Biphenyl Complexes of Zirconium and Their Utility in the Synthesis of Polycyclic Aromatic Hydrocarbons

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by

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Abstract

This dissertation primarily concerns the synthesis of polycyclic aromatic hydrocarbons (PAHs) using a newly discovered zirconium-mediated double ipso substitution on an ortho-dihaloarene to form a triphenylene fragment.

The first part of this work is a background on PAHs, their occurrence, use, and synthesis followed by an overview of chapters.

The second chapter describes the characterization and preliminary reactivity studies of a homologous family of zirconohydrocarbons bearing one, two, three, or four 2,2′-biphenylidyliyl (biphe) ligands. In all cases, the biphe ligands are bidentate, forming doubly benzannulated zirconacyclopentadienes. One of the homologues is a tetraanionic zirconate, two are examples of homoleptic σ-bound zirconohydrocarbons, and three are anionic complexes. The members of this family exhibit unusual aryl-aryl bond forming reactivity that may provide new routes to aryl-aryl bond formation.

The third chapter covers the uncatalyzed reaction of [Zr(biphe)₃][(Li•(THF)₄)₂], where biphe is 2,2′-biphenylidyliyl, with o-dihaloarenes to give triphenylenes. The reaction is noteworthy from a synthetic viewpoint because it is a new disconnection for the synthesis of PAHs. The reaction is noteworthy from an organometallic viewpoint because it is a rare, if not unprecedented, example of an uncatalyzed, Zr-mediated aryl-aryl bond formation.

The fourth chapter describes the use of [Zr(biphe)₃][(Li•(THF)₄)₂] in a fourfold reaction
allowing the synthesis of 18,18'-dihexyl[9,9']biphenanthro[9,10-b]triphenylene in which two phenanthro[9,10-b]triphenylene moieties are joined through their sterically hindered 9 positions. This remarkably strained and twisted PAH has been characterized using a variety of spectroscopic techniques and computations.

The fifth chapter describes the use of [Zr(biphe)][(Li•(THF)4)2] for the synthesis of two extended triptycenes. The extended triptycenes are paddlewheel shaped molecules that may be useful in the construction of nano scale devices and as scaffolds in supramolecular chemistry.

The sixth chapter is a graphical abstract of Crystallographic Information Framework files. All structures shown have solutions suitable for publication.
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Chapter 1
Introduction to Polycyclic Aromatic Hydrocarbons and Overview of Chapters

General Introduction

Polycyclic aromatic hydrocarbons (PAHs) are the focus of the research described herein. Our interest in PAHs derives from the desire to understand their fundamental properties, but we are also interested in their application to technology. A theme is the development and use of new methods for the synthesis of architecturally interesting PAHs. Spectroscopy and computational modeling of our synthetic targets allow us to understand their structure, properties, and reactivity.

Background

Polycyclic aromatic hydrocarbons (PAHs) are compounds with two or more fused aromatic rings. They are found in nature as major components of coal tar, oil shale,\(^1,2\) and as a minor component of crude oil. PAHs obtained from natural sources are often found as complex mixtures. These mixtures are sufficiently complex that, using current separation techniques, only the smallest and most volatile PAHs are easily isolated.\(^3\)

In the last 25 years, it has been suggested that PAHs may constitute 1-2% of all the carbon contained in interstellar clouds.\(^4\) The presence of PAHs in the harsh environment of interstellar space is a testament to the stability of certain members of this class of compounds.\(^5\) One challenge in the field of astrochemistry is identifying which PAHs make up the mixtures detected in interstellar space.\(^6\) One of the factors, besides their remoteness, that makes this difficult is lack of authentic PAH standards.\(^6\)

PAHs are also notable pollutants in the environment. Certain PAHs have been shown to be potent carcinogens.\(^7\) A major breakthrough in medicine was the discovery by Dr.
Percival Pott in 1775 that soot from chimneys was causing chimney sweeps to develop scrotal cancer at a much higher rate than the general population. In the 1930s, it was determined that PAHs are the component of soot that causes cancer. Soot contains benzo[a]pyrene, the first chemical compound shown to directly cause disease (cancer) in humans. Modern chemists are actively pursuing the synthesis of new PAHs in an attempt to gain a deeper understanding of their carcinogenic behavior. Better synthetic methodology, as well as advances in molecular biology and computer modeling, have led to increased interest in structure-activity relationships for PAH carcinogenicity.

Pollution of the environment by PAHs comes primarily from the burning of fossil fuels for energy. Incineration of trash, the burning of wood, and emissions from coke ovens used in the manufacture of steel are other notable sources. Due to their potentially harmful affects on organisms with which they come in contact, understanding the fate of PAHs that have been released into the environment is an important area of research.

Chemists have been synthesizing PAHs in the lab for well over a hundred years. They were originally desired as intermediates in the synthesis of quinoid dyes, as well as models for the study of aromaticity, which is the phenomenon that gives rise to the curious stability most commonly associated with benzene. The synthesis of more complex PAHs, which allows the further study of aromaticity, continues even to the present.

PAHs have proven useful in the rapidly expanding field of supramolecular chemistry. Much of their utility derives from three factors. First, they have well defined rigid structures. Second, their aromatic cores can be decorated with other functional groups in a straightforward manner. Third, their propensity for undergoing interesting electrostatic
and Van der Waals interactions with each other (π-stacking) as well as ions (π-cation and π-anion interactions) allow for supramolecular systems to be designed to assemble in somewhat predictable ways.\textsuperscript{13}

The use of PAHs in optoelectronic devices is widespread. They are important components of liquid crystalline materials\textsuperscript{14} and are constituents of organic light-emitting diodes (OLEDs).\textsuperscript{15} Currently, PAHs are being developed for use in solar cells.\textsuperscript{16} PAHs have shown promise as components of electronic devices, such as organic semiconductor materials and field effect transistors.\textsuperscript{17} They are currently limited in their application because control of their molecular ordering in bulk is not completely understood. In addition, techniques for processing them into usable electronic device components are still being developed.\textsuperscript{18}

One of the reasons that PAHs are useful building blocks in material science is that over one hundred years of research directed at synthetic control over PAH structures has been carried out.\textsuperscript{19} This research makes possible the synthesis of non-naturally occurring compounds with predictable and useful properties. Several important synthetic milestones have been attained in the synthesis of PAHs. Some of the earliest controlled syntheses of PAHs were carried out at the beginning of the 20\textsuperscript{th} century by Roland Scholl.\textsuperscript{20} The reaction he utilized, and which now bears his name, is a Lewis acid catalyzed cyclodehydrogenation reaction. The Scholl reaction is still used today for cascade reactions, in which flexible branched phenylene precursors are converted to large disk shaped PAHs.\textsuperscript{21} During the middle part of the 20\textsuperscript{th} century, Eric Clar synthesized and characterized a multitude of PAHs.\textsuperscript{22} He is also known for developing a valence bond model for predicting their relative stabilities that is still used today.\textsuperscript{23} As techniques
(X-ray diffraction, NMR spectroscopy, UV-visible spectroscopy) for the characterization of organic compounds improved and were adopted, chemists began to expand the class of PAHs to include strained and twisted non-planar molecules. The synthesis of [6]-helicene, a helical compound with its non-planar geometry forced by intramolecular steric interactions, was carried out by Newman and Lednicer in 1956. Cram pioneered the synthesis and study of the strained aromatic cyclophanes, which are aromatic rings with alkane tethers connecting non-adjacent ring carbons. The cyclophanes, due to their tether-enforced, non-natural bond lengths and angles, have been used as model systems to test the limits of aromaticity. The synthesis of corannulene by Barth and Lawton marked another milestone in PAH chemistry. The incorporation of a five-membered ring into the carbon skeleton of corannulene forces it to adopt a bowl like structure. The discovery of C$_{60}$ and carbon nanotubes and subsequent reports of their remarkable material properties have spurred a large amount of research towards the controlled synthesis of non-planar PAHs.

Figure 1-1. Examples of non-planar PAHs.

Modern synthetic methods have been developed which allow the synthesis of many PAHs under mild conditions and in high yields. The synthesis of strained PAHs, which
normally cannot be formed using mild reaction conditions, often relies on photocyclization,\textsuperscript{32} flash vacuum pyrolysis,\textsuperscript{33} and by the dimerization and trimerization of alkynes and arynes.\textsuperscript{34}

The highlight of the research presented in this dissertation is the synthesis and characterization of 18,18'-dihexyl[9,9']biphenanthro[9,10-\textit{b}]triphenylene (I) (Chapter 4). The preparation and study of this highly strained and twisted PAH typifies our research. The solid-state structure of I was elucidated by X-ray diffraction analysis. The molecule exhibits rich conformational behavior in solution, which was studied by both spectroscopic methods and computer modeling. Due to its unusual architecture, this PAH served as a useful benchmark for various computer models used in the calculation of molecular geometry and spectroscopic properties. The synthesis of I was made possible by a new synthetic transformation developed in our laboratory, a double \textit{ipso} substitution on an \textit{ortho}-dihaloarene to form a triphenylene fragment (Chapter 3). This transformation is carried out using the tris(biphe)zirconate lithium complex (II) (where biphe is biphenyl[2,2'-diyl]), which was discovered serendipitously (Chapter 2) in the course of our research directed at the synthesis of a short nanotube segment.
Overview of Chapters

Chapter 2: Four Homologous Zirconium 2,2′-Biphenyldiyls: Synthesis, Structure, and Reactivity

The synthesis of a carbon "nano-hoop", a short hydrogen-terminated segment of a nanotube, was one of the original synthetic targets of our research group. We intended to create this large non-planar PAH using the much smaller PAH triphenylene as a building block. The triphenylene we intended to use was one with the unknown 1, 8-substitution pattern (Scheme 1).

Scheme 1-1. A proposed synthesis of a carbon nano hoop. The 1,8-disubstituted triphenylene precursor is the leftmost structure.

Due to the difficulty of synthesizing a 1,8-disubstituted triphenylene using traditional methods, we began investigating a zirconium-mediated aryl-aryl bond forming reaction for the synthesis of the desired triphenylene. Work by Negishi\textsuperscript{35} and Takahashi\textsuperscript{36} demonstrated the ability of zirconocyclopentadienes to undergo 4+2 cycloadditions with alkynes (Scheme 2).
Scheme 1-2. Takahashi’s synthesis of a highly substituted benzene by 4+2 cycloaddition of a zirconocyclopentadiene with an alkyne.

Rausch had previously synthesized bis(cyclopentadienyl)titanafuorene which is a dibenzo analogue of the zirconocyclopentadienes used by Takahashi. Based on these precedents, we hoped to prepare a bis(cyclopentadienyl)zirconofluorene complex for a formal [4+2] reaction with benzyne to yield triphenylene (Scheme 3).

Scheme 1-3. A proposed zirconium and nickel mediated triphenylene forming reaction analogous to Takahashi’s synthesis of highly substituted benzenes.

Attempts to prepare the bis(cyclopentadienyl) zirconofluorene complex (III), under the conditions Rausch used for the preparation of bis(cyclopentadienyl) titanafuorene, led to the addition of two biphenyls, not the expected single addition. The resulting zirconate complex, bis(biphe)cyclopentadienyl zirconate lithium (IV), which bears two biphenyls and one cyclopentadienyl ligand, was obtained and characterized by NMR and X-ray crystallography (Scheme 4). A parallel reaction with four equivalents of 2, 2'-
dilithiobiphenyl was attempted, and furnished crystals of the highly reactive tetraanionic complex tetrakis(biphe)zirconate lithium (V), which bears four biphenyls. Complex V was characterized by NMR and X-ray crystallography\textsuperscript{38} (Scheme 4). By changing the reaction solvent from ether to THF, while using the same stoichiometry and reaction conditions that previously yielded the tetraanionic complex, a dianionic complex tris(biphe)zirconate lithium (II) bearing three biphenyls is obtained. Complex II was characterized using NMR and X-ray crystallography\textsuperscript{38} (Scheme 4).

**Scheme 1-4.** The synthesis of three zirconate complexes by reaction of dilithiobiphenyl with zirconocene dichloride.

With three zirconate complexes in hand, our focus returned to the synthesis of III our original organometallic target, and the last member needed to complete a family of biphenyl zirconium complexes. Despite repeated attempts, using different conditions and starting materials, the neutral complex remained elusive. Eventually, we found that any
of the three biphenyl zirconate complexes we had already synthesized react with freshly cracked, neat cyclopentadiene to afford III in reasonable yields \(^{38}\) (Scheme 5).

**Scheme 1-5.** The synthesis of the neutral biphenyl zirconocene complex by reaction of cyclopentadiene with any of three biphenyl zirconate complexes.

Because hafnium is directly below zirconium on the periodic table, we believed the synthesis of the hafnium analogs of our previously discovered complexes II-V would be fruitful. When hafnocene dichloride is used as starting material in place of zirconocene dichloride and reactions identical to those that gave the zirconium complexes are run, three analogous biphenyl complexes of hafnium II-Hf, III-Hf, and V-Hf are obtained (Figure 2). The complexes were characterized by NMR and X-ray crystallography. The hafnium complexes exhibit more stability to air and water than the zirconate complexes.
They also exhibit lower reactivity generally, as judged by their slower rates of decomposition in various solvents compared to those for the zirconium complexes.

![Diagram of complexes](image)

**Figure 1-2.** Three biphenyl complexes of hafnium synthesized using the same methodology that yielded their zirconium analogues.

**Chapter 3: Uncatalyzed Zirconium-Mediated Biphenylation of o-Dihalobenzenes To Form Triphenylenes**

After a preliminary survey of reactivity for the zirconate and hafnate complexes, II was chosen for further study, because it exhibits a good balance between stability and reactivity. It is also easy to make on a large scale. We discovered that this complex enables double *ipso* substitution on an *ortho*-dihaloarene to form a triphenylene fragment. The reaction is a new synthetic method for the synthesis of PAHs in which a biphenyl group is added to an arene at the expense of *ortho* halogens\(^{39}\) (Scheme 6). This new synthetic method is important because it allows direct access to interesting PAHs through easily obtainable starting compounds.
**Scheme 1-6.** The general transformation by which an ortho-dihalobenzene can be biphenylated using the tris(biphe) zirconate complex.

The reaction is general for the halogens, with best yields for o-diodobenzene and far worse yields with o-difluorobenzene. The reaction tolerates alkyl and alkoxy functionality and can be carried out two times on 1,2,4,5-tetrahalobenzenes to afford tetrabenzoanthracenes in modest yields.

The reaction is also capable of introducing a great deal of strain, as demonstrated by the synthesis of 9,18-dimethyltetrabenzoanthracene by reaction of II with 1,2,4,5-tetrahalo-p-xylene. Steric interactions between its methyl groups and four of the hydrogens on its aromatic rings gives rise to a remarkable 38 kcal/mol of strain (Scheme 7).

The reaction of II with o-haloarenes is not without limitation— it proceeds in only modest yields and produces PAHs that are not readily functionalized for further reaction. Despite these limitations, the methodology is useful for the direct synthesis of highly strained PAHs.
**Scheme 1-7.** Use of the tris(biphe) zirconate complex for the synthesis of six PAHs.

Chapter 4: **18,18'-Dihexyl[9,9']biphenanthro[9,10-b]triphenylene: Construction and Consequences of a Profoundly Hindered Aryl-Aryl Single Bond**

Considering both the limitations and strengths of the biphenylation reaction of II with \( o \)-haloarenes, it was apparent that synthetic routes relying on this transformation should be short and yield products that are interesting without further chemical elaboration. In particular, we were interested in exploiting the ability of II to generate strain. Therefore, a short reaction sequence was devised that would create an extremely strained and twisted PAH. The reaction sequence began with the exhaustive electrophilic bromination of 4,4'-dimethyl biphenyl. The resulting product was then biphenyalted four times using zirconium complex (II) to give 18,18'-di-methyl[9,9']bi[phenanthro[9,10-b]triphenylenyl] (I-Me) in low yields. The product was difficult to purify due to its poor solubility in most organic solvents. A small amount of analytically pure material was obtained by crystallization I-Me from THF and water. The compound was only partially
characterized by NMR. Due to difficulties with purification of I-\text{Me}, the synthesis was redesigned with \textit{n}-hexyl groups in place of the methyl groups in the starting biphenyl. The \textit{di-\textit{n}}-hexylbiphenyl was brominated using the same reaction conditions used previously for the methyl compound. The resulting dihexyloctabromobiphenyl was allowed to react with II in toluene to give 18,18'-\textit{di-\textit{n}}-hexyl[9,9']bi[phenanthro[9,10-b]triphenylenyl] in 5\% yield (Scheme 8).

Scheme 1-8. The synthesis of two highly strained, twisted 18,18'-\textit{di-alkyl}[9,9']bi[phenanthro[9,10-b]triphenylenyl] molecules utilizing the tris(biphe) zirconate complex to add four biphenyls to a dialkyloctabromobiphenyl precursor.

This compound was fully characterized. Various 2D NMR techniques were used to fully assign both the proton and carbon spectra. A high quality single crystal of the compound was grown by slow evaporation of benzene and an X-ray crystal structure was determined. The crystal structure revealed the compound to be among the most twisted arenes ever synthesized. The structure shows the molecule to be composed of two identical helical subunits bound through a central bond (Figure 2).
Figure 1-3. A ray-traced thermal ellipsoid plot (50% ellipses) showing the 18,18'-di-n-hexyl[9,9']bi[phenanthro[9,10-b]triphenylenyl] molecule. Hydrogens and co-crystalized benzene solvent molecules have been removed for clarity.

Calculations suggest the central bond in this molecule may be the most strained carbon-carbon single bond yet reported.\textsuperscript{40} The overall strain energy in the molecule, as judged by comparison to calculations for an unstrained reference isomer, is more than 70 kcal/mol.

Because the subunits of (I) are helical and interlocked, the compound exists as either a pair of interlocked plus helical (P) or minus helical (M) subunits. The chiral, interlocked subunits are reminiscent of a handshake where two right or two left hands clasp. The crystal structure obtained for (I) reveals a 1:1 mixture of lowest energy MM and PP chiral molecules. A barrier for the interconversion between the MM and PP homochiral subunits of 1 was measured spectroscopically (VT-NMR) to be 15.2 kcal/mol, which is in good agreement with our computationally determined barrier of 15.7 kcal/mol. This
barrier is low enough to preclude resolution of chiraly pure samples of I at ambient temperatures.

Due to its remarkably twisted structure, as well as its interlocked subunits, I was deemed a useful test case for the benchmarking of different computational methods for the prediction of proton and carbon NMR chemical shifts. This was done by comparing the computationally predicted values of the proton and carbon chemical shifts for I with those obtained by NMR measurements taken on I.

Chapter 5: Synthesis of an Extended Triptycene Using a New Zirconium Mediated Transformation

Another useful feature of the reaction of II with o-haloarenes is the ability to create large PAHs from relatively simple precursors in a single reaction. With this in mind, a two step synthesis of an extended triptycene (VI) was designed (Scheme 9). The paddlewheel shaped target molecule is attractive for its potential uses as a component of inclusion complexes, molecular machines, and polymers.

The synthesis of VI relies on use of II for the three-fold biphenylation of 2,3,6,7,10,11-hexabromotriptycene (VII). In order to obtain useful amounts of synthetic intermediate VII, an improved synthesis needed to be developed.\textsuperscript{41} Our improved synthesis offers higher yields and direct access to VII from easily available starting materials. Compound VII may prove to be an interesting synthetic intermediate for the synthesis of triptycene-based supramolecular systems. Triptycene is often utilized as a scaffold for supramolecular chemistry due to its rigidity and \textit{C}_{3v} symmetry.

With gram amounts of synthetic intermediate VII now available, a three-fold biphenylation reaction with zirconium complex II was carried out giving VI, a triptycene
with three triphenylene blades, in modest yields. The paddlewheel shaped compound VI was fully characterized. However, despite significant effort, we could not grow a single crystal of it suitable for X-ray diffraction analysis. The difficulty encountered in attempting to crystallize VI was puzzling because both triptycene and triphenylene can be crystallized from a variety of solvents, yet combining structural features of both in VI seems to have inhibited crystallization. We hypothesized that the void about the bridgehead hydrogens could not be efficiently filled in a crystal. To test this hypothesis, we synthesized a version of the paddlewheel shaped molecule VI with n-butyl groups in place of its bridgehead hydrogens (VI-Bu) (Scheme 9). In line with our hypothesis, the compound easily crystallized from multiple common organic solvents. A single crystal X-ray diffraction experiment was carried out on VI-Bu.

**Scheme 1-9.** The synthesis of a paddlewheel shaped PAH formed by the reaction of the highly symmetric molecule 2,3,6,7,10,11-hexabromotriptycene with tris(biphe) zirconate.

**Chapter 6: Crystallography**

We routinely acquire X-ray diffraction data and attempt to solve this data for our PAHs and other synthetic compounds. Single crystal X-ray diffraction analysis is one of the most direct and important experiments for studying the three dimensional shape of
molecules. This chapter is a summary of these crystal structures. Only structures suitable for publication are included; structures with poor data or intractable disorder are omitted. Since we are interested in molecules that push the limits of PAH architecture, and therefore often have interesting three dimensional shapes, X-ray crystallography is an essential technique. Many of the compounds described in this chapter were synthesized by other members of the King research group, and I am indebted to them for providing crystals for my study.
References:

Chapter 2


**Four Homologous Zirconium 2,2′-Biphenyldiyls: Synthesis, Structure, and Reactivity**

**Introduction**

We report the preparation, characterization, and preliminary reactivity studies of a homologous family of zirconohydrocarbons bearing one, two, three, or four 2,2′-biphenyldiyl (biphe) ligands. In all cases, the biphe ligands are bidentate, forming doubly benzannulated zirconacyclopentadienes. One of the homologs is a tetraanionic zirconate; two are examples of homoleptic σ-bound zirconohydrocarbons; three are anionic “ate” complexes; and all four are easily prepared on 0.5 g scale. Perhaps most importantly, members of this family exhibit unusual aryl-aryl bond forming reactivity that may provide new routes to aryl-aryl bond formation.

The organometallic chemistry of zirconocium has been studied for more than 50 years\(^1\) and is dominated by zirconocenes,\(^2\) which are widely used as catalysts for olefin polymerization\(^3\) and in organic synthesis.\(^4\) The ability of alkyl or aryl zirconocenes to transmetalate stoichiometrically (Cu, Hg, Sn, B, and Al) or catalytically (Ni and Pd) is synthetically useful.\(^2\) In particular, the formal [4 + 2] cycloaddition of zirconacyclopentadienes via their transmetallated derivatives with acetylenes is an increasingly popular route to highly substituted benzenes\(^5,6\) and heterocycles.\(^7,9\) Sharp has extended this concept to the formal [3 + 2] cycloaddition of polycyclic aromatic hydrocarbons with acetylenes.\(^10,11\)
Our initial motivation was to use the hitherto unreported biscyclopentadienyl zirconium(2,2'-biphenyldiyiy) (Cp₂Zr(biphe), 1) in a [4 + 2] route to phenanthrene derivatives by a route similar to that of Eisch. In 1971, Rausch and co-workers prepared the titanium analog of 1, Cp₂Ti(biphe), in 12% yield by treating Cp₂TiCl₂ with Li₂(biphe), the crystal structure has been reported.

**Results and Discussion**

Treatment of Cp₂ZrCl₂ with Li₂(biphe), even in substoichiometric amounts, did not produce the expected product 1, but instead produced [Li•(THF)_₄][CpZr(biphe)₂] (2) by loss of a Cp⁻ ligand (Scheme 1 a). The reactivity of Cp₂ZrCl₂ with Li₂(biphe) continued to surprise us. Treatment of Cp₂ZrCl₂ with excess Li₂(biphe) in THF gave the homoleptic complex [Li•(THF)_₄][Zr(biphe)₃] (3) in 87% yield. A reaction, identical except using Et₂O in place of THF, gave [Li•(Et₂O)_₄][Zr(biphe)₄] (4) in 56% yield.

These reactions involve loss of Cp⁻ ligands. Few examples of the loss of a single Cp⁻ from a zirconocene have been reported: transfer to Ir, transfer to Mo or W, and the displacement by alkyl lithium reagents. Excluding exhaustive protonolysis or oxidation, only one example of the loss of both Cp⁻ ligands from a zirconocene has been reported: treatment of Cp₂ZrMe₂ with MeLi was reported to afford two equivalents of CpLi, but the resulting zirconium species was not characterized.

The complex we initially sought, 1, could not be prepared by the direct reaction of Cp₂ZrCl₂ with Li₂(biphe), even when using substiochiometric Li₂(biphe) – only 2, 3, or 4 were obtained. The elusive complex 1 was ultimately prepared by protonolysis of biphe ligands from 2, 3, or 4 using the mild acid CpH with concomitant interception of a Zr
intermediate by the conjugate base, Cp\(^-\), a method reported by Scott et al.\(^{22}\) Thus, all homologous zirconium 2,2’-biphenyldiyls, 1-4, have been prepared.

Table 2-1. X-Ray crystallographic data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C(<em>{22})H(</em>{18})Zr</td>
<td>C(<em>{47})H(</em>{53})Li(<em>{2})O(</em>{4})Zr</td>
<td>C(<em>{68})H(</em>{86})Li(<em>{2})O(</em>{8})Zr</td>
<td>C(<em>{64})H(</em>{72})Li(<em>{4})O(</em>{4})Zr</td>
</tr>
<tr>
<td>fw</td>
<td>373.58</td>
<td>788.05</td>
<td>1136.47</td>
<td>1024.20</td>
</tr>
<tr>
<td>crystal system</td>
<td>rhombohedral</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>r-3</td>
<td>(P_2_1/c)</td>
<td>(c_1 _2/c_1)</td>
<td>(P2(1)/n)</td>
</tr>
<tr>
<td>a, Å</td>
<td>19.1732(16)</td>
<td>19.2821(17)</td>
<td>28.632(10)</td>
<td>12.9268(5)</td>
</tr>
<tr>
<td>b, Å</td>
<td>19.1732(16)</td>
<td>14.6363(13)</td>
<td>13.128(5)</td>
<td>17.6970(6)</td>
</tr>
<tr>
<td>c, Å</td>
<td>24.043(4)</td>
<td>15.0442(13)</td>
<td>21.206(7)</td>
<td>23.7283(8)</td>
</tr>
<tr>
<td>(\alpha), deg</td>
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<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>(\beta), deg</td>
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<td>106.650</td>
<td>131.001(8)</td>
<td>95.9130</td>
</tr>
<tr>
<td>(\gamma), deg</td>
<td>120.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>V, Å(^3)</td>
<td>7653.6</td>
<td>4067.7(6)</td>
<td>6015(4)</td>
<td>5399.3</td>
</tr>
<tr>
<td>Z</td>
<td>18</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>temp, K</td>
<td>100 (2)</td>
<td>100 (2)</td>
<td>100 (2)</td>
<td>100 (2)</td>
</tr>
<tr>
<td>total ref.</td>
<td>33084</td>
<td>69947</td>
<td>38854</td>
<td>69988</td>
</tr>
<tr>
<td>unique ref. (Rint)</td>
<td>3919, 0.1915</td>
<td>14180, 0.0217</td>
<td>6914, 0.0660</td>
<td>12393, 0.0411</td>
</tr>
<tr>
<td>(2\theta) max ((^\circ))</td>
<td>55</td>
<td>65.08</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>(R_1), w(R_2) (I&gt;2(\sigma)(I))</td>
<td>0.0398, 0.0865</td>
<td>0.0339, 0.093</td>
<td>0.0559, 0.1253</td>
<td>0.0350, 0.0887</td>
</tr>
</tbody>
</table>

The structures of complexes 1-4 were determined by single-crystal X-ray diffraction analysis (Table 1), (Figure 1, see Appendices for figures showing counterions and solvent). Complex 1 is similar to other zirconacyclopentadienes, except that the C(\(\alpha\))-C(\(\beta\)) bonds, which are common to both the five and the six member rings, are longer (1.42 Å, cf. Cp\(_2\)Zr(C\(_4\)Ph\(_4\)), 1.36 Å).\(^{23}\) This difference, also observed in 2-4, is similar to that between furan\(^{24}\) (1.32 Å) and dibenzofuran\(^{25}\) (1.38 Å).
Scheme 2-1. Synthesis and interconversions of complexes 1-4. a) 1.0 Li₂(biphe), THF, −30 °C, 76% b) 4.0 Li₂(biphe), THF, −30 °C, 87% c) 4.0 Li₂(biphe), Et₂O, −30 °C, 56% d) 2.0 Li₂(biphe), THF, −30 °C e) 1.0 Li₂(biphe), Et₂O, −30 °C, 93% f) excess CpH, f₁, 67%; f₂, 86%; f₃, 10%

In the crystal structure of 2, the Li⁺(THF)₄ cation is separated (7.27 Å) from the formally anionic zirconium atom. A disordered THF molecule fills a void. This zirconate possesses a four-legged piano stool geometry. In the crystal structure of 3, the two Li⁺(THF)₄ cations are separated (8.02 Å) from the formally dianionic zirconium atom. The three biphe ligands are disposed about the Zr atom with a geometry closer to trigonal prismatic than octahedral (θ = 22.4°, where θ is the angle between the medians of the triangles formed by the C atoms bound to Zr, θ = 0 for a prism and θ = 60° for an
octahedron). Similar structures with bisphosphine or 2,2'-bipyridyl ligands have been reported. In the crystal structure of 4, a single Li•(Et₂O) cation nests in each of the four clefts defined by the biphe ligands. The Li cations are in Van der Waals contact with roughly six C atoms (av, 2.33 Å, std dev 0.13 Å). The C atoms remain essentially planar, as demonstrated by the sum of the angles around C(α) exceeding 358° in all cases (cf. sp³, 328.5°; sp², 360°). Hence, the Li – C interactions are ionic, not covalent. The four (biphe) ligands are disposed about Zr with a geometry closer to square antiprismatic than square prismatic (θ = 32.2°, where θ is the angle of offset between the squares formed by the C atoms bound to Zr, θ = 45° for a square antiprism and θ = 0 for a square prism). The distance between the C atoms of the biphe ligands and the Zr atom increase with the number of biphe ligands (Table 2).
Figure 2-1. Single crystal X-ray diffraction analysis structures of 1-4. Hydrogens, counterions, and solvate molecules are omitted for clarity.
The inability to prepare 1 from the direct reaction of \( \text{Cp}_2\text{ZrCl}_2 \) with \( \text{Li}_2(\text{biphe}) \) demonstrates that the addition of the second biphe and loss of \( \text{Cp}^- \) is faster than the addition of the first biphe.\(^{27}\) Indeed, the stepwise addition of biphe ligands is effective. Both complex 1 and 2 can be converted to 3 by treatment with \( \text{Li}_2(\text{biphe}) \) in THF in > 90% yield. Likewise, complex 3 is converted to 4 by treatment with excess \( \text{Li}_2(\text{biphe}) \) in \( \text{Et}_2\text{O} \) in 97% yield. The conversion of 1 to 2 has not been realized.

All compounds 1-4 can be prepared on greater than 500 mg scale as crystalline solids. The simplest to prepare is 3, which immediately precipitates as a pure, crystalline solid. Treatment of 3 with \( \text{Li}_2(\text{biphe}) \) in \( \text{Et}_2\text{O} \) is our preferred method to prepare 4, which crystallizes from the reaction mixture at −30 °C.

The reactivity of 1-4 varies drastically with the number of biphe ligands. Both neutral 1 and monoanion 2 are indefinitely stable at 25 °C as a solid or in \( \text{Et}_2\text{O} \) or THF solution. Dianion 3, which is poorly soluble, is indefinitely stable at −35 °C, but decomposes at room temperature over 12 h under THF in an Ar atmosphere. In benzene, a good solvent for 3, the decomposition occurs within 1 h. The tetraanion 4 is extraordinarily reactive –

---

**Table 2-2. Geometric measures of 1-4.**

<table>
<thead>
<tr>
<th></th>
<th>( r(\text{C-Zr}) ) / Å (av, st dev)</th>
<th>( \Sigma (\text{C(( \alpha )}) / ^\circ ) (av, st dev)</th>
<th>( r(\text{Cp centroid-Zr}) ) / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.27, 0.01</td>
<td>360, 0.0</td>
<td>2.20, 2.21</td>
</tr>
<tr>
<td>2</td>
<td>2.34, 0.02</td>
<td>359.6, 0.4</td>
<td>2.27</td>
</tr>
<tr>
<td>3</td>
<td>2.36, 0.02</td>
<td>359.6, 0.2</td>
<td>2.27</td>
</tr>
<tr>
<td>4</td>
<td>2.49, 0.02</td>
<td>358.5, 1.5</td>
<td></td>
</tr>
</tbody>
</table>
it decomposes rapidly at room temperature as a solid or in solution, but can be stored for
days at $-35\,^\circ\text{C}$ under $\text{Et}_2\text{O}$.

Thermolysis of 2 (70 °C, toluene) provided biphenyl, biphenylene, and quaterphenyl as
the only detectable organic products. Thermolysis of 3 (70 °C, toluene) provided
biphenylene as the main organic product. Thermolysis of 4 (20 °C, $\text{Et}_2\text{O}$) provided
biphenyl and biphenylene. Decomposition over 10 d at $-35\,^\circ\text{C}$ provided quaterphenyl as
well. The inorganic or organometallic products from these reactions were intractable and
not characterized.

These compounds are sensitive to acids and oxidants. Complex 1 was quantitatively
converted to zirconocene dichloride by protonolysis with ethereal HCl. Oxidation of 4
with CoCl$_2$ in $\text{Et}_2\text{O}$ provides ortho-quaterphenyl, ortho-sexiphenyl, quaterphenylene, and
sexiphenylene (GC-MS), as well as traces of higher oligophenyls (LD-TOF). The
products of these thermolysis and oxidation reactions suggest that these complexes may
provide new methods to form aryl-aryl bonds.

**Summary**

A new family of zirconium complexes has been prepared and characterized. All
members are metallohydrocarbons. Compounds 3 and 4 are homoleptic. The Zr
fragment, assuming a full positive charge on Li, varies from neutral to a remarkable
tetraanion. In all cases, the Zr atom is electronically unsaturated: in complexes 1, and 4
it carries 16 e$^-$; in complex 2, it carries 14 e$^-$; in complex 3, it carries 12 e$^-$. Our original
intent, the use of dibenzozirconacyclopentadienes as substrates for formal $[4 + 2]$
cycloaddition reactions, was realized. The reaction of 3 with $(\text{PPh}_3)_2\text{NiBr}_2$ followed by
diphenylacetylene gave 9,10-diphenyl phenanthrene (47%); when followed by 3-hexyne,
it gave 9,10-diethyl phenanthrene. The [4 + 2] cycloaddition chemistry of this family of molecules may, however, be the least interesting outcome of this work. We expect the aryl-aryl bond forming reactivity of these complexes to be especially interesting, especially for the dianion 3 and the reactive tetranion 4 (see chapters 3 and 4).

**Hafnium Analogues**

Hafnium analogues of zirconium complexes 1, 3, and 4 were also prepared (Figure 2). The hafnium compounds were prepared starting from hafnocene dichloride using reaction conditions identical to those employed for the synthesis of their zirconium analogs. Interestingly, the hafnium analogue of 2 could not be prepared using the reaction that produced zirconate 2. All attempts to synthesize this compound produced the hafnium analogue of 4 in low yields. The hafnium complexes exhibited less reactivity than the analogous zirconium complexes as judged by their resistance to thermolysis and much slower decomposition when exposed to water and air.

**Figure 2-2.** Three hafnium complexes synthesized using the same procedures used for the synthesis of their zirconium analogues
An alternative synthesis of \([\text{Li}^+\text{(Et}_2\text{O})_4][\text{Hf(biphe)}_4]\) utilizing hafnocene tetrachloride as starting material was developed (Scheme 2). This un-optimized synthesis allowed for simplified purification of the hafnate complex because CpLi is not produced as a reaction by-product.

**Scheme 2-2.** Synthesis of tetrakis (biphenyl[2,2'-diyl])hafnate using hafnium tetrachloride starting material.

![Scheme 2-2](image)

**Experimental Section**

**Biphenyl(2,2'-diyl)zirconocene (1):** The complex 2, 3, (~0.5 g) or 4 (~30 mg) and neat cyclopentadiene (ca. 8 mL) were stirred for 2 h. Precipitated CpLi was removed by filtration. Removal of cyclopentadiene under reduced pressure followed by two crystallizations from hexanes gave biphenyl(2,2'-diyl)zirconocene (from 2, 67%; from 3, 86%; from 4, 2%). Anal. Calc (Found) for \(\text{C}_{22}\text{H}_{18}\text{Zr}\): C, 70.96 (70.68); H, 4.88 (4.99). \(^1\text{H} \text{NMR (500 MHz) (}d_8\text{-THF):} \delta 7.56 (d, J = 7.0 \text{ Hz}, 1.9\text{H, Ar}H), 6.86 (t, J = 8.0 \text{ Hz}, 2.0\text{H, Ar}H), 6.72 (t, J = 7.1 \text{ Hz}, 1.8\text{H, Ar}H), 6.49 (d, J = 6.1 \text{ Hz}, 1.6\text{H Ar}H) 6.36 (s, 9.8 \text{ H Cp}H), 3.56 (s, solvent), 1.71 (s, solvent). \(^1^3\text{C} \text{NMR (125 MHz) (}C_6\text{D}_6):} \delta 186.6, 148.0, 136.3, 126.7, 125.3, 122.4, 113.6.
Bis(biphenyl(2,2'-diyl))cyclopentadienyl zirconate, Li salt (2): n-Butyllithium (1.76 M in hexane, 6.8 mL, 12 mmol) was added to a solution of 2,2'-dibromobiphenyl (1.807 g, 5.8 mmol) in THF (20 mL) at –80 °C. After warming to –30 °C, Cp₂ZrCl₂ (1.693 g, 5.8 mmol) was added. This temperature was maintained for 1 h and then the reaction warmed to 25 °C. Solvent was removed under vacuum and the residue was washed with hexane and then dissolved in THF (20 mL). The volume of the THF was reduced by half and the solution was placed in the freezer. Yellow crystals (1.736 g, 76%) formed overnight. ¹H NMR (500 MHz) (C₆D₆): δ 7.85 (t, J = 7.0 Hz, 8H, ArH), 7.21 (t, J = 7.5 Hz, 4H, ArH), 7.12 (t, J = 7.5 Hz, 4H, ArH), 6.32 (s, 5H, CpH). ¹³C NMR (125 MHz) (C₆D₆): δ 190.6, 155.6, 139.7, 128.7, 127.5, 125.9, 121.8, 114.0, 68.5, 25.8.

Tris(biphenyl(2,2'-diyl))zirconate², Li salt (3): n-Butyllithium (2.9 M in hexane, 6.9 mL, 20.0 mmol) was added to solution of 2,2'-dibromobiphenyl (3.120 g, 10.0 mmol) in 100 mL of THF at –80 °C. After warming to –30 °C, Cp₂ZrCl₂ (0.730 g, 2.5 mmol) was added. The temperature was maintained for 18 h and fine yellow crystals (2.47 g, 87%) precipitated from solution. ¹H NMR (500 MHz) (C₆D₆): δ 8.41 (m, J = 6.5 Hz, 6H, ArH), 7.75 (m, J = 7.5 Hz, 6H, ArH), 7.21 (m, J = 7 Hz, 6H, ArH), 7.15 (m, J = 7 Hz, 6H, ArH), 3.34 (m, 48H, THF), 1.31 (m, 44H, THF). ¹³C NMR (125 MHz) (C₆D₆): δ 190.9, 157.7, 140.7, 128.9, 125.9, 121.0, 67.8, 25.6.

Tetrakis(biphenyl(2,2'-diyl))zirconate⁴, Li salt (4): The reaction sequence was identical to that used to prepare 3, except that Et₂O replaced THF and the reaction was scaled by 0.57. Blocky crystals (0.825 g, 56%) were formed. ¹H NMR (500 MHz) (₈₅-toluene): δ 7.98 (m, J = 8 Hz, 16H, Ar-H), 7.13 (m, J = 7.5 Hz, 8H, Ar-H), 6.88 (m, J =
7.5 Hz, 8H, Ar-H) 3.38 (q, 7 Hz, 138H, Et₂O), 1.12 (t, 7 Hz, 208H, Et₂O). ¹³C NMR (125 MHz) (C₆D₆): δ 153.7, 144.8, 128.7, 126.4, 126.0, 122.8, 66.1, 15.7.

3 from 2: n-Butyllithium (1.62 M in hexane, 0.4 mL 0.66 mmol) was added to a solution of 2,2′-dibromobiphenyl (0.103 g, 0.33 mmol) in THF (10 mL) at −78 °C. The solution was allowed to warm to −30 °C and then added to solution of 2 (0.250 g 0.33 mmol) in THF (5 mL), also at −30 °C. The resulting yellow precipitate was collected by filtration and rinsed with THF (0.360 g, 96%). The ¹H NMR spectrum and crystal unit cell were identical to 3 prepared from Cp₂ZrCl₂.

4 from 3: n-Butyllithium 1.62 M in hexane (0.26 mL 0.44 mmol) was added to a stirred solution of dibromobiphenyl (0.137 g, 0.44 mmol) in Et₂O (20 mL) at −40 °C. After 0.5 h, 3 (0.500 g, 0.44 mmol) was added as a solid. The temperature was maintained at −40 °C for 16 h. The reaction volume was reduced by half and crystals formed overnight (0.4191 g, 93%), which gave an identical ¹H and ¹³C NMR to that of 4 prepared from Cp₂ZrCl₂.

3 from 1: A solution of 2,2′-dilithiobiphenyl (0.0442 g, 0.266 mmol) in THF (10 mL) was added over 5 min to 1 (0.050 g, 0.133 mmol) dissolved in THF (10 mL) at −35 °C. After 1 h, the reaction was allowed to warm to 25 °C. The precipitate was collected by filtration and rinsed with hexane and THF to yield 3 (0.139 g, 92%), which gave an identical ¹H and ¹³C NMR to that of 3 prepared from Cp₂ZrCl₂.

Thermolysis of 2 and 3: The complex 2 or 3 (200 mg) was dissolved in toluene (50 mL) in a Schlenk flask under Ar and then heated to 70 °C for 3 h. Solvent was removed under vacuum and the hexane-soluble fraction analyzed by GC-MS. Compound 2
yielded biphenyl, biphenylene, and quaterphenyl and 3 yielded primarily biphenylene with trace amounts of biphenyl and quaterphenyl.

**Thermolysis of 4:** Complex 4 in Et₂O was thermolyzed at 25 °C under Ar for 24 h. Solvent was removed under vacuum and the hexane-soluble fraction analyzed by GC-MS, which revealed biphenyl and biphenylene.

**Hydrochlorolysis of 1:** Complex 1 (150 mg 0.40 mmol) was dissolved in 1 M HCl in diethyl ether (~15 mL) and the yellow solution went immediately clear. After evaporation the residue was triturated with hexane to isolate biphenyl (60.3 mg, 100%, GC-MS). The insoluble material was recrystallized from THF to yield Cp₂ZrCl₂ (117 mg, 100%, ¹H NMR).

**Oxidation of 3:** Complex 3 (0.250 g, 0.22 mmol), suspended in Et₂O, was mixed with CoCl₂ (0.058 g, 0.22 mmol) for 6 h at 25 °C. Solvent was removed under vacuum and the toluene-soluble fraction analyzed by GC-MS, which revealed quaterphenyl, quaterphenylene, hexaphenyl, and hexaphenylene. LDTOF-MS analysis showed hexaphenyl, hexaphenylene, and traces of octaphenyl, octaphenylene, and decaphenylene.

**Reaction of 3 with diphenylacetylene and Ni(PPh₃)₂Br₂:** Complex 3 (0.125 g, 0.11 mmol) and diphenylacetylene (0.066 g, 0.33 mmol) were suspended in THF (10 mL) and Ni(PPh₃)₂Br₂ (0.275g 0.33 mmol) was added. After 12 h, aqueous HCl (6 M, 50 mL) was added. Extraction with toluene, chromatography, and PPh₃ removal with CuCl afforded diphenylphenanthrene (0.052 g, 48%, GC-MS, ¹H NMR).

**Biphenyl(2,2′-diyl)hafnocene.** Lithium tris[biphenyl (2,2′-diyl)]hafnate (1.00 g, 0.81 mmol) was placed in a flask with a stir bar, 10 mL freshly cracked cyclopentadiene,
and 15 mL of toluene; the resulting yellow suspension was stirred at 60° C for 72 hr. The reaction was cooled to room temperature and filtered to remove the white cyclopentadienyl lithium powder. The yellow filtrate was concentrated by evaporation. The remaining liquid was shaken with hexane and evaporated. This process was repeated twice more resulting in a white viscous material and yellow crystals. The yellow material was dissolved in hexane and the mixture filtered to remove any solid material. Pale yellow biphenyl(2,2'-diyl) hafnocene (74 mg, 20%) was obtained through crystallization from hexane at −30 °C. ¹H NMR (500 MHz) (d₆-benzene): δ 8.01 (d, J = 9.0 Hz, 1.9H, ArH), 7.18 (t, J = 8.0 Hz, 2.0H, ArH), 7.14 (t, J = 7.1 Hz, 1.8H, ArH), 6.64 (d, J = 6.1 Hz, 1.6H, ArH), 5.77 (s, 9.8 H, CpH). ¹³C NMR (125 MHz) (C₆D₆): δ 192.8, 145.4, 137.4, 126.7, 126.2, 122.6, 112.7.

**Lithium tris(biphenyl (2,2'-diyl))hafenate³⁻.** n-Butyllithium (1.52 M in hexane; 8.0 mL, 20.2 mmol) was added to a stirred solution of 2,2'-dibromobiphenyl (3.12 g, 10 mmol) in 50 mL THF at −80 °C. The solution was allowed to warm to −30 °C, at which time hafnocene dichloride (944 mg, 2.50 mmol) was added as a powder. The solution was allowed to warm to room temperature, and a yellow precipitate formed. The product (1.42 g, 46%) was collected on a filter and dried under high vacuum. ¹H NMR (500 MHz) (C₆D₆): δ 8.41 (m, J = 6.5 Hz, 6H, ArH), 7.78 (m, J = 7.5 Hz, 6H, ArH), 7.21 (m, J = 7 Hz, 6H, ArH), 7.15 (m, J = 7 Hz, 6H, ArH), 3.31 (m, 48H, THF), 1.31 (m, 44H, THF). ¹³C NMR (125 MHz) (C₆D₆): δ 197.3, 159.2, 142.6, 128.6, 126.4, 121.6, 68.0, 25.9.

**Lithium tetrakis(biphenyl(2,2'-diyl))hafenate⁴⁻.** n-Butyllithium 1.52 M in hexane (3.95 mL, 9.87 mmol) was added to a stirred solution of 2,2'-dibromobiphenyl (1.54 g,
4.94 mmol) in diethyl ether (25 mL) at −80 °C. The solution was allowed to warm to −30 °C, at which time hafnocene dichloride (233 mg, 0.617 mmol) was added as a powder. The solution was allowed to warm and stirred at room temperature for 1 h. The mixture was filtered and the yellow filtrate evaporated to dryness. The solid obtained was dissolved, as much as possible, in diethyl ether and filtered again. Pale yellow crystals were obtained (143 mg, 20%) from this second filtrate at −30 °C. $^1$H NMR (500 MHz) ($d_8$-THF): δ 7.97 (m, J = 8 Hz, 16H, Ar-H), 7.16 (m, J = 7.5 Hz, 8H, Ar-H), 6.87 (m, J = 7.5 Hz, 8H, Ar-H), 3.38 (q, 7 Hz, 138H, Et$_2$O), 1.07 (t, 7 Hz, 208H, Et$_2$O). $^{13}$C NMR (125 MHz) ($d_8$-THF): δ 156.8, 144.1, 129.8, 128.7, 127.0, 124.2, 66.1, 15.8.

**Lithium tetrakis(biphenyl(2,2′-diyl))hafnate$^{4-}$ (alternative synthesis).** $n$-Butyllithium (1.52 M in hexane; 3.95 mL, 9.87 mmol) was added to a stirred solution of 2,2′-dibromobiphenyl (1.54 g, 4.94 mmol) in 25 mL diethyl ether at −80 °C. The solution was allowed to warm to −30 °C, at which time hafnium tetrachloride was added. The reaction was allowed to warm to room temperature and filtered under argon. The filtrate was concentrated to ~10 mL and placed in a −35 °C freezer overnight. After 12 hours, crystals of pure lithium tetrakis (biphenyl(2,2′-diyl)) hafnate$^{4-}$ were isolated by filtration (115 mg, 16%).
References:

(23) Jones, B. S.; Petersen, J. L. Organometallics 1985, 4, 966-971.
Chapter 3


Uncatalyzed Zirconium-Mediated Biphenylation of o-Dihalobenzenes To Form Triphenylenes

Introduction.

Aryl-aryl bond forming reactions are ubiquitous in synthesis.\(^1\) Zirconium has, however, played a limited role in this field. Buchwald reported a Pd-mediated reaction of a Zr-benzyne complex with benzenes or biphenyls to give biphenyls or terphenyls.\(^2\) Takahashi reported a Cu-mediated reaction of an alkyl zirconopentadiene with o-diodobenzenes to give alkyl-substituted naphthalenes.\(^3\)

Results and Discussion.

We report herein the uncatalyzed reaction of \([\text{Zr}(\text{biphe})_3][(\text{Li} \bullet (\text{Et}_2\text{O}))_2] (1),^4\) where biphe is 2,2′-biphenyldiyil, with o-dihaloarenes to give triphenylenes (Scheme 1). The reaction is noteworthy from a synthetic viewpoint because it is a new disconnection for the synthesis of polycyclic aromatic hydrocarbons (PAHs). The closest reported analog is the double nucleophilic aromatic substitution reaction of 2,2′-dilithiobiphenyl with hexafluorobenzene to afford 1,2,3,4-tetrafluorotriphenylene.\(^5\) The reaction is noteworthy from an organometallic viewpoint because it is a rare, if not unprecedented, example of an uncatalyzed, Zr-mediated aryl-aryl bond formation. The scope is broad. The reaction works with all halogens (Scheme 1). Dichloro-, dibromo- and diiodobenzene give higher yields (14%, 26%, 48%) than difluorobenzene (2%). Substituents are tolerated: 4,5-dibromoveratrole or 4,5-dibromo-o-xylene react with 1 to give the corresponding 2,3-disubstituted triphenylene.
Scheme 3-1. Substitution of o-dihalides by 2,2'-biphenyldiyl.

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Yield</th>
</tr>
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<tr>
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</tr>
<tr>
<td>Cl</td>
<td>H</td>
<td>14</td>
</tr>
<tr>
<td>Br</td>
<td>H</td>
<td>26</td>
</tr>
<tr>
<td>I</td>
<td>H</td>
<td>48</td>
</tr>
<tr>
<td>Br</td>
<td>OMe</td>
<td>61*</td>
</tr>
<tr>
<td>Br</td>
<td>Me</td>
<td>66*</td>
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<tr>
<td>I</td>
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<td>cmpd</td>
<td>Yield</td>
</tr>
<tr>
<td>H</td>
<td>17* %</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>Ph</td>
<td>3</td>
<td>ref (7)</td>
</tr>
</tbody>
</table>

This method provides rapid entry into 1,2-disubstituted triphenylenes, which may be useful as discotic liquid crystals. The reaction of 1,2-diiodo-4,5-dihexylbenzene with 1 gave 2,3-dihexyltriphenylene in 8.4% yield.

Multiple biphenyldiyl moieties can be introduced in a single step. The reaction of 1,2,4,5-tetrabromobenzene with 1 afforded tetrabenz[a,c,h,j]anthracene in 17% isolated yield.

Strained molecules can be produced. The reaction of 1 with tetrabromo-p-xylene gave 9,18-dimethyltetrabenza[c,h,j]-anthracene (2) in 9% yield. This molecule is slightly more strained (38 kcal/mol, B3LYP/6-31+G*) than Pascal’s analogous 9,18-diphenyltetraconta[c,h,j]-anthracene (3) (34 kcal/mol, B3LYP/6-31+G*). Like 3, 2 is easily reduced - excess 1, which is presumably a reductant, gives the corresponding 9,18-dihydro product as a major component.
This reaction works in a variety of conditions: in toluene, dioxane, or THF solution, or with neat liquid reagents. The best procedure utilizes toluene at 25 °C with sufficient solvent to dissolve all reactants. Most reactions are complete after 20 min.

This unoptimized reaction is not ideal. Significant amounts of quaterphenyl are produced, which may arise from the oxidation of 1 or zirconates derived from 1 upon workup or from a reductive elimination step. The yields vary from poor to modest.

We are uncertain of the mechanism. Double nucleophilic aromatic substitution is unlikely since electron-rich dihalobenzenes, e.g. 4,5-dibromo veratrole, are good substrates. A mechanism involving the reductive generation of benzyne from the o-dihaloarene and its subsequent insertion into Zr-(biphe) bonds is also possible. Trapping experiments, however, do not support this mechanism – the reaction of o-dibromobenzene with 1 in the presence of a 10-fold excess of furan proceeded normally and did not produce detectable (GC-MS) amounts of the trapping product, 1,4-dihydro-1,4-epoxynaphthalene.

A mechanism involving oxidative insertion of Zr into an aryl-halogen bond may operate. Since the Zr center is $d^0$, reduction would have to precede oxidative insertion. The formation of quaterphenyl suggests this may occur. $\sigma$-Bond metathesis, perhaps involving electron-transfer, is another possibility.

This transformation enables a new disconnection for the synthesis of PAHs: the double substitution of two o-halogens with a biphenyldiyi moiety to give a terphenyl fragment. The reaction tolerates functionality and can generate strained molecules. This reaction is a rare example an uncatalyzed aryl-aryl bond formation reaction involving zirconium.
Experimental Section.

General Methods. All reactions were carried out in a glove box plumbed with argon gas. All reaction solvents were used dry and degassed with argon. 1,2-Dihalobenzenes, hexafluorobenzene, 1,2,4,5-tetrabromobenzene, 2,3,5,6-tetrabromo-p-xylene, and 1,2-dibromo-4,5-dimethoxy benzene were all purchased from commercial sources and used as received. 1,2-Dibromo-4,5-dimethylbenzene and 1,2-dihexyl-4,5-diiodobenzene were prepared according to the literature procedures.

Reactions of lithium tris biphenyl(2,2'-diyl)zirconate$^{2-}$ with 1,2-dihalobenzenes. The complex 1 (148 mg, 0.13 mmol) was added to a solution of the dihalobenzene (1.25 mmol) in toluene (30 mL) and was stirred for 3 h. The reaction was quenched by addition of ethereal HCl. The mixture was washed with water (3 × 15 mL), and the organic phase was collected. The yield of triphenylene was determined by GC using an external standard of triphenylene: from difluorobenzene, 2%; from dichlorobenzene, 14%; from dibromobenzene, 26%; from diiodobenzene, 48%.

Reaction of lithium trisbiphenyl(2,2'-diyl) zirconate$^{2-}$ with neat dichlorobenzene. The complex 1 (286 mg, 0.25 mmol) and neat 1,2-dichlorobenzene (20 mL) were stirred for 5 min. The reaction was quenched by addition of ethereal HCl. Solvent and volatile impurities were removed under vacuum (45 mTorr), and the residue was placed on a Kugelrohr at 120 °C (45 mTorr). The material that sublimed into the first bulb was isolated and crystallized from hexane to give triphenylene (104 mg, 66%) with GC-MS, $^1$H and $^{13}$C NMR spectra identical to authentic triphenylene standard (Aldrich).

Reaction of lithium trisbiphenyl(2,2'-diyl)zirconate$^{2-}$ with 1,2,4,5-tetrabromobenzene. The complex 1 (276 mg, 0.24 mmol) was added to a solution of
1,2,4,5-tetrabromobenzene (100 mg, 0.25 mmol) in toluene (50 mL) at 100 °C and was stirred for 15 min. The reaction was allowed to cool to room temperature and was quenched by addition of ethereal HCl. The mixture was washed with water (3 × 30 mL), and the organic phase was collected and evaporated to dryness. The residue was washed with hexane (250 mL), and the insoluble material was filtered off and rinsed further with hexane (30 mL) and benzene (30 mL) to give tetrabenzo[a,c,h,j]anthracene (16 mg, 17%) with UV-Vis spectrum identical to reported literature.\textsuperscript{11} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): Δ7.71-7.79 (m, 8H), 8.70 (d, 4H), 8.96 (d, 4H), 9.93 (s, 2H).

**Reaction of lithium trisbiphenyl(2,2'-diyl)zirconate\textsuperscript{2−} with 2,3,5,6-tetrabromo-p-xylene.** The complex \textsuperscript{1} (286 mg, 0.25 mmol) was added to a solution of 2,3,5,6-tetrabromo-p-xylene (81 mg, 0.19 mmol) in toluene (50 mL) and was stirred for 4 h. The reaction was quenched by addition of aqueous HCl (5 M, 50 mL), and the organic phase was collected and evaporated to dryness. The residue was washed with boiling heptane. The insoluble product was filtered off and further washed with heptane to give 9,18-dimethyltetrabenzo[a,c,h,j]anthracene (6.5 mg, 8%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): Δ8.66 (d, J=8.5 Hz, 4H), 8.56 (d, J=8.0 Hz, 4H), 7.57-7.66 (m, 8H), 3.34 (s, 6H). \textsuperscript{13}C NMR (500 MHz, CDCl\textsubscript{3}): Δ134.0, 132.1, 131.3, 130.4, 129.9, 127.4, 125.6, 122.9, 30.3. UV-Vis (dichloromethane) \(λ_{\text{max}}\) (log\(ε\)): 313nm (5.7), 276nm, 260nm. HMRS calculated: 406.172, found: 406.1602.

**Reaction of lithium trisbiphenyl(2,2'-diyl)zirconate\textsuperscript{2−} with 1,2-dibromo-4,5-dimethylbenzene.** The complex \textsuperscript{1} (284 mg, 0.25 mmol) was added to a solution of 1,2-dibromo-4,5-dimethylbenzene (656 mg, 2.5 mmol) in toluene (100 mL) and was stirred for 30 m. The reaction was quenched by addition of ethereal HCl. The mixture was
washed with water (3 × 30 mL), and the organic phase was collected and evaporated to dryness. The residue was placed on a kugelrohr (45 mTorr) for 2 h. The non-volatile material was then dissolved in toluene and filtered to give 2,3-dimethyltriphenylene (95 mg, 49%) with $^1$H and $^{13}$C NMR spectra identical to that reported in the literature.\textsuperscript{12}

**Reaction of lithium trisbiphenyl(2,2'-diyl)zirconate\textsuperscript{2-} with 1,2-dibromo-4,5-dimethoxybenzene.** The complex 1 (284 mg, 0.25 mmol) was added to a solution of dibromoveratrol (740 mg, 2.5 mmol) in toluene (100 mL) and was stirred for 30 m. The reaction was quenched by addition of ethereal HCl. The mixture was washed with water (3 × 30 mL), and the organic phase was collected and evaporated to dryness. The residue was placed on a kugelrohr (45 mTorr) for 6 h at 60 °C. The non-volatile material was crystallized from toluene to give 2,3-dimethoxytriphenylene (131.76 mg, 61%) with $^1$H and $^{13}$C NMR spectra identical to that reported in the literature.\textsuperscript{13}

**Reaction of lithium trisbiphenyl(2,2'-diyl)zirconate\textsuperscript{2-} with 1,2-dihexyl-4,5-diiodobenzene.** The complex 1 (1.136 g, 1.00 mmol) was added to a solution of 1,2-dihexyl-4,5-diiodobenzene (498 mg, 1.0 mmol) in toluene (60 mL) for 30 m. The mixture was washed with water (30 mL), and the organic material was collected and evaporated to dryness. The residue was placed on a kugelrohr (45 mTorr) overnight at 150 °C. The non-volatile material was then dissolved in heptane and filtered through silica gel to give 2,3-dihexyltriphenylene (33.3 mg 8.4%) with $^1$H and $^{13}$C NMR spectra identical to that reported in the literature.\textsuperscript{14}
References:

Chapter 4


18,18’-Dihexyl[9,9’]biphenanthro[9,10-b]triphenylene: Construction and Consequences of a Profoundly Hindered Aryl-Aryl Single Bond

Introduction

We report the synthesis, characterization, and conformational analysis of the title arene 1-Hex, in which two phenanthro[9,10-b]triphenylene (PTP) moieties are joined through their sterically hindered 9 positions (Figure 1). This single bond joins two gulf$s$, a term we coin by extension of the established bay, cove, and fjord nomenclature\(^1\) (Figure 1). Steric congestion twists the PTP moieties\(^2\) and hinders rotation about the central bond, giving rise to rich conformational behavior.

Figure 4-1. Structure of 1-R and definitions of concave PAH regions.

Pascal’s pioneering syntheses\(^2,3\) of gulf-substituted PAHs was motivated by an interest in the relationship between steric congestion, reactivity, structure, and properties; the story is told in an engaging review.\(^4\) Other gulf-substituted PAHs have been synthesized and studied due to their role in carcinogenesis.\(^5\) PAHs bearing COOR’ (R’ = H, alkyl) in a gulf have been used as rigid spacers for molecular tweezers.\(^6,7\)
Figure 4-2. Some known PAHs with gulfs. Unsaturation and non-gulf H atoms are omitted for clarity.

The simplest PAH with a gulf architecture is dibenzo[a,j]anthracene (2-H, Figure 2); the placement of a substituent in the gulf region (position 14) introduces much strain and distorts the PAH skeleton from planarity. The derivatives 2-COOH and 2-COOR were used as a rigid spacer for molecular tweezers, and were prepared via a pyrylium salt. Its derivative 2-Ph was recently prepared using a Wagner-Meerwein rearrangement of a substituted 9-fluorenylmethanol. The second skeleton in this family, naphtho[1,2-b]triphenylene (3-H), bears an additional ortho-fused ring (Figure 2), but still has only one gulf. Its derivative, 3-Me, was synthesized by a Grignard route from the corresponding quinone, and its derivative, 3-Ph, was prepared by the Diels-Alder cycloaddition of phencyclone with 4-chlorodihydronaphthalene followed by oxidation. The third skeleton, phenanthro[9,10-b]triphenylene (4-H), has two gulfs (Figure 2). Pascal and co-workers pioneered the study of its gulf-substituted derivatives using a Diels-Alder approach, in which 9,10-didehydrophenanthrene reacts with phencyclone dienes or by using the pyrolysis of phencyclone dienes, to prepare the twisted and strained 4-Ph and other 4-(p-C₆H₄X) derivatives. Rabinovitz and co-workers developed another route to 4-Ph, the Li-mediated coupling and subsequent oxidation of hexaphenylbenzene. The last method for the preparation of this skeleton is the two-
fold, Zr-mediated biphenylation of 1,4-disubstituted tetrabromobenzene, which we previously employed for the preparation of 4-Me.\textsuperscript{12} We also use this method for the synthesis of 1-Hex.

1-Hex is unique – it is the only known compound with a gulf-gulf bond. This structural element gives rise to several phenomena that merit investigation. It introduces a great deal of strain, but the 9,9’ bond exhibits a paradoxically normal length. It gives rise to a chiral equilibrium structure and rich conformational dynamics. Sterics profoundly hinder rotation about the 9,9’ bond.

Results and Discussion

Synthesis. The synthesis of 1-Hex uses the recently developed reagent, (Li(THF))\textsubscript{4}•Zr(biphe), (5, biphe is 2,2’-biphenyldiyl),\textsuperscript{13} to effect the four-fold biphenylation of 4,4’-dihexyloctabromobiphenyl (6). The basic reaction is a double ipso substitution on an ortho-dihaloarene to form a triphenylene fragment.\textsuperscript{12} To the best of our knowledge, the only other method for this transformation is the recently reported Stille coupling with a 2,2’-distannylbinaphthyl reagent under microwave irradiation.\textsuperscript{14}

Exhaustive electrophilic bromination of 4,4’-dihexylbiphenyl, which was prepared by Kumada coupling of 4,4’- dibromobiphenyl with hexylmagnesium bromide, gives octabromide 6. Treatment of 6 with 5 afforded 1-Hex in 5% isolated yield (Scheme 1). By-products, which are mostly oligophenyls, were removed by trituration with hexane. Preparative HPLC (silica gel, hexane / chloroform) followed by crystallization from benzene gave pure 1-Hex. This compound can be stored in air, and is soluble in THF, toluene, benzene, chloroform, and dichloromethane. No light sensitivity has been noted.
**Scheme 4-1.** Synthesis of 1-Hex.

![Scheme 4-1 Synthesis of 1-Hex](image)

**Static Structure.** The structure of 1-Hex was determined by two independent single crystal X-ray diffraction analyses. While the crystals differed in the number of benzene solvate molecules and in the conformations of the hexyl chains, the geometries of the PAH cores were nearly identical.

Three perspectives of one structure, the hemisolvate, are shown in Figure 3. The PTP moieties twist, in the same chiral sense, to accommodate one another. The resulting structure is reminiscent of a handshake, a term we employ as a trivial name. Several metrics (Figure 4) describe the static geometry: the length of the central bond \( r \), the dihedral angle \( d_a \) about the central bond (8b, 9, 9', 8b'), and the dihedral angle describing the twist of a PTP moiety. Two definitions of this twist dihedral are used in the literature: (1) the angle \( d_b \) between the least-squares plane of the central ring and the least squares plane of the two distal rings\(^{16}\) and (2) the angle \( d_c \), which is the greater of the dihedral 4a, 4b, 13a, 13b or dihedral 4b, 4a, 13b, 13a.\(^{17}\) To facilitate comparisons, we report values for both definitions. The other metrics \( d_{a_1}, a_p, a_d, \Sigma a_0, \) and \( \Sigma a_{18} \) are needed to describe dynamic behavior and will be discussed later.
Figure 4.3. Three views of the X-ray diffraction analysis structure of $1\text{Hex}^+$ (benzene)$_{0.5}$. Hydrogen atoms, solvent, and the terminal four carbon atoms of the hexyl groups are omitted for clarity (50% ellipsoids shown).
The X-ray diffraction data reveal a surprisingly ordinary central bond length $r$, 1.49 Å (cf. 9,9'-bianthracene,\textsuperscript{18} 1.50 Å), despite the large amount of strain in this hindered central bond (see below). The dihedral angle $d_a$ is 57.8° (cf. 9,9'-bianthracene,\textsuperscript{18} 79.1°). The PTP moieties are highly twisted, with an average torsion angle $d_c$ of 69° (cf. 4-Ph,\textsuperscript{3} 66°), but less than that of the current record holder, hexaphenyltetra-benzo[\textit{a,c,l,n}]pentacene, in which an anthracene subunit exhibits a twist of 86°.\textsuperscript{19}

\textbf{Figure 4-4.} Numbering and characteristic metrics of 1-Hex.
Table 4-1. Measurements of 1-Hex.

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<th>geometry</th>
<th>( r / \text{Å} )</th>
<th>( d_a, s / °, n^a )</th>
<th>( d_b, s / °, n^a )</th>
<th>( d_c, s / °, n^a )</th>
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<td>X-ray, disolvate(^b)</td>
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<td>X-ray, hemisolvate(^b)</td>
<td>1.487(3)</td>
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<td>36.5, 1.6, 4</td>
<td>69.0, 3.0, 2</td>
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<td>B3LYP/6-31G(d)(^c)</td>
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<tr>
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<td>39.5, 0.2, 2</td>
<td>75.5, 0, 1</td>
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<td>39.9, 0.1, 2</td>
<td>74.9, 0, 1</td>
</tr>
</tbody>
</table>

\(^a\) number of measurements. \(^b\) no molecular symmetry. \(^c\) no molecular symmetry, close to \( C_2 \) point group, hexyl groups all \textit{anti}. \(^d\) \( C_2 \) point group. \(^e\) Modified AMBER force field.

Computational modeling of 1-Hex was carried out and geometries reasonably close to those found by X-ray diffraction were obtained (Table 1) using both DFT and semi-empirical models (calculations performed by J. Crowfoot and P. Rempala).\(^20\)

To simplify computational analysis, calculations were carried out on the 1-Hex analogs: 1-Me (strain, rotation about the central bond), 1-Et (alkyl motion), and 1-H (NMR chemical shift benchmarking).

**Strain.** Preliminary calculations (AM1) indicated that analog 1-Me is higher in energy by about 60 kcal/mol than an unstrained reference isomer. Further calculations (performed by J. Crowfoot and P. Rempala) at the B3LYP 6-31G(d) level of theory allowed decomposition of strain into two components (Scheme 2), that arising from a gulf-gulf bond (37.4 kcal/mol) and that originating from methyl substituted gulfs (34 kcal/mol). 1-Me is a good model compound for studying the strain found in 1-Hex.
because the terminal 5 carbons of the hexyl chains in \textbf{1-Hex} can be arranged such that they create no additional strain. The overall strain found in \textbf{1-Me} using B3LYP 6-31G(d) is 72 kcal/mol.\textsuperscript{20}

\textbf{Scheme 4-2.} Homodesmotic strain energies (B3LYP/6-31G(d), $\Delta E_{el}$, $\Delta G_{298}$ in parentheses) for \textbf{1-Me}.

\textbf{Bond Energy.} The homolytic bond dissociation energy of \textbf{1-Me} was calculated to be 67.4 kcal/mol; for comparison, biphenyl was calculated to be 115.2 kcal/mol. These calculations, carried out using the B3LYP/6-31G(d) level of theory and basis set, indicate that the bond strength for the central bond of \textbf{1-Me} is about 60\% of that for the central bond in biphenyl (all bond dissociation calculations performed by J. Crowfoot).\textsuperscript{20}

\textbf{Bond Length.} The length of the central bond in \textbf{1-Hex} (1.490 Å) is essentially identical to that of biphenyls without substitution \textit{ortho} to the central bond (1.487 Å, $s = 0.007$ Å) and biphenyls with substitution \textit{ortho} to the central bond (1.490 Å, $s = 0.010$ Å).
Å). Why does the weak central bond of \textbf{1-Hex} – which has only 60\% of the normal strength of a biphenyl central bond – exhibit a normal bond length? We address this question by exploring the potential energy surface of \textbf{1-Me} at intermediate bond lengths, stretching the central bond from equilibrium to 11 Å. These calculations reveal that lengthening the central bond in \textbf{1-Me} releases strain only gradually until about 5.5 Å at which point the PTP blades disengage releasing ~14 kcal/mol of strain.

Force, not energy, determines the equilibrium bond length: at equilibrium, the net force is zero. If the change of strain energy is small around the equilibrium geometry, then strain will not alter the equilibrium distance. This appears to be the case for \textbf{1-R} (all bond length calculations performed by P. Rempala).\textsuperscript{20}

\textbf{NMR Spectra.} All \textsuperscript{1}H and \textsuperscript{13}C NMR resonances have been assigned (Figure 5) by a combination of DQF-COSY, NOE, HMQC, and HMBC spectra (see Appendix). The \textsuperscript{1}H NMR spectrum of \textbf{1-Hex} in benzene-d\textsubscript{6} at 55 °C revealed eight well-dispersed aryl signals and seven alkyl resonances. The most downfield alkyl resonance at about 4.1 ppm was diagnostic; it could be assigned to protons H19a and H19b. The reason this alkyl resonance appears unusually far downfield in the \textsuperscript{1}H NMR spectrum is its proximity to the aryl rings, which create deshielding diatropic ring currents. A 1-D NOE experiment, which gives through space proximity, correlated the most downfield signal in the aryl region with the diagnostic alkyl resonance at 4.1 ppm (Figure 5, top spectrum). The peak at 8.3 ppm was assigned to protons H1 and H17. A DQF-COSY, which reveals three bond proton-proton coupling, allowed assignment of the H2, H16 (7.35 ppm); H3, H15 (7.29 ppm); and H4, H14 (7.97 ppm) proton pairs. Another 1-D NOE experiment (Figure 5, bottom two spectra) correlated proton pair H5, H13 with pair H4, H14
allowing the resonance at 7.80 ppm to be assigned. The DQF-COSY and prior assignment of proton pair H5, H13 allowed the assignment of the remaining aryl resonances H6, H12 (6.69 ppm); H7, H11 (6.20 ppm); and H8, H10 (7.59 ppm). The alkyl resonances were also assigned on the basis of the DQF-COSY, utilizing diagnostic 1H resonances of H19a and H19b as the starting point. Diastereotopic protons H20a and H20b were resolved at 55 °C and the resonances at 2.14 and 1.81 ppm were assigned to them. Proton H23 was assigned the resonance at 1.41 ppm. Protons H21 and H22 were coincidentally degenerate and assigned the resonance at 1.21 ppm. Proton H24 was assigned to the resonance at 0.83.
Figure 4-5. Three 1D NOE spectra (C₆D₆); allowing correlation of proton chemical shifts by through space interaction with their nearest neighbors.
Figure 4-6. The aryl regions of the $^1$H-COSY off diagonal peaks correlate protons separated by three bonds.

With the proton NMR spectrum fully assigned, we turned to assignment of all carbon chemical shifts. The carbons bearing protons were assigned by HSQC, which gives one bond proton carbon correlation (see appendix). Non-proton bearing carbons were assigned by HMBC NMR spectroscopy, which gives three and four bond correlations between non proton bearing carbons and protons (Figure 7).
Figure 4-7. The HMBC spectrum correlates aryl proton resonances with non-proton bearing carbons through three and four bonds.
GIAO NMR calculations support the assignments. Benchmark calculations were performed on the model system **1-H** at $D_2$ symmetry, using a variety of functionals and basis sets and using the geometry determined by B3LYP/6-31G(d) calculations. Because all models predicted similar chemical shifts (see Supporting Information), we decided to use the more affordable B3LYP/6-31G(d)-GIAO//B3LYP/6-31G(d) level for NMR prediction of **1-Hex**. (All NMR calculations performed by J. Crowfoot and P. Rempala).\(^{20}\)

Comparison of the NMR spectra of **1-Hex** with **4-Ph**\(^{11}\) is informative. Unsymmetrical substitution of the PTP moieties in **1-Hex** splits the resonances found in symmetrically substituted **4-Ph**; these correlations are traced in Figure 6. Protons facing the aryl gulf (6, 7, 8) are upfield of protons facing the aliphatic gulf. This is reasonable, as the aryl gulf-facing protons experience a diatropic shift due to their proximity to the other PTP moiety. In the $^{13}$C spectrum of **1-Hex** (and **4-Ph**), aryl carbons bearing protons are upfield of internal carbon atoms.
**Figure 4-8.** The aryl regions of the $^1$H and $^{13}$C NMR spectra of 1-Hex (C$_6$D$_6$) (black); correlation of the chemical shifts of 4-Ph with the calculated (GIAO-B3LYP/6-31G(d)) and experimental chemical shifts of 1-Hex (red).

**Variable Temperature NMR.** Variable temperature $^1$H NMR spectroscopy revealed two dynamic processes (Scheme 3). Inversion of chirality causes the diastereotopic protons of CH$_2$(19) and CH$_2$(20) to coalesce at 45°C and 50°C, respectively. Analysis of the coalescence of the CH$_2$(19) resonances gives DG$^{\ddagger}_{\text{inversion}}$ of 15.3 ± 0.5 kcal/mol; and the coalescence of resonances of CH$_2$(20), which are partially obscured by solvent, gives a DG$^{\ddagger}_{\text{inversion}}$ of 15.2 ± 0.6 kcal/mol (Figure 7). Pascal and co-workers reported a similar barrier to inversion, 16.7 kcal/mol, in 4-(p-i-PrC$_6$H$_4$).
Hindered rotation of the hexyl groups about dihedral $d_d$ lowers the apparent symmetry of the molecule from $D_2$ to $C_2$ (or $C_1$, depending on the relative orientations of the two of $d_d$ dihedrals). Aryl protons H(1) and H(17) coalesce at $-5$ °C, giving a $\Delta G^\ddagger$ of $12.0 \pm 0.4$ kcal/mol. In addition, both pairs, H(8) and H(10), and H(7) and H(11), coalesce at $-28$ °C, giving a $\Delta G^\ddagger$ of $12.0 \pm 0.5$ kcal/mol (Figure 8). The barrier to alkyl group rotation in 1-Hex is $12.0 \pm 0.4$ kcal/mol.

**Scheme 4-3. Dynamic processes in 1-Hex.**
Figure 4-9. Variable temperature $^1$H NMR spectra (500 MHz, THF-$d_8$) showing CH$_2$(19) of 1-Hex.
Figure 4-10. Variable temperature $^1$H NMR spectra (500 MHz, THF-$d_8$) showing CH(1) and CH(17) of 1-Hex.
Optical Properties. The UV/Vis spectrum of **1-Hex** ($\lambda_{\text{max}}$ 311.5 nm) is similar to that of 9,18-dimethylphenanthro[9,10-b]triphenylene, **4-Me** ($\lambda_{\text{max}}$ 313 nm). The emission spectrum ($\lambda_{\text{ex}}$ 341 nm) exhibits a maximum at 480 nm, which represents a significant Stokes shift when compared to the emission maximum for **4-H** ($\lambda_{\text{ex}}$ 335 nm, $\lambda_{\text{max \; em}}$ 381.5 nm).\(^{22}\) This large Stokes shift could arise from the formation of an intramolecular exciplex or from the twist of the PTP moieties. Comparison with the fluorescence spectrum of **4-Ph** should resolve this question, but this spectrum apparently has not been reported.

**Dynamics: Alkyl Rotation.** Crystallography establishes the existence of hexyl group rotomers with similar energies. The two crystal structures of **1-Hex** differ in the orientation of alkyls about the 20-19-19'-20' dihedral: in the hemisolvate, the alkyl groups are *anti*; in the disolvate, they are *syn*. To avoid confusion with a coincident dihedral relevant to inversion of chirality, we use the labels *syn*(20-20') and *anti*(20-20'). We use the ethyl analog, **1-Et**, the smallest model illustrating alkyl rotation, for our computational studies.

Calculations reveal that the conformers *syn*(20-20') and *anti*(20-20')-**1-Et** are connected by a complex potential energy surface and have essentially identical energies, in agreement with the observation that both conformers of **1-Hex** crystallize from benzene solution. The calculated barrier ($\Delta G^\ddagger$) for interconversion of these conformers is 11.4 kcal/mol, in reasonable agreement with the barrier measured for **1-Hex**, 12.0 ± 0.5 kcal/mol. (Dynamics calculations relating to alkyl rotation carried out by P. Rempala).\(^{20}\)

**Dynamics: Inversion of Chirality.** Crystallography has established that low energy conformers of **1-Hex** are chiral, and variable temperature (VT) NMR has revealed a
process, which we ascribe to chiral inversion (see below), with a barrier of \( \Delta G^\ddagger = 15.2 \pm 0.5 \text{ kcal/mol} \). What is the mechanism of inversion? As before, we address this question using calculations – here with the B3LYP 6-31G(d) model chemistry and the analog \textbf{1-Me}.\textsuperscript{23}

We have identified both stepwise and concerted pathways for inversion. In both cases, the sterically encumbering Me groups move out of their axial positions in the gulf to a bent position above the plane of the central ring of the PTP moiety. This movement is required because the gulf rings cannot pass one another with a methyl group in the axial position.

The rate determining transition states of each pathway for the inversion of \textbf{1-Me} are comparably high in energy: stepwise, \( \Delta G^\ddagger_{298} = 16.1 \text{ kcal/mol} \); concerted, \( \Delta G^\ddagger_{298} = 15.7 \text{ kcal/mol} \). Both values are consistent with the barrier to inversion of 15.2 ± 0.5 kcal/mol for \textbf{1-Hex} determined by VT NMR. It should be noted that the racemization pathways involve only changes in helicity or the position of an alkyl group. Rotation about the central bond is not involved in either path. (Calculations illuminating the energy pathway for inversion of chirality performed by J. Crowfoot).\textsuperscript{20}

**Conclusions**

The synthesis of \textbf{1-Hex} demonstrates the utility of the biphenylating reagent \textbf{5} to prepare strained and hindered PAHs. In a single step, eight new aryl C-C bonds are formed with the introduction of ~80 kcal/mol of strain. The product, \textbf{1-Hex}, contains the only known example of a bond between two PAH gulfs. This bond is one of the more hindered single bonds in chemistry, and its energetic, structural, and dynamic consequences are extraordinary. Its adiabatic homolytic BDE is only 55% of biphenyl,
but the bond has a normal length. The explanation – that strain is released slowly with extension – is revealed by calculations. VT NMR reveals two dynamic processes; analysis of the NMR spectra and calculations identify these processes as alkyl rotation and inversion of chirality. The full reaction coordinates for these processes are explored by DFT calculations and are rare examples of complex conformational behavior in PAHs, molecules that are often considered rigid.

Experimental Section

General Methods. Preparation of 4,4′-dihexylbiphenyl and 18,18′-Di-n-hexyl[9,9′]Bi[phenanthro[9,10-b]triphenylenyl] were carried out under argon gas using Schlenk techniques. All reaction solvents were dry and degassed by evacuation and backfilling with argon. [1,3-bis(diphenylphosphino)propane]-nickel(II)chloride, hexyl magnesium bromide, 4,4′-dibromobiphenyl and bromine were obtained commercially and used as received. Tetrahydrofuran and toluene solvent were distilled from sodium/ketyl radical and stored over 4A mol sieves under argon.

Reaction of 4,4′-dibromobiphenyl with hexylmagnesium bromide. Hexyl magnesium bromide (1.23M in ether) (100 mL, 0.123 mol) was added dropwise to a stirred suspension of 4,4′-dibromobiphenyl (15.6g) and [1,3-bis(diphenylphosphino)propane]-nickel(II)chloride (720 mg) in THF (125 mL). After exothermic reaction had ceased (~2 h), the mixture was refluxed for 4 h. The mixture was allowed to cool, pentane (120 mL) was added and the mixture was stirred under air for 2 h, followed by filtration through silica gel (pentane eluent). The filtrate was evaporated and the resulting residue was distilled on the Kügelrohr (165 °C and 60 mtorr) to yield a fraction that was 90+ % dihexylbiphenyl. This fraction was subjected to further distillation under the same
conditions to yield a pure fraction of dihexylbiphenyl (4.25g, 26%). $^1$H NMR (400MHz, CDCl$_3$): δ 7.49 (m, 4H), 7.24 (m, 4H), 2.63 (t, J = 8.0 Hz, 4H), 1.64 (m, 4H) 1.31 (m, 12H) 0.89 (t, J = 6.8 Hz, 6H). $^{13}$C NMR (500MHz, CDCl$_3$): δ141.9, 138.7, 128.9, 127.0, 35.8, 31.9, 31.6, 29.2, 22.8, 14.3. Elem Anal. calc C, H: 89.37, 10.63 found C, H: 89.41 10.54

**Reaction of 4,4'-dihexylbiphenyl with bromine.**  4,4'-Dihexylbiphenyl (0.710 g, 2.2 mmol) was added as a powder to stirred bromine 5 (mL) in a round bottom flask which was held at 0 ºC and equipped with an efficient reflux condensor. Once the exothermic reaction had ceased, as judged by diminished HBr evolution, iron powder (0.040g, 0.72mmol) was added. The reaction was held at 0 ºC for 1 h after iron was added and then warmed to 55 ºC. After 2 h the reaction was allowed to cool and the bromine was evaporated under vacuum. The remaining residue was dissolved in methylene chloride (100 mL) and the resulting solution was extracted with a saturated solution of sodium thiosulfate in water (100 mL) then twice with water (100 mL). The organic layer was separated and evaporated and the resulting residue was crystallized from isopropanol yielding off white crystals of 4,4'-Dihexyl-2,3,5,6,2',3',5',6'-octabromobiphenyl (1.13g, 54%). $^1$H NMR (400MHz, CDCl$_3$): 3.26 (m, 4H), 1.64 (m, 4H) 1.50 (m, 12H) 0.93 (t, J = 6.8 Hz, 6H). $^{13}$C NMR (500MHz, CDCl$_3$): δ146.1, 144.6, 127.3, 126.8, 42.0, 31.1, 29.5, 27.7, 22.7, 14.2. λ (log ε): sh. 230 nm (4.8)

**Reaction of lithium tris[biphenyl(2,2'-diyl)]zirconate (5) with 6**

The zirconium complex (2.272 g, 2.00 mmol) was added as a neat powder to a solution of 2,3,5,6,2',3',5',6'-octabromobiphenyl (475 mg, 0.50 mmol) in toluene (100 mL) and the
mixture was stirred for 24 h. The reaction was quenched by elution through silica gel (toluene eluent) the eluted fractions were evaporated to dryness. The residue was chromatographed on silica gel (100g) using first heptane to remove biphenyl and quaterphenyl followed by dichloromethane which eluted a complex mixture containing 1. This mixture was subjected to preparative HPLC using a silica gel stationary phase and 80% hexane 20% chloroform mobile phase. Fractions containing the desired product were combined and evaporated. The resulting solids were crystallized from benzene to obtain pure 1 (21 mg 5%).

\(^1\)H NMR (500MHz, C6D6): 8.29 (d, J = 7.5Hz, 4H, H1), 7.98 (d, J=8 Hz, 4H, H4) 7.81 (d, J=8 Hz, 4H, H5) 7.59 (d, J = 8.0 Hz, 4H, H8) 7.35 (t, J = 7.5Hz, 4H, H2), 7.30 (t, J=7.5 Hz, 4H, H3) 6.69 (t, J = 7.5Hz, 4H, H6), 6.20 (t, J=7.5 Hz, 4H, H7), 4.11 (bs, 4H, H19), 2.14 (bs, 2H, H20), 1.81 (bs, 2H, H20), 1.44 (bs, 4H, H23), 1.21 (bs, 8H, H21 and H22), 0.83 (unresolved triplet 6H, H24) \(^1\)C NMR (500MHz, C6D6): δ 134.6 (C18), 133.6 (C9), 133.4 (C18a, C17b), 133.0 (C8b, C9a), 132.3 (C4a, C13b), 132.1 (C8a, C9b), 131.9 (C18b, C17a), 131.8 (C4b, C13a), 128.8 (C8, C10), 127.7 (C1, C17), 127.0 (C3, C15), 126.5 (C6, C12), 126.2 (C2, C16), 125.0 (C7, C11), 124.5 (C4, C14), 123.1 (C5, C13), 33.9 (C20), 31.9 (C22), 31.0 (C19), 30.4 (C21), 23.2 (C23), 14.4 (C24). \(\lambda\)max (log e): 311.5nm (4.57), 242nm (4.49), sh 332 nm (4.44).
References:

(15) Disolvate: C84H70(C72H58(C6H6)2); FW 1079.40; triclinic; P–1; pale yellow; a = 8.98780(10) Å; b = 15.3483(2) Å; c = 21.4148(3) Å; α = 86.2720(10)°; β = 89.2610(2)°; γ = 78.7930(10)°; cell volume = 2891.65(6) Å³; temp. 100 K; Z = 2; R = 0.038; GOF = 1.09. Hemisolvate: C75H61 (C72H58(C6H6)0.5); FW = 962.24; triclinic; P–1; pale yellow; a = 8.9148(15) Å; b = 13.982(2) Å; c = 21.420(4) Å; α = 104.888(3)°; β = 96.430(3)°; γ = 94.489(3)°; cell volume = 2548.0(7) Å³; temp. 100 K; Z = 2; R = 0.054; GOF = 0.92.
(20) Hilton, C. L.; Crowfoot, J. M.; Rempala, P; King, B. T. J. Am. Chem Soc. Accepted for Publication.
The modified Amber model chemistry also would have been appropriate, but transition states were more difficult to locate.
Chapter 5
Synthesis of an Extended Triptycene Using a New Zirconium Mediated Transformation

Introduction

Triptycene is a useful building block in supramolecular chemistry. Its rigidity, paddlewheel shape, and ease of functionalization\textsuperscript{1,2,3,4} make triptycene a useful rotor\textsuperscript{5} or stator\textsuperscript{6} component in nanodevices, a rigid spacer for the construction of host-guest complexes,\textsuperscript{7} a framework for the construction of chelating ligands\textsuperscript{1,8,9} and a subunit of molecular cages.\textsuperscript{2} Electron rich clefs between the arene blades of triptycene allow it to form inclusion complexes\textsuperscript{10} with C\textsubscript{60}. The rigid paddlewheel shape of triptycene is credited with improving the mechanical properties of polymers in which it is incorporated as a pendant residue.\textsuperscript{11,12,13}

We chose to synthesize 6,13(2,3-triphenyleno)-6,13(dihydro)\textsuperscript{-[a,c,l,n]-tetrabenzopentacene 1-H}, an extended triptycene in which the three benzene blades of parent triptycene are replaced with triphenylene blades. This extends the arene blade both perpendicular and parallel to the highest symmetry axis of the molecule, and creates a cavity above its bridgehead sites. Hart and coworkers\textsuperscript{14} pioneered the synthesis and characterization of extended triptycenes.\textsuperscript{15} With very few exceptions,\textsuperscript{16,17} triptycenes have been extended by adding fused rings perpendicular to the highest symmetry axis of the molecule (i.e. benzene blades are extended into anthracene blades). Compound 1-H provides a new rigid scaffold geometry and may enable different host-guest chemistry due to its larger $\pi$ system.
An interesting feature of 1-H is the void about its bridgehead sites, which contributes to a large intermolecular free volume\textsuperscript{12} (IMFV) for this triptycene system. Swager has defined intermolecular free volume as: “the difference in volume between that which is generated by the geometry of the structure and that occupied by the structure itself.”\textsuperscript{12} Free volume is one of the features that make triptycene an attractive stator for the construction of molecular gyroscopes,\textsuperscript{6} as well as, a component of polymers exhibiting improved mechanical properties.\textsuperscript{12,13}

**Results and Discussion**

The synthesis of 1-H is carried out in two steps. First, the regioselective bromination of triptycene yielding 2,3,6,7,12,13-hexabromotriptyene 2,\textsuperscript{4} which is followed by the substitution of three biphenyl units for three pairs of o-dibromides using the recently reported\textsuperscript{18} tris(biphe)zirconate lithium reagent, where biphe is [biphenyl(2,2'-diyl)]. The traditional Diels-Alder strategy for this synthesis would require tetrabenzo[a,c,l,n]pentacene which is difficult to prepare\textsuperscript{19} and 2,3-didehydrotriphenylene\textsuperscript{20} which is difficult to use as a dienophile.

With the goal of synthesizing 1-H, we developed an improved synthesis of hexabromide 2-H from triptycene; our improved synthesis provides a one step, multi-gram preparation of 2-H in 64% yield. Aryl bromide 2-H may be a versatile building block for macromolecules.

The synthesis of 1-H relies on the recently developed reagent (Li(THF)\textsubscript{4})\textsubscript{2}Zr(biphe)\textsubscript{3} (3),\textsuperscript{18} to effect the three-fold biphenylation of 2-H. The reaction gives a double ipso substitution on an ortho-dihaloarene to form a triphenylene fragment.\textsuperscript{21}
A modification to the previously reported work-up for reactions of 3 facilitates purification of the reaction mixture. Previously, a protic reaction quench was used yielding neutral biphenyl quaterphenyl and higher oligomers. In the improved procedure the reaction is quenched with CO$_2$ to afford easily separated oligophenylcarbonates. After the CO$_2$ quench and flash chromatography on alumina, the remaining three component mixture, which contains 1-H, incompletely biphenylated products and reduced products, was separated using HPLC to give pure 1-H in 21% yield.

**Scheme 5-1.** Synthesis of extended triptycenes 1-H and 1-Bu.

![Scheme 5-1](image)

Compound 1-H was characterized by NMR and MALDI-MS. We were particularly interested in obtaining a crystal structure of 1-H in order to carry out detailed analysis of its three dimensional shape and solid state packing. Despite extensive efforts, crystals of 1-H suitable for single crystal X-ray diffraction analysis could not be grown. Attempts to co-crystallize 1-H with picric acid, trinitrofluorenone, C$_{60}$, and adamantane also failed. Almost all crystallization attempts yielded films. Not only was 1-H difficult to crystallize, it also proved difficult to remove even low boiling solvents from it. Vacuum
(30 mTorr) at elevated temperatures failed to completely remove acetone and dichloromethane.

The reluctance of 1-H to crystallize was puzzling, as both triphenylene and triptycene crystallize easily from a variety of solvents. We hypothesize that the free volume about the bridgehead hydrogens in 1-H frustrates packing and inhibits crystallization.

To test this hypothesis, we synthesized 6,13(2,3-triphenyleno)-6,13(di-n-butyl)-[a,c,l,n]-tetrabenzopentacene, 1-Bu, using the same synthetic scheme that provided 1-H, replacing the triptycene starting material with 9,10-dibutyltriptycene. Dibutyltriptycene is synthesized in three steps. First, 9,10-anthraquinone reacts with two equivalents of n-butyl lithium to yield a diol, which is reduced with tin dichloride in acetic acid\(^{22}\) to give 9,10-dibutyl anthracene (7 g, 40% yield over two steps). Next, Diels-Alder addition of benzyne affords 9,10-dibutyltriptycene (70% yield). Bromination using the same conditions as for 2-H gave 2-Bu in 68% yield. Biphenylation of 2-Bu with 3 gave 1-Bu, although in poor yield (20mg, 5%).

We were able to grow quality crystals of 1-Bu suitable for single crystal X-ray diffraction analysis from both benzene and bromoform. The ease of crystallization of 1-Bu from several solvents supports our hypothesis that the void around the bridgehead hydrogens in 1-H inhibits its crystallization. The crystallographic dimensions of 1-Bu are shown in Figure 1.
Figure 5-1 Thermal ellipsoid (50%) plot from the crystal structure of 1-Bu.

The IMFV of 1-H calculated using the crystallographic geometry of 1-Bu, is 844 Å³ (cf. triptycene 92 Å³). Because the IMFV of triptycene has been shown to play an important role in modulating the mechanical properties of polymers, it seems 1-H with its significantly larger IMFV may exert an even greater influence over the mechanical properties of polymers.

Conclusions

We have synthesized two new extended triptycenes 1-H and 1-Bu which bear triphenylene blades. The triphenylene blades extend the triptycene both perpendicular and parallel to its highest symmetry axis. The synthesis of extended triptycenes 1-H and
1-Bu was made possible by the recently developed biphenylating agent 3, this reagent formed six new C-C bonds in one step. Compound 1-H proved impossible to crystallize, possibly due to voids about its bridgeheads that inhibited packing. Compound 1-Bu, which has no bridgehead voids, is easily crystallized from several solvents. This supports our hypothesis that the large voids in 1-H inhibited packing. The large IMFV of 1 suggest applications in molecular devices, and polymers. Both triptycene 1-H and 1-Bu provide a new rigid scaffold geometry, which may enable their use in host-guest chemistry or as rigid frameworks for the construction of chelating ligands. The large electron rich clefts between their triphenylene blades make them candidates for use in new inclusion complexes.

**Experimental Section**

**Synthesis of 2-H** Triptycene (1.06 g, 4.18 mmol) was dissolved in chloroform (80 mL) in a round bottom flask equipped with PTFE-clad magnetic stir bar. Iron filings (30 mg) were added and the solution was stirred at 25 °C. A reflux condenser was attached to the flask and left open to the atmosphere. Bromine (1.35 mL, 26.3 mmol) was added through the top of the condenser. This solution was refluxed for 60 min, during which time the initially reddish-brown solution turns reddish-orange. The flask was removed from heat, and chloroform excess bromine were removed under vacuum (100 mTorr). The resulting brown powder was dissolved in chloroform (100 mL) and flushed using additional chloroform (100 mL) through a pad of silica gel (20 g) on a fritted glass filter. The filtrate was evaporated to dryness. The crude white powder (2.83 g, 98%) was crystallized from acetone yielding C_{20}H_{8}Br_{6}•(acetone)_{2} (0.88 g, 29%). The mother liquor was evaporated and the residue was crystallized from acetone to afford a second crop of
crystals (0.97 g, C_{20}H_{8}Br_{6}(acetone)_{2}, 32%). The combined yield is 1.85 g, 61%. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta \) 7.63 (s, 3H), 5.24 (s, 1H). \textsuperscript{13}C NMR (101 MHz, CDBr\textsubscript{3}): \( \delta \) 141.8, 127.1, 119.9, 48.6. UV-Vis \( \lambda_{\text{max}} \)/nm(log \( \varepsilon \)): 229 (4.95), 285 (3.49), 295 (3.83). Calc C, H, Br: 33.01, 1.11, 65.88. Found: 33.17, 1.19, 65.68.

**Synthesis of 1-H** \text{Li(THF)}_{4}\text{Zr(biphe)}_{3} (3.41 g, 3.00 mmol) was added as a powder to a solution of 2,3,6,7,12,13-hexabromotriptycene (0.364 g, 0.50 mmol) in toluene (50 mL). The reaction mixture was stirred under argon, at room temperature, for 2 days and then quenched by addition of anhydrous carbon dioxide gas. The mixture was passed through a column of basic alumina using toluene. The eluent was evaporated, and the resulting residue was purified using preparative HPLC (silica/ 40:60 CHCl\textsubscript{3}:hexane) yielding 1-H (29 mg, 9%). \textsuperscript{1}H NMR (500 MHz, C\textsubscript{2}D\textsubscript{2}Cl\textsubscript{4}): \( \delta \) 8.87 (s, 6H), 8.74 (d, \( J = 5 \) Hz, 6H), 8.63 (d, \( J = 5 \) Hz, 6H), 7.59 (m, 12 H), 6.19 (s, 2H). \textsuperscript{13}C NMR (500 MHz, CDCl\textsubscript{3}): \( \delta \) 146.7, 133.3, 133.2, 131.4, 130.3, 130.2, 126.6, 121.7, 58.0. UV-Vis \( \lambda_{\text{max}} \)/nm(log \( \varepsilon \)): 263 (5.12) sh 273. HRMS calcd for C\textsubscript{56}H\textsubscript{32}: 704.2504 Found: 704.2451.

**Synthesis of 9,10-dibutylanthracene** Anthraquinone (10.4 g, 50 mmol) was added to a stirred solution of \textit{n}-butyllithium (273 mmol) in hexane (100 mL) and anisole (100 mL) at room temperature. The reaction was stirred for 1 day and quenched by addition of ammonium chloride. The organic layer was separated, washed with water (2 \( \times \) 200 mL), and evaporated. The resulting residue was dissolved in THF (75 mL), and added dropwise to a solution of tin dichloride (56.25 g, 250 mmol) in acetic acid (300 mL). The resulting suspension was stirred for 1 day, and the organic material was extracted with hexane (1000 mL). The organic extract was washed with 5% ammonium hydroxide (500 mL) and evaporated to dryness. The residue was crystallized from 2-propanol to give
pure 9, 10-dibutylanthracene (4.2 g, 40%). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.32 (m, 4H), 7.51 (m, 4H), 3.61 (m, 4H), 1.82 (m, 4H), 1.62 (m, 4H), 1.04 (t, J = 3 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 134.0, 129.6, 125.5, 125.0, 33.8, 28.1, 23.7, 14.3. Anal. Calcd. for C$_{22}$H$_{26}$: C, 90.98, H, 9.02 found: C, 91.06, H, 8.91. m.p. 105 °C.

### Synthesis of 9,10-dibutyltriptycene
Anthrаниlic acid (4.00 g, 28.8 mmol) was dissolved in THF (180 mL) and added dropwise over 4 hours to a solution of isoamyl nitrite (4.2 mL, 31 mmol) and 9,10-dibutylanthracene (4.00 g 13.8 mmol) in refluxing chloroform (250 mL). After the addition was complete, the reaction was refluxed for a further 15 min, and the solvent was evaporated to dryness. The remaining solids were dissolved in xylene (200 mL) and maleic anhydride (1.896 g, 19.32 mmol) was added. This mixture was refluxed for 15 min and allowed to cool. Aqueous work-up and filtration through a plug of silica gel afforded dibutyltriptycene (3.485 g, 69%) $^1$H NMR (500 MHz, CDCl$_3$): δ 7.46 (s, 6H), 7.06 (s, 6H), 3.10 – 2.84 (m, 4H), 2.22 (dd, J = 12.6 Hz, 19.9, 4H), 1.98 – 1.79 (m, 4H), 1.22 (t, J = 7.3 Hz, 6H). $^{13}$C NMR (101 MHz, CDBr$_3$): δ 147.33, 123.45, 121.14, 52.15, 27.47, 26.71, 24.14, 14.01. Anal. Calcd. for C$_{28}$H$_{30}$: C, 91.75, H, 8.25 Found: C, 91.34, H, 8.51. m.p. 105 °C.

### Synthesis 2-Bu 9,10-Dibutyltriptycene (0.425 g, 1.16 mmol) was dissolved in chloroform (30 mL) in a 100 mL round bottom flask equipped with PTFE-clad magnetic stir bar. Iron filings (20 mg) were added and the solution was stirred at 25 °C. A reflux condenser was attached to the flask and left open to the atmosphere. Bromine (0.38 mL, 7.3 mmol) was added through the top of the condenser. This solution was refluxed for 60 min. The flask was removed from heat, and excess bromine and chloroform were removed under vacuum (100 mTorr). The resulting brown powder was dissolved in
chloroform (50 mL) and flushed through a pad of silica gel (10 g) on a fritted glass filter, using additional chloroform as eluent (100 mL). The filtrate was evaporated to dryness. The crude white powder (0.90 g, 98%) was washed with acetone yielding pure 2-Bu (0.628 g, 68%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.55 (s, 6H), 2.80 – 2.66 (m, 4H), 1.99 (s, 4H), 1.82 (dd, $J = 7.4$ Hz, 14.9, 4H), 1.30 – 1.10 (m, 6H). $^{13}$C NMR (126 MHz, CDBr$_3$): $\delta$ 147.49, 128.02, 121.66, 77.40, 77.14, 76.89, 52.33, 27.57, 27.16, 24.81, 14.25.

**Synthesis 1-Bu** Li(THF)$_4$Zr(biphe)$_3$ (3.41 g, 3.00 mmol) was added as a powder to a solution of 2,3,6,7,12,13-hexabromo-9,10-dibutyltriptycene (0.419 g, 0.5 mmol) in toluene (50 mL). The reaction mixture was stirred at room temperature for 2 days and then quenched by addition of anhydrous carbon dioxide gas. The mixture was passed through a column of basic alumina using toluene. The eluent was collected and evaporated, and the residue was purified using preparative HPLC (silica/15:85 CH$_2$Cl$_2$:hexane) yielding 1-Bu (22 mg, 5%). $^1$H NMR (400 MHz, CDBr$_3$): $\delta$ 8.65 (s, 6H), 8.50 (m, 12H), 7.56 (m, 12H), 3.55 (d, $J = 7.8$ Hz, 4H), 2.59 (s, 4H), 2.29 (dd, $J = 7.4$ Hz, 14.8 Hz, 4H), 1.45 (t, $J = 7.3$ Hz, 6H). $^{13}$C NMR (126 MHz, C$_6$D$_6$): $\delta$ 147.3, 131.1, 131.0, 127.8, 127.5, 124.3, 123.9, 118.0, 54.3, 29.4, 29.1, 26.3, 15.1. HRMS calcd for C$_{64}$H$_{48}$: 816.37506 Found: 816.3734.
References:

(22) Rimmer, R. W.; Christiansen, R. G.; Brown, R. K.; Sandin, R. J. Am. Chem. Soc. 1950, 72, 2298.
Chapter 6
Crystallography

This chapter is a graphical abstract of solved crystal structures. The graphics were generated from Crystallographic Information Framework (CIF) files. Pictures are shown on the following pages with their file name. The full text of the corresponding CIF files is attached, as appendix 5, to this dissertation.
CH179

CH181

CH183

CH184
CH229

acetone solvate

CH235

2 benzene

0.5 benzene

CH238

CH240
## Appendix 1. Supplemental information
### Chapter 2-
X-Ray parameters, spectra, and structures.

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Thermal ellipse (50%) plot of compound 1
Thermal ellipse (50%) plot of compound 2
Thermal ellipse (50%) plot of compound 3
Thermal ellipse (50%) plot of compound 4
$^1$H NMR Spectrum (500MHz) of 1 in THF-$d8$
$^{13}$C NMR Spectrum (500 MHz) of 1 in benzene-d6
$^1$H NMR Spectrum (500MHz) of 2 in THF-$d_8$
$^{13}$C NMR Spectrum (500 MHz) of 2 in benzene-<i>d6</i>
$^1$H NMR Spectrum (500MHz) of 3 in benzene-$d_6$
$^{13}$C NMR Spectrum (500 MHz) of 3 in benzene-$d_6$
$^1$H NMR Spectrum (500MHz) of 4 in $d_8$-THF
$^{13}$C NMR Spectrum (500 MHz) of 4 in benzene-$d_6$
$^{13}$C NMR Spectrum (500 MHz) of 4 in benzene-d$_6$ showing resonance near solvent signal

$\text{Zr}^{4-}$

$\text{[Li}^{+}\cdot\text{Et}_2\text{O}]_4$
$^1$H NMR Spectrum (500MHz) of biphenyl hafnocene in benzene-$d_6$
$^{13}$C NMR Spectrum (500MHz) of biphenyl hafnocene in benzene-$d_6$
$^1\text{H NMR Spectrum (500MHz)}$ of lithium tris(biphenyl(2,2'-diyl)) hafnate in benzene-$d_6$
$^{13}$C NMR Spectrum (500MHz) of lithium tris(biphenyl(2,2'-diyl)) hafnate in benzene-$d_6$
$^1$H NMR Spectrum (500 MHz) of lithium tetrakis(biphenyl(2,2'-diyl)) hafnate in THF-$d_8$
$^{13}$CNMR Spectrum (500 MHz) of lithium tetrakis(biphenyl(2,2'-diyl)) hafnate in THF-d$_8$
Appendix 2: Supplemental information for chapter 3 -

Uncatalyzed Zirconium-Mediated Biphenylation of o-Dihalobenzenes To Form

Triphenylenes
$^1$H NMR at 500 MHz of 9,18-dimethylphenanthro[9,10-b]triphenylene in CDCl$_3$
Computational Details

Density functional calculations were performed using Gaussian 03\textsuperscript{1} 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. Stationary points were subjected to frequency calculations and assigned as minima (all real frequencies). Strain energies are reported as the change in electronic energies. The lowest energy conformer of was used in the analysis.


\textbf{Strain Definitions}

\begin{itemize}
\item \textbf{Strain 1:} +38 kcal/mol
\item \textbf{Strain 2:} +34 kcal/mol
\end{itemize}
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\text{C} & \quad 0.909372 \quad 2.748061 \quad 0.000066 \\
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Appendix 3 - Supplemental information for Chapter 4

400 MHz $^{13}$C in CDCl$_3$
$^1$H NMR in CDCl$_3$ at 25°C
400 MHz $^{13}$C in CDCl$_3$

Acetone

Acetone
UV-Visible spectra
dihexyloctabromide in CH$_2$Cl$_2$

![Graph showing UV-Visible spectra of dihexyloctabromide in CH$_2$Cl$_2$](image)
$^1\text{H NMR in C}_6\text{D}_6 \text{ at 55°C}$

\begin{figure}
\centering
\includegraphics[width=\textwidth]{nmr_spectrum}
\end{figure}
$^{13}$C NMR in C$_6$D$_6$ at 55°C
gCOSY in C₆D₆ at 55 °C

[F1 (ppm)]
6.2  6.4  6.6  6.8  7.0  7.2  7.4  7.6  7.8  8.0  8.2  8.4

[F2 (ppm)]
6.6  6.8  7.0  7.2  7.4  7.6  7.8  8.0  8.2  8.4
HSQC at 55 °C in C₆D₆
THREE 1D NOE STUDIES (C6D6 at 55 °C)
HMBC NMR in C₆D₆ at 55°C
(HSQC breakthrough shown in red)
HMBC NMR in C₆D₆ at 55°C
Affected protons shown explicitly
VT NMR in d8-THF

Affected protons shown explicitly
VT $^1$H-NMR in d8-THF

Affected protons shown explicitly
500 MHz VT NMR data in d8-THF

62 °C

55 °C
20 °C

15 °C
$10^\circ C$

$5^\circ C$
$-10^\circ C$

$-15^\circ C$
-50 °C

-55 °C
UV-Vis Trace for 18,18'-Di-n-hexyl[9,9']bi[phenanthro[9,10-b]triphenylenyl] in dichloromethane 1.35 E-6 M

Data Set: Storage 1 84420 - Raw Data - C:\Program Files\Shimadzu\UVProbe\Data\king\File_071029_1 84420.spc
Appendix 4- Supplemental information for Chapter 5
UV-Vis of compound **2-H** in methylene chloride

\[ \text{AU} \]

\[ \lambda \text{ (nm)} \]
$^1$H NMR of Compound 1-H in C$_2$D$_2$Cl$_4$

$^{13}$C NMR of Compound 1-H in CDCl$_3$
MALDI-MS of Compound 1-H
$^1$H NMR of 9,10-dibutylanthracene in CDCl$_3$

$^{13}$C NMR of 9,10-dibutylanthracene in CDCl$_3$
$^1$H NMR of 9,10-dibutyltriptycene in CDCl$_3$

$^{13}$C NMR of 9,10-dibutyltriptycene in CDBr$_3$
$^1$H NMR of 2-Bu in CDCl$_3$

$^{13}$C NMR of 2-Bu in CDCl$_3$
$^1$H NMR of 1-Bu in CDCl$_3$

$^{13}$C NMR of 1-Bu in CDBr$_3$
MALDI-MS for 1-Bu

4700 Reflector Spec #1 (BP = 1296.7, 672)

H dibupwheel internal calibration T2D Print: 16:52, June 23, 2008