.40, 28.44

**[diboron][5-tert-butoxycarbonylamino-2,4-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-carbamic acid tert-butyl ester (18)**

To a solution of 1,5-diamino-2,4-dibromobenzene (1.00 g, 2.15 mmol) in ether (5 mL) at room temperature was added dropwise methylithium (2.58 mL, 6.45 mmol, 2.5 M in ether) and the solution was stirred for 20 min. The mixture was cooled to −78 °C, tert-butyl lithium (7.58 mL, 12.9 mmol, 1.71 M in pentane) was added, and then the temperature was raised to 0 °C (ice bath) for 3 h. To this solution was added isopropyl
pinacol borate (3.07 mL, 15.05 mmol) followed by THF (7 mL). The solution was then allowed to warm to room temperature and stir overnight. Celite (1 g) was added, the mixture was stirred for a few minutes and then the solvent was removed in vacuo. Methylene chloride was added and the slurry was stirred for 0.5 h, filtered through a Celite pad, and washed with methylene chloride. The solvent was removed in vacuo and the crude material was flash chromatographed with methylene chloride. The solvent was removed in vacuo and the crude solid was washed with hexanes to give the target compound as a white solid 0.206 g (17 %). (206 mg). $^1$H NMR (500MHz, CDCl$_3$): 1.34(s, 24H) 1.53(s, 18H), 8.05, 8.81, 8.97 ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): 25.1, 28.6, 80.1, 84.1, 105.8, 145.3, 149.9, 152.8 ppm. ESI-MS: 567 (+ Li$^+$). Anal. Calcd. for C$_{28}$H$_{46}$B$_2$N$_2$O$_8$: C, 60.02; H, 8.28. Found: not measured.

3.5 References


30. Viboh, R.


Chapter 4

Toward saddlenes: Tetrabenzo-[8]-circulene Precursors

4.1 Introduction and background

Tetrabenzo-[8]-circulene 6, also known as saddlene, is an intriguing D$_{2d}$
symmetric polycyclic aromatic hydrocarbon target with 8-membered ring core, which
gives this molecule its namesake saddle-like structure. This structural feature likely
occurs in Y-junction of carbon nanotubes (CNTs), as shown in Figure 4.1. This chapter
reports the work toward the synthesis of saddlenes precursors.

![Figure 4.1](Image)

Figure 4.1. The Y-junction of a CNT. The [8]circulene defect is highlighted (Picture by
Charles Roberton) 

The synthetic strategy for the synthesis of saddles is shown on Scheme 4.1. Our
initial synthetic approach relied on the formation of tetrabenzo[cyclooctatetraene 4, which
can be achieved in two ways (Scheme 4.1). In the first route, dimerization of 2,3-
dibromo-1,4-dimethyl-naphthalene 1 would give 4.3.1: 3,3′-dibromo-1,4,1′,4′-tetramethyl-4a,8a-dihydro-[2,2′]

Scheme 4.1 The synthetic strategy toward saddlenes
binaphthalenyl 2. Subsequent dimerization was expected to give cyclooctatetraene 4.

The precedent for this approach is Mukarami's dimerization of o-dibromo benzene, which reliably afforded 2,2'-binaphthyl, as shown in Scheme 4.2.\(^3\)

![Scheme 4.2 Mukarami's dimerization of o-dibromo benzene afforded 2,2'-binaphthyl.](image)

In the second route, dimerization of dibenzobiphenylene 3 to 4 can be achieved using Tsay conditions which is a C-C bond activation using transition metal catalyst. He showed that oxidative addition of Ni(0) complexes to biphenylene followed by reductive elimination can furnish tetrabenzocyclooctatetraene (Scheme 4.3).\(^1\)
Scheme 4.3. Precedent for C-C bond activation of biphenylene to tetraphenylene using Ni(COD)(PEt₃)₄.

The synthesis would be completed by functionalization of tetrabenzocyclooctatetraene 4 to afford octavinyl 5 by benzylic bromination. Subsequent conversion to an aldehyde followed by a Wittig condensation with formaldehyde would give an alkene. The ring closing metathesis of the resultant alkene using Grubbs’ 2nd generation catalyst is expected to give our title compound 6. Other routes can be envisioned.

4.2 Results and Discussions

4.2.1. Attempted synthesis of 4.3.1: 3,3'-dibromo-1,4,1',4'-tetramethyl-4a,8a-dihydro-[2,2'] binaphthalenyl

Preparation of saddlene precursor, 1, started with the synthesis of 9 via Diels-Alder reaction of in situ generated benzyne with furan to afford 9 in 53% yield (Scheme 4.4).² Compound 9 was then reduced using Zn metal and TiCl₄ in THF to gave 1 in 86%
yield.

\[ \begin{array}{c}
\text{Br} & \text{Br} & \text{Br} & \text{Br} \\
\text{Br} & \text{Br} & \text{Br} & \text{Br}
\end{array} \xrightarrow{n-\text{BuLi}, -78^\circ\text{C}, \text{toluene}}
\begin{array}{c}
\text{Br} & \text{Br} & \text{Br} & \text{Br} \\
\text{Br} & \text{Br} & \text{Br} & \text{Br}
\end{array} \xrightarrow{\text{Zn, TiCl}_4, \text{THF}}
\begin{array}{c}
\text{Br} & \text{Br} & \text{Br} & \text{Br}
\end{array}\]

**Scheme 4.4.** The synthesis of 2,3-dibromo-1,4-dimethyl-naphthalene using Diels-Alder reaction followed by reduction.

Treatment of 2,3-dibromo-1,4-dimethyl-naphthalene with 0.5 equivalents of \(n\)-butyl lithium was expected to give 2 via dimerization of the corresponding naphthlyne (Scheme 4.4). This was not realized - instead, 3 was isolated in 40% yield as a yellow needles. Even with rigorous exclusion of air and moisture, we could not dimerize to form 2. However, traces of the title compound were observed by GC-MS.

\[ \begin{array}{c}
\text{Br} & \text{Br} & \text{Br} & \text{Br} \\
\text{Br} & \text{Br} & \text{Br} & \text{Br}
\end{array} \xrightarrow{0.5 \text{ (equiv) } n-\text{BuLi, } -78^\circ\text{C}}
\begin{array}{c}
\text{Br} & \text{Br} & \text{Br} & \text{Br} \\
\text{Br} & \text{Br} & \text{Br} & \text{Br}
\end{array}
\]

**Scheme 4.5.** Dimerization of 1 in 0.5 equivalents of \(n\)-BuLi. GC-MS showed traces of the desired product 2. Compound 3 was instead isolated in 40% yield.
Biphenylene 3 had previously been prepared by Dekker and coworkers, as illustrated in Scheme 4.5. Their synthesis started with 4a,5a,5b,11a,11b,12a-hexahydro-
dibenzo[b,h]biphenylene-5,6,11,12-tetraone, which was previously synthesized by photolytic dimerization of 1,4-naphthoquinone. This compound was subjected to Grignard methylation and subsequent dehydration to afford 3 in 40% yield after chromatographic purification.

\[
\begin{align*}
\text{(a)} & \quad 1. \text{CH}_3\text{MgI (excess), ether, 36 h.} \quad 2. \text{HCl} \\
\text{(b)} & \quad \text{Acetyl chloride, acetic anhydride, 5 h, reflux}
\end{align*}
\]

Scheme 4.6. Dekker's route to 2

Our goal to synthesize saddlene precursor 2 was not realized. The failure to dimerize 1 to 2 was attributed to steric demands of the methyl substituents. Instead, an unexpected compound 3 was isolated in 40% yield (Scheme 4.6).

The dimerization via C-C bond activation described previously was attempted by Charles Robertson, a former King Group member. He tried to dimerize 3 to 4 using Tsay's conditions, as shown in Scheme 4.7. Only starting material was recovered in that reaction.  

6
Scheme 4.7. Dimerization of 3 to 4 via Tsay's conditions. No reaction occurred.

4.3 Conclusion

The syntheses described above did not furnish tetrabenzo-[8]-circulene precursor 2. The attempt to dimerize 2,3-dibromo-1,4-dimethyl-naphthalene to 2 using 0.5 equivalents of \( n \)-BuLi was not successful. Instead, an unexpected biphenylene 3 was formed. Traces of the expected dimmer 2 were observed by GC-MS. Difficulty in formation of 2 is likely due to steric demands by the four methyl substituents. The current synthetic route needs to be redesigned.

4.4 Experimentals

General methods.

All reactions were carried out under an atmosphere of dry nitrogen in oven dried glassware with standard Schlenk or vacuum-line techniques. Reactions were monitored by TLC, GC-MS, and NMR. GC-MS was performed on a Varian CP-3800 GC with a Saturn 2200 MS system. Compounds were separated by column chromatography using
60 mesh silica gel. $^1$H and $^{13}$C NMR spectra were recorded on General Electric QE-300 MHz, Varian 400MHz spectrometer, or Varian 500 MHz spectrometer.

**2,3-dibromo-1,4-dimethyl-naphthalene (1) (previously synthesized compound)**

To a suspension of dry zinc dust (15.4 g, 0.236 mol) in THF (140 mL) under N$_2$ atmosphere, TiCl$_4$ (25.25 g, 0.133 mol) was added dropwise and the mixture was refluxed for 10 min and then cooled in an ice bath. A solution of 1 (7.5 g, 0.024 mol) in THF (80 mL) was added via syringe and the mixture was then refluxed overnight forming a dark purple mixture. The mixture was cooled in ice bath and 10% HCl (600 mL) was added and then stirred for 15 min. The product was extracted using toluene and the resulting solution dried over CaCl$_2$ affording 1 in 75% after recrystallization in ethanol. The $^1$H and $^{13}$C NMR identical to those reported in the literature.$^{14}$

**5,6,11,12-tetramethyl-dibenzo[b,h]biphenylene (3) (previously synthesized compound)**

To a dry 250 mL 3-neck round bottom flask, 2,3-dibromo-1,4-dimethyl-naphthalene (2.00 g, 6.37 mmol), 200 mL THF, and a magnetic stirrer were added and cooled to $-78$ °C for 25 min. $n$-Buli (2.64 mL, 7.64 mmol) was added slowly for 40 min via a syringe. The mixture was warmed slowly to room temperature and stirred overnight and then quenched with 10 mL of water. The product was extracted with toluene (400 mL) and washed with water (3 × 100 mL), dried over MgSO$_4$ and the solvent was evaporated. The resulting dark brown residue was purified by column chromatography to afford 3 in 40% yield. The $^1$H and $^{13}$C NMR were identical to those reported in the literature.
4,5-dibromo-3,6-dimethyl-11-oxa-tricyclo[6.2.1.0²,7]undeca-2,4,6,9-tetraene (9)  
(previously synthesized compound⁶)

To a three neck 2 L round bottom flask equipped with a dropping funnel and a magnetic stirring bar, 2,3,5,6-tetrabromo-p-xylene (19.98 g, 0.047 mol) was added. Anhydrous toluene (500 mL), furan (20 mL, 0.284 mol), hexane (230 mL) were transferred by cannula into the flask and the mixture was cooled to −78 °C. Using a dropping funnel, n-Buli (26.35 mL, 0.047 mol) was added dropwise over 2 h. The reaction was stirred for an additional 2 h and then allowed to slowly warm to room temperature and stirred overnight. The organic mixture was quenched with 4 mL methanol, washed with water (2 × 200 mL), and dried over MgSO₄. The solvent was removed in vacuo to give a white solid that was purified further by column chromatography to give the target compound in 50 % yield. ¹H and ¹³C NMR spectra were identical to that reported in the literature.⁶

4.6 References


Chapter 5

Conclusions

5.1 General conclusions

Bulky and functionalized cyclopentadiene ligands can easily be synthesized using Miura and Dyker methodology. Scholl oxidation on these ligands successfully produced two new Cp-type PAHs, 20 and 21. It was difficult to coordinate metals directly on bulky cyclopentadiene 16, but this was easily achieved via oxidative insertion of brominated cyclopentadiene 17. Attempts to prepare bowl-shaped metal coordinated PAHs did not precede as expected. This opens up a new area of research that has not received much attention.

Polymeric helicene precursors 5, 11, and 18 were prepared. Margel Bonifacio has utilized monomer 5 to carry on with the synthesis of carbohelicene. The synthesis of monomer 18 needs more improvements for the progress of azahelicene projects.

While the attempt to synthesize tetrabenzo-[8]-circulene precursors gave an unexpected product, more research needs to be done in order to improve the synthesis of saddlene.

Throughout this thesis, computational studies were an integral part of the experimental work which helped to better understand the results.
## Appendix 1

### Chapter 2

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<td>1H NMR at 400 MHz of 6,9-di-tert-butyl-1,2,3-tris-(4-tert-butyl-</td>
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phenyl)-1H-cyclopenta[l]phenanthrene in CDCl$_3$ (25)

$^{13}$C NMR at 500 MHz of 6,9-di-tert-butyl-1,2,3-tris-(4-tert-butyl-phenyl)-1H-cyclopenta[l]phenanthrene in CDCl$_3$ (25)

Chapter 3

$^1$H NMR at 500 MHz of 1-[2,4-dibromo-5-(1-hydroxy-propyl)-phenyl]-propan-1-ol in CDCl$_3$ (12)

$^{13}$C NMR at 500 MHz of 1-[2,4-dibromo-5-(1-hydroxy-propyl)-phenyl]-propan-1-ol in CDCl$_3$ (12)

$^1$H NMR 400 MHz of trans, trans-1,5-dibromo-2,4-dipropenyl-benzene in CDCl$_3$ (5)

$^{13}$C NMR 400 MHz of trans, trans-1,5-dibromo-2,4-dipropenyl-benzene in CDCl$_3$ (5)

$^1$H NMR at 400 MHz of (diboron) [5-tert-butoxycarbonylamino-2,4-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-carbamic acid tert-butyl ester in CDCl$_3$ (18)

$^{13}$C NMR at 500 MHz of (diboron) [5-tert-butoxycarbonylamino-2,4-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-carbamic acid tert-butyl ester in CDCl$_3$ (18)
\(^1\)H NMR at 400 MHz of 1-hydroxyl-1,2,3,4,5-penta(4-tert-butylphenyl)cyclopentadiene in CDCl\(_3\)
$^{13}$C NMR at 500 MHz of 1-hydroxyl-1,2,3,4,5-penta(4-tert-butylphenyl)cyclopentadiene in CDCl$_3$
\(^1\)H at 400 MHz of 1-bromo-1,2,3,4,5-penta(4-tert-butyl)phenyl cyclopentadiene in CDCl\(_3\)
$^{13}$C NMR at 500 MHz of 1-bromo-1,2,3,4,5-penta(4-tert-butyl)phenyl cyclopentadiene in CDCl$_3$
$^1$H NMR at 500 MHz of Cp**Ru(CO)$_2$Br in CDCl$_3$
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$^1$H NMR at 400 MHz of 13-(4-tert-butylphenyl)-13H-tetrakis-3,6,11,14-(4-tert-butyl)-[a,c,g,i]fluorene in CDCl$_3$
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\(^1\)H NMR at 500 MHz of 1-[2,4-dibromo-5-(1-hydroxy-propyl)-phenyl]-propan-1-ol in CDCl\(_3\)
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$^1$H NMR at 400 MHz of *trans, trans*-1,5-Dibromo-2,4-dipropenyl-benzene in CDCl$_3$
$^{13}$C NMR at 400 MHz of *trans, trans*-1,5-dibromo-2,4-dipropenyl-benzene in CDCl$_3$
$^1$H NMR at 400 MHz of (diboron) [5-tert-butoxycarbonylamino-2,4-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-carbamic acid tert-butyl ester in CDCl$_3$. 
$^{13}$C NMR at 500 MHz of (diboron) [5-tert-butoxycarbonylamino-2,4-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-carbamic acid tert-butyl ester in CDCl$_3$
Computational Details

Optimizations and relative energy calculations were done using PM3 level of theory in Spartan 02: IA32/I686, build 119. Transition-metal complexes were studied using modified PM3(tm) method. Density functional calculations were performed using Gaussian 03 program. The B3LYP functional together with standard 6-31G (d) basis set (Cartesian d functions) was used. Standard cut-off values were used in geometry optimizations. Graphical representations of calculated structures were generated using Spartan Graphical Interface, or POVRAY tracing program.

(1) Spartan 02,

Wavefunction Developers:

Q-Chem Developers:
A.Wavefunction Inc., Irvine CA

Chapter 2

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Heat of formation: 0.372478 Hartree
Heat of formation : 0.781813 Hartree

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Formula $C_{36}H_{38}O_8$

Fw 598.66

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c, Å 14.6375(3)
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91
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Heat of formation: 0.077422 Hartree
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H89  -0.122136967  1.761158083  7.186296417  
H90  -0.995318904  3.244188172  6.765946321  
H91  0.054958338  3.216176756  8.19373394  
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C93  -1.184244919  -2.643036414  6.873462067  
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C95  -1.731755514  -5.159632909  4.570718322  
C96  -2.086802861  -5.206885157  6.313064895  
C97  -0.422656991  -4.971539819  5.74905364  
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H102 -0.13665759  -2.918545193  7.05204658  
H103 -1.777557921  -3.020994014  7.715699148  
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C105  1.433877761  -7.285708289  -2.05959219  
C106  2.789766258  -6.098770176  -3.78734061  
H107  -0.654088957  -6.348103414  -4.86054613  
H108  0.43956214  -7.125834337  -4.64438254  
H109  0.227576433  -5.3600544  -4.66297077  
H110  0.458895472  -7.376291581  -1.5633186  
H111  2.194768038  -7.17921629  -1.26911764  
H112  2.253557408  -3.380769296  0.720756135  
H113  -0.052473216  -3.189186335  1.16110648  
H114  2.13558586  3.215803898  1.736851702  
H115  1.068002987  3.951139184  0.6845028  

Heat of formation :  0.081025 Hartree

C1  0.123528809  -0.001918797  -2.927378167  
C2  1.054843672  -0.00085949  -1.749465383  
C3  0.853162368  1.194190646  -0.80533681  
C4  0.551833391  0.713575094  0.439760158  
C5  0.551659662  -0.713814917  0.440087878  

Heat of formation :  0.081025 Hartree
Heat of formation : 0.090263 Hartree

C1  0.355875933 -0.169823351 -2.942794423
C2  1.145105699  0.213384111 -1.72148159
C3  0.881128275  1.415967879 -0.773155796
C4  0.83868265  0.916059741  0.511230679
C5  0.949650061 -0.504090543  0.522381131
C6  1.055051268 -0.946319102 -0.759252351
H7  2.204723132  0.337723672 -2.062967395
C8  0.831105044  2.849373895 -0.857450027
C9  0.759113283 -2.304236501 -1.004502934
C10 0.623074566  1.585917121  1.733532332
C11 0.73167883  -1.30632745  1.662197334
C12 0.731583737  5.673740301 -0.941016587
C13 0.638798856  3.599497727  0.339701948
C14 0.996348048  3.549082269 -2.069030761
C15 0.944087985  4.922785555 -2.113133716
C16 0.579871477  5.004325578  0.258494143
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C18 0.11820518  -3.732033026  5.094791445
H19 1.070322635  5.458920533 -3.066602796
H20 0.411754987  5.578268841  1.191266889
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C104 -0.172745785 -7.498327845 -1.03377866
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H107 -0.484340167 -7.282039874 -0.003219038
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H111  3.25786825  -7.049450386 -0.649857814
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H113  0.932271668  -6.934135837 -3.52745416
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Heat of formation : 0.095109 Hartree

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C2 1.58587066 -0.414326789 -1.106213183
C3 1.35565813 0.765993329 -0.248240593
C4 1.060680285 0.350729738 1.014348753
C5 0.912793553 -1.105965157 1.062315866
C6 1.20050586 -1.57173533 -0.219405778
H7 2.67524648 -0.547626855 -1.325148627
C8 1.060534761 2.072684042 -0.689914468
C9 0.93220949 -2.796965926 -0.979761622
C10 0.712671471 1.291363941 2.00935322
C11 0.510499409 -1.59752484 2.376695525
C12 0.470968175 4.607968061 -1.568546984
C13 0.801927533 3.062626823 0.278748296
C14 0.798251444 2.25651191 -2.07125865
C15 0.529592918 3.544293004 -2.49627782
C16 0.553981268 4.361372575 -0.204811863
C17 -0.210368594 -2.526121792 4.950900107
C18 -0.542539557 -3.024697091 6.343150791
H19 0.321422208 3.741274207 -3.5635332
H20 0.407485426 5.18992275 0.509339505
H21 0.195365731 6.013823998 4.001739536
H22 0.668538141 2.662942051 1.675425495
C23 0.36920993 0.786407928 3.277761452
H24 0.082507094 1.708363974 4.272653627
C25 0.381015187 3.555887859 2.721913652
H26 0.33643539 -2.956045815 2.636804399
H27 -0.13928813 -4.496837664 4.079585957
H28 -0.17182761 1.353133743 5.289328114
H29 0.365999941 4.640393768 2.518280073
C30 -0.149792987 4.07364758 5.1315545
C31 -0.338565223 -0.009399987 -4.873292718
C32 0.397084712 -1.394171386 -3.020410702
C33 0.611281745 1.049735841 -2.901314441
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C35 -0.193042696 -1.264142481 -4.280243246
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C37 -0.013458618 -3.418208375 3.897154638
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H40  -0.534915912  -2.170618029  -4.815124692  
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C42  0.533745425  -5.123698176  -2.525446297  
C43  0.555841644  -2.693318933  -2.345209637  
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C45  0.953858184  -5.211460476  -1.198759404  
C46  0.341314034  -3.859157541  -3.081558932  
C47  0.292452982  -0.675123699  3.441687175  
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C54  1.551957754  -5.970274986  -5.041602743  
C55  0.471497617  -3.685914488  1.826512346  
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H63  -2.729068516  1.142476959  -5.431346482  
H64  -2.905710581  -0.618708801  -5.517397212  
H65  -1.268420668  -1.088575176  -8.037241268  
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H67  0.362966644  -1.200171884  -7.352507498  
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C72  1.871941711  6.166809617  -3.461847029  
C73  0.49309424  7.20313997  -3.873086704  
C74  -1.769883846  6.081795757  -1.122293874  
C75  -1.794091747  5.472467779  -2.786407623  
C76  -1.588561632  7.206335036  -2.480634615  
C77  0.482849474  6.899807262  -0.094131478  
C78  0.511109127  8.074773217  -1.428786722  
C79  1.903980483  7.014465737  -1.146812032  
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C81  -0.757231688  5.378414628  4.612935871  
C82  1.199502634  4.370662916  5.791513999  
C83  1.656943821  3.454496969  6.187447794  
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C85  1.903904757  4.811306536  5.074221955  
C86  -1.771823174  5.22188368  4.22384798  
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Heat of formation: 0.09059 Hartree

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C4  0.908387465  0.753540306  1.340449047
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C17 0.407259362 -4.000710286 4.080061367
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H28 0.100766091 -5.196316164 2.309463502
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C37 0.138225331 5.247899886 2.153864111
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H39 0.14859826 2.127863947 -4.624229202
H40 -0.140740246 -2.199367011 -4.545180122
C41 -0.516951879 -0.042801761 -6.18230181
C42 -0.033378755 -4.814394867 -1.541512588
C43 0.549192214 -2.482556851 -1.90745816
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C45 0.066585738 -4.652359524 -0.168630744
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Heat of formation: 0.135946 Hartree
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C36  3.851011387  -2.89789167  0.929183178
C37  2.8539535  -0.741747856  1.457971429
C38  -2.205598656  2.459553781  0.168444739
C39  4.925469595  -5.171246656  1.012252788
H42  -3.326364795  3.80541086  -1.091885126
H43  2.53545415  -4.566614341  0.557648573
H44  4.965564826  -1.040982403  1.100717359
C45  5.107159058  -3.89616106  0.636944725
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C48  2.8539535  -0.741747856  1.457971429
C49  3.968194937  -1.50845769  1.171185036
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Chapter 3

B3LYP/6-31G* geometries for trans-trans isomer 5

![Diagram of trans-trans isomer 5]

Scf done: -5607.959901

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B3LYP/6-31G* geometries for cis-trans isomer 13

![Diagram of cis-trans isomer 13]

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B3LYP/6-31G* geometries for cis-cis isomer 14

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C -0.853923 -0.995079 -0.721148
C  0.304969 -1.770343 -0.887208
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Crystallographic data of 2

Formula C₆H₆Br₂N₂
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a, Å 10.9556(13)
b, Å 4.0186(5)
c, Å 17.343(2)
α, deg 90
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Space group P 2₁/c

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Appendix 2

List of missing characterization data

**Chapter 2**

C\textsubscript{p}*\textsubscript{3}RuC\textsubscript{p} (3)
- Melting point
- UV/Vis

C\textsubscript{p}*\textsubscript{3}Ru(CO)\textsubscript{2}Br (5)
- Melting point
- UV/Vis
- Mass
- Elemental analysis

1-bromo-1,2,3,4,5-penta(4-tert-butyl)phenyl cyclopentadiene (6)
- Melting Point
- UV/Vis
- Mass
- Elemental Analysis

- Melting point
- IR
- UV/Vis
- Elemental Analysis

**Chapter 3**

(diboron) [5-tert-butoxycarbonylamino-2,4-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-carbamic acid tert-butyl ester (18)
- Melting point
- IR
- UV/Vis
- Elemental analysis