

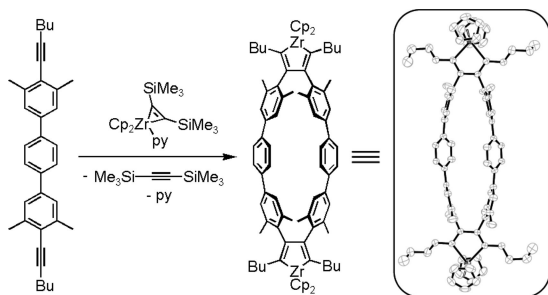
## Zirconocene-Mediated Macrocyclizations of Diynes Containing Di-*o*-Methylphenylene Spacers

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The diynes 3,3',5,5'-tetramethyl-4,4'-di(pent-1-ynyl)biphenyl (**4**) and 3,3'',5,5''-tetramethyl-4,4''-di(hex-1-ynyl)terphenyl (**9**) undergo coupling with  $\text{Cp}_2\text{Zr}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\text{py})$  to give dimeric macrocycles in moderate yields (16% for **4** and 26% for **9**).

Macrocycles and cyclophanes are desirable synthetic targets for a wide variety of investigations and applications including (for example) aromaticity, host–guest chemistry, and supramolecular chemistry.<sup>1</sup> However, the preparation of these molecules is often fraught with difficult procedures (e.g., high dilution), low yields, and laborious purification.<sup>2</sup> Previously, we have described the preparation of zirconium-containing macrocycles and cyclophanes from the zirconocene coupling of diynes.<sup>3–12</sup> This method provides simple, high-yield routes to macrocycles that can vary considerably in size and shape.

The reductive coupling of alkynes by zirconocene results in zirconacyclopentadienes which can be transformed to a wide array of conjugated structures and heterocycles.<sup>13</sup> The efficient synthesis of macrocycles via the zirconocene coupling route is based on the coupling of silicon-substituted diynes. This process involves the formation of C–C bonds, and with silyl-substituted alkynyl groups, the coupling is highly regioselective and reversible.<sup>14,15</sup> It is the reversible nature of these couplings that provides efficient, high-yield routes to macrocyclic structures. Although the silicon substituents have these desirable effects on the zirconocene coupling, the resulting zirconacyclopentadienes possessing silyl groups in the  $\alpha$  position are difficult to derivatize<sup>4,16</sup> and successful derivatizations can be low-yielding.<sup>9</sup> Therefore, it is of interest to develop new synthetic methodologies that do not depend on bulky  $\alpha$ -directing groups.

$\beta$ -Directing groups have the potential to promote macrocycle formation while leaving the metal center sterically accessible for further transformations. Previous studies with electron-withdrawing aryl groups (i.e.,  $-\text{C}_6\text{F}_5$ ) demonstrate the desired  $\beta$  selectivity, but these groups do not promote reversibility.<sup>17</sup> Subsequent investigations have revealed that the mesityl group preferentially couples into the  $\beta$ -position and enhances the reversibility of alkyne couplings.<sup>18</sup> In this contribution, we describe the synthesis of macrocycles via the coupling of diynes containing di-*o*-methylated phenylene spacers as analogues of the mesityl group.

Two diynes, containing biphenyl and terphenyl spacers, were synthesized. The diene 3,3',5,5'-tetramethyl-4,4'-di(pent-1-ynyl)biphenyl (**4**) was synthesized by the route shown in Scheme 1. 4,4'-Diiodo-3,3',5,5'-tetramethylbiphenyl (**2**) was synthesized from 3,3',5,5'-tetramethylbenzidine (**1**) via a Sandmeyer-type iodination. Although the direct coupling of 1-pentyne with biphenyl **2** would have been the most direct route to diene **4**, this reaction proved too low-yielding to give any appreciable amount of product. Thus, the alkynyl groups were introduced via Sonogashira coupling of  $\text{Me}_3\text{SiC}\equiv\text{CH}$  to give 3,3',5,5'-tetramethyl-4,4'-bis(trimethylsilyl-2-ethyne-1-yl)biphenyl (**3**) in 62% yield. The alkynes were then deprotected by removal of the  $-\text{SiMe}_3$  groups under basic conditions, and the propyl groups were introduced by a nucleophilic substitution reaction between lithium acetylide and 1-bromopropane.

Macrocycle **5** was prepared by coupling of diene **4** with Rosenthal's  $\text{Cp}_2\text{Zr}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\text{py})$ .<sup>19</sup> Although the resulting zirconium-containing macrocycle precipitated out of benzene upon formation, it was relatively impure. This macrocycle was demetalated by protonolysis with TFA to give macrocycle **5** in 16% yield after purification by column chromatography. The dimeric nature of the macrocycle was

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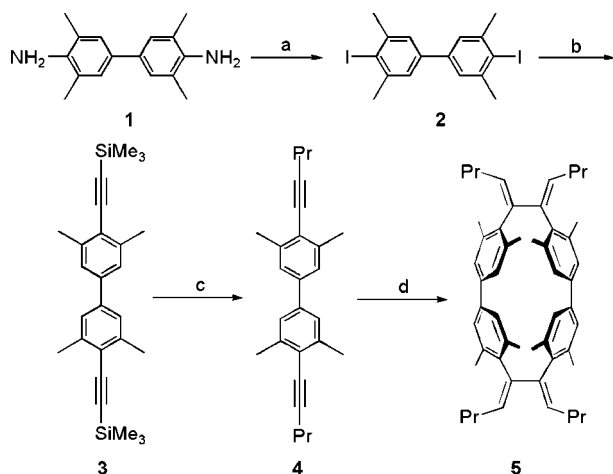
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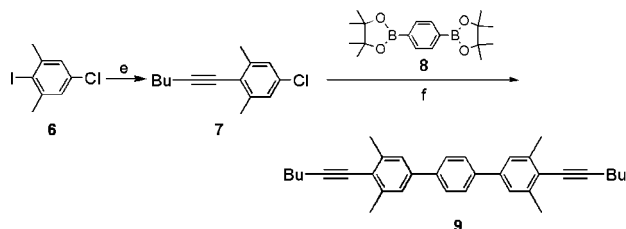
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SCHEME 1. Synthesis and Cyclodimerization of Diyne 4<sup>a</sup>

<sup>a</sup> Conditions: (a) NaNO<sub>2</sub>, KI, H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O, 24%; (b) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, PPh<sub>3</sub>, Me<sub>3</sub>SiC≡CH, Et<sub>3</sub>N, 62%; (c) (i) K<sub>2</sub>CO<sub>3</sub>, THF, MeOH, (ii) *n*-BuLi, pentane, (iii) 1-bromopropane, TMEDA, THF, 30%; (d) (i) Cp<sub>2</sub>Zr(η<sup>2</sup>-Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>)(py), benzene, (ii) TFA, THF, 16%.

SCHEME 2. Synthesis of Diyne 9<sup>a</sup>

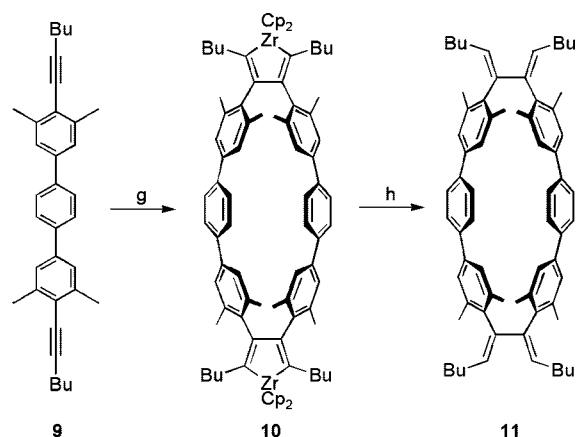
<sup>a</sup> Conditions: (e) PdCl<sub>2</sub>, X-Phos, Cs<sub>2</sub>CO<sub>3</sub>, 1-hexyne, AcCN, 59%; (f) 8, Pd<sub>2</sub>(dba)<sub>3</sub>, X-Phos, Cs<sub>2</sub>CO<sub>3</sub>, DMF, 69%.

established by EI-MS (including HRMS). The short, two-carbon spacer between the tetramethylbiphenyl groups in macrocycle **5** probably causes considerable strain within the molecule, which may decrease the yield of the cyclization step.

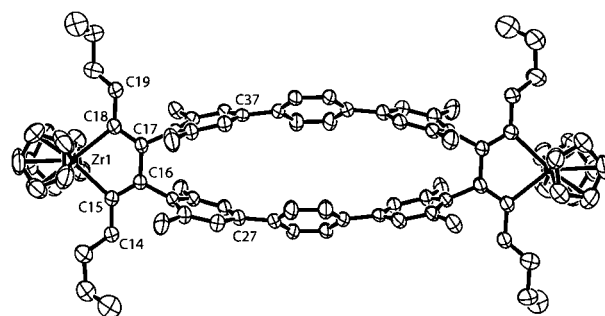
An analogous diene with a terphenyl spacer was synthesized by the route in Scheme 2. In the first step, 1-hexyne was coupled to 4-chloro-1-iodo-2,6-dimethylbenzene (**6**) via a palladium coupling route using Buchwald's X-Phos ligand.<sup>20</sup> Although these reaction conditions were optimized for coupling terminal alkynes to chloroarenes, we observed the coupling to preferentially occur at the sterically hindered iodo site. Diyne **9** was then obtained through two consecutive couplings of chloroarene **7** to diboronate **8** under anhydrous conditions.

The synthesis of macrocycle **10** resulted from the cyclodimerization of diene **9** with Cp<sub>2</sub>Zr(η<sup>2</sup>-Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>)(py) in toluene (Scheme 3). This macrocycle has no appreciable solubility in common organic solvents, which prevented characterization by mass spectrometry and NMR spectroscopy. Macrocycle **10** was demetallated by protonolysis with TFA to afford macrocycle **11**. Removal of the zirconocene moiety led to a considerable increase in solubility and allowed for characterization of macrocycle **11** by routine techniques (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR, MALDI-TOF, and combustion analysis).

To further characterize **10**, X-ray quality crystals were obtained by layering a toluene solution of diene **9** over a toluene solution of Cp<sub>2</sub>Zr(η<sup>2</sup>-Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>)(py). The resulting centrosymmetric structure exhibits conformational strain along the

SCHEME 3. Synthesis of Macrocycles **10** and **11**<sup>a</sup>

<sup>a</sup> Conditions: (g) Cp<sub>2</sub>Zr(η<sup>2</sup>-Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>)(py), toluene, 26%; (h) TFA, THF, 23% (overall).



**FIGURE 1.** ORTEP depiction of the solid-state molecular structure of **10**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn with 50% probabilities.

terphenyl spacer (Figure 1). The phenylene rings in the β-positions of the zirconacyclopentadiene are bent by 11.2 and 17.4° (defined as the angle between the planes formed by the *ipso* and two *ortho* C's of the phenylene group), while the middle phenylene ring is significantly more planar (bent by 2.9°). On the other hand, the zirconacyclopentadiene moiety exhibits relatively little strain with a nearly planar framework.

Zirconocene-mediated macrocyclizations may be driven by precipitation of the macrocycle from solution. Thus, in an attempt to improve the yield of **10**, the relatively poor solvent diethyl ether was employed in the reaction of diene **9** with Cp<sub>2</sub>Zr(η<sup>2</sup>-Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>)(py). In fact, this reaction led to significantly more precipitate, but the yield of the macrocycle **10** was not improved. Analysis of the resulting solid by mass spectrometry (MALDI-TOF) indicated that the major byproducts were oligomers (*n* = 3–7). The crude solid was subsequently demetallated with TFA, and the resulting macrocycle was isolated from the oligomeric byproducts by column chromatography to give **11** in 23% yield.

Compared to other zirconocene-mediated cyclizations of diynes containing silicon substituents, the cyclizations of diynes containing *o*-methylphenylene spacers are rather low-yielding. It has been observed that (alkyl)C≡CMes will couple with the mesityl group in the β-position under kinetic conditions (ambient temperature) such that the ββ regioisomer is the major product (Cp<sub>2</sub>Zr[2,5-Pr<sub>2</sub>-3,4-Mes<sub>2</sub>C<sub>4</sub>]). Heating solutions of these zirconocenes gives the αβ regioisomer, Cp<sub>2</sub>Zr[2,4-Mes<sub>2</sub>-3,5-Pr<sub>2</sub>C<sub>4</sub>], as the apparent thermodynamic product.<sup>18</sup> Similarly, heating solutions of diene **9** and Cp<sub>2</sub>Zr(η<sup>2</sup>-Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>)(py) to 80 °C in C<sub>6</sub>D<sub>6</sub> did not lead to an increase in macrocycle yield and

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eventually led to decomposition of any macrocycle that had formed. Therefore, it seems reasonable to assume that macrocycle formation with diynes containing *o*-methylphenylene spacers is under kinetic rather than thermodynamic control.

In conclusion, we have demonstrated that the zirconocene coupling of diynes containing *di-o*-methylphenylene spacers results in dimeric macrocycles that can be demetalated to give all-carbon-based structures. This new method is complementary to the coupling of diynes terminated with silicon substituents, which generally give trimeric macrocycles with *p*-phenylene spacers of four rings or less.<sup>6,8,10,11</sup>

## Experimental Section

**4,4'-Diiodo-3,3',5,5'-tetramethylbiphenyl (2).** Biphenyl **1** (1.50 g, 6.2 mmol) was dissolved in toluene (5 mL) and acetone (10 mL), and to this solution were added water (20 mL) and H<sub>2</sub>SO<sub>4</sub> (1.3 mL, 25.0 mmol), which caused the solid to precipitate out of solution. The reaction mixture was cooled to 0 °C, and a solution of NaNO<sub>2</sub> (1.55 g, 22.5 mmol) in water (8 mL) was added dropwise. This was stirred at 0 °C for 3 h. To this reaction mixture was slowly added a solution of KI (2.50 g, 15.0 mmol) in water (10 mL) over 10 min. The reaction mixture was then heated at 40 °C for 1 h and then at 80 °C until the solid dissolved. The reaction mixture was diluted with water and then extracted with diethyl ether. The organic layers were combined and then washed with a saturated solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, water, 2 N NaOH, and brine. The organic layer was collected, dried with MgSO<sub>4</sub>, filtered, and concentrated. The resulting crude product was filtered through a plug of silica with hexanes as the eluent to give a yellow solid in 24% yield (0.68 g, 1.5 mmol): <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.07 (s, 4H), 2.38 (s, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>) δ 143.0, 140.4, 126.2, 108.0, 30.2; GC-MS *m/z* = 462 (M<sup>+</sup>). Anal. Calcd for C<sub>16</sub>H<sub>16</sub>I<sub>2</sub>: C, 41.59; H, 3.49. Found: C, 41.94; H, 3.45.

**3,3',5,5'-Tetramethyl-4,4'-bis(trimethylsilyl)-2-ethyne-1-yl)biphenyl (3).** Biphenyl **2** (2.00 g, 4.3 mmol), CuI (0.020 g, 0.09 mmol), PPh<sub>3</sub> (0.050 g, 0.17 mmol), and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.070 g, 0.09 mmol) were loaded into a flask. These solids were dissolved/suspended in triethylamine (50 mL), and trimethylsilylacetylene (1.3 mL, 9.5 mmol) was added via syringe. The flask was equipped with a reflux condenser, and the reaction mixture was heated at reflux. The reaction progress was monitored by GC-MS. At 8 and 24 h intervals, CuI (0.020 g, 0.09 mmol), PPh<sub>3</sub> (0.050 g, 0.17 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.070 g, 0.09 mmol), and trimethylsilylacetylene (0.5 mL, 3.5 mmol) were added. The reaction mixture was heated at reflux for a total of 44 h. The reaction was quenched with a saturated solution of NH<sub>4</sub>Cl (50 mL), and this was stirred for 10 min. The reaction mixture was then filtered through a plug of silica gel. The organic layer was collected and washed with a saturated solution of NH<sub>4</sub>Cl, a dilute solution of HCl, water, and brine. The organic layer was collected, dried with MgSO<sub>4</sub>, filtered, and concentrated. The crude solid was adsorbed onto silica gel and purified by column chromatography (silica gel, hexanes/diethyl ether) to give a light yellow solid in 62% yield (1.09 g, 2.7 mmol): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.25 (s, 4H), 2.48 (s, 12H), 0.28 (s, 18H); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>) δ 141.2, 140.1, 125.5, 122.3, 103.7, 103.0, 21.4, 0.4; GC-MS *m/z* = 402 (M<sup>+</sup>). Anal. Calcd for C<sub>26</sub>H<sub>34</sub>Si<sub>2</sub>: C, 77.54; H, 8.51. Found: C, 77.14; H, 8.58.

**3,3',5,5'-Tetramethyl-4,4'-di(pent-1-ynyl)biphenyl (4).** Biphenyl **3** (1.00 g, 2.5 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.34 g, 2.5 mmol) were loaded into a flask and dissolved/suspended in THF (15 mL) and methanol (15 mL). The reaction mixture was stirred at ambient temperature for 4 h, and then the solvent was removed. The crude solid was extracted with diethyl ether, and this was washed with water, a saturated solution of NaHCO<sub>3</sub>, and brine. The organic layer was collected, dried over MgSO<sub>4</sub>, filtered, and concentrated. The resulting solid was loaded into a Schlenk flask and dissolved in pentane (20 mL). This solution was cooled in to 0 °C, and BuLi

(3.0 mL, 4.9 mmol) was added dropwise via syringe. The cold bath was removed after 10 min, and the reaction mixture was stirred at ambient temperature for 2 h. The solvent was then removed by cannula filtration, and the resulting solid was suspended in THF (25 mL). To this suspension was added 1-bromopropane (0.44 mL, 4.9 mmol), and the reaction mixture was heated at 60 °C for 16 h. The reaction was monitored by GC-MS. TMEDA (0.73 mL, 4.8 mmol) was added to the reaction mixture, and this was heated at reflux for 20 h. 1-Bromopropane (0.15 mL, 1.6 mmol) was added to the reaction mixture, and this was heated at reflux for an additional 16 h. The solvent was then removed, and the resulting oil was dissolved in diethyl ether. This solution was washed with a saturated solution of NaHCO<sub>3</sub>, water, 2 N NaOH, and brine. The organic layer was collected, dried with MgSO<sub>4</sub>, filtered, and concentrated. The resulting crude oil was purified by column chromatography (silica gel, hexanes/toluene) to give a light yellow solid in 30% yield (0.25 g, 0.73 mmol): <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.36 (s, 4H), 2.57 (s, 12H), 2.30 (t, *J* = 6.8 Hz, 4H), 1.49 (tq, *J* = 7.2 Hz, 4H), 0.98 (t, *J* = 7.2 Hz, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>) δ 140.5, 139.4, 125.4, 123.0, 99.6, 78.5, 22.7, 22.0, 21.5, 13.8; GC-MS *m/z* = 342 (M<sup>+</sup>); HRMS calcd for C<sub>26</sub>H<sub>30</sub> 342.2348, found 342.2354.

**Macrocycle 5.** Biphenyl **4** (0.10 g, 0.29 mmol) and Cp<sub>2</sub>Zr(py)(η<sup>2</sup>-Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>) (0.14 g, 0.29 mmol) were loaded into a Teflon-sealed tube and dissolved in benzene (2 mL). Reaction occurred at ambient temperature over 16 h, during which time precipitate formed. The solvent was removed by filtration on a fritted funnel, and the resulting solid was washed with benzene and diethyl ether to give an orange powder in 17% crude yield (0.028 g, 0.025 mmol). This solid was loaded into a Schlenk tube and dissolved in THF (5 mL). To this solution was added TFA (18 μL, 0.25 mmol), and the reaction mixture was stirred at ambient temperature for 2.5 h. The solvent and excess acid were removed under vacuum. The resulting crude solid was purified by column chromatography (silica gel, hexanes/toluene) to give a white solid in 16% overall yield (0.016 g, 0.023 mmol): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.54 (s, 8H), 6.29 (t, *J* = 7.2 Hz, 4H), 2.14 (s, 24H), 2.01 (dt, *J* = 7.2 Hz, 8H), 1.51 (tq, *J* = 7.4 Hz, 8H), 0.95 (t, *J* = 7.5 Hz, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>) δ 140.4, 140.1, 136.6, 135.9, 127.6, 125.7, 32.7, 23.0, 21.1, 14.4; EI-MS *m/z* = 688 (M<sup>+</sup>); HRMS calcd for C<sub>52</sub>H<sub>64</sub> 688.5008, found 688.5015.

**5-Chloro-2-(hex-1-ynyl)-1,3-dimethylbenzene (7).** 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (0.54 g, 1.1 mmol), PdCl<sub>2</sub> (67 mg, 0.40 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (16.0 g, 48.9 mmol) were loaded into a flask and suspended in acetonitrile (40 mL). To this suspension was added 4-chloro-1-iodo-2,6-dimethylbenzene (**6**)<sup>21</sup> (5.00 g, 18.8 mmol), and the reaction mixture was stirred for 10 min. 1-Hexyne (2.8 mL, 24.4 mmol) was then added via syringe, and the reaction mixture was heated at 80 °C for 16 h. The reaction mixture was allowed to cool to ambient temperature and then diluted with water. The aqueous layer was extracted with diethyl ether. The organic layers were combined, dried with MgSO<sub>4</sub>, filtered, and concentrated. The resulting crude product was purified by column chromatography (silica gel, hexanes) to give a yellow oil in 59% yield (2.45 g, 11.1 mmol): <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 6.91 (s, 2H), 2.25 (m, 8H), 1.36 (m, 4H), 0.81 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>) δ 142.3, 133.2, 127.5, 123.3, 100.2, 78.4, 31.6, 22.6, 21.4, 19.9, 14.1; GC-MS *m/z* = 220 (M<sup>+</sup>). Anal. Calcd for C<sub>14</sub>H<sub>17</sub>Cl: C, 76.18; H, 7.76. Found: C, 76.14; H, 7.69.

**3,3',5,5'-Tetramethyl-4,4''-di(hex-1-ynyl)terphenyl (9).** 1,4-Bis(4,4,5,5-tetramethyl-1,3-dioxaborolan-2-yl)benzene (**8**) (0.067 g, 0.20 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (3 mg, 3 μmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (9 mg, 18 μmol), and Cs<sub>2</sub>CO<sub>3</sub> (0.39 g, 1.2 mmol) were loaded into a flask. A separate flask was loaded with alkyne **7** (0.090 g, 0.40 mmol); this flask was washed with DMF (2 × 4 mL), and the resulting solutions were transferred by

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cannula to the flask containing the reagents. The solution was degassed by three freeze/pump/thaw cycles, and then the flask was sealed and heated at 95 °C for 16 h. The reaction mixture was filtered through diatomaceous earth and diluted with ethyl acetate. This was then washed with a saturated solution of NaHCO<sub>3</sub> and brine. The organic layer was collected, dried with MgSO<sub>4</sub>, filtered, and concentrated. The resulting crude product was purified by column chromatography (silica gel, hexanes/diethyl ether) to give a light yellow solid in 69% yield (0.061 g, 0.14 mmol): <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.61 (s, 4H), 7.36 (s, 4H), 2.59 (s, 12H), 2.38 (t, *J* = 7.0 Hz, 4H), 1.45 (m, 8H), 0.86 (t, *J* = 7.0 Hz, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>) δ 141.1, 140.6, 140.1, 128.2, 126.2, 124.0, 100.1, 79.5, 31.8, 22.6, 21.9, 20.1, 14.1; GC–MS *m/z* = 446 (M<sup>+</sup>). Anal. Calcd for C<sub>34</sub>H<sub>38</sub>: C, 91.42; H, 8.58. Found: C, 91.07; H, 8.46.

**Macrocycle 10.** Terphenyl**9** (0.25 g, 0.56 mmol) and Cp<sub>2</sub>Zr(py)(η<sup>2</sup>-Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>) (0.26 g, 0.56 mmol) were loaded into a flask and dissolved in toluene (8 mL). This mixture was stirred at ambient temperature for 16 h, during which time precipitate formed. The solvent was removed by cannula filtration, and the resulting solid was washed with toluene to give an orange powder in 26% yield (0.081 g, 0.061 mmol). Attempts at characterization by NMR spectroscopy were unsuccessful due to low solubility. Anal. Calcd for C<sub>88</sub>H<sub>96</sub>Zr<sub>2</sub>: C, 79.10; H, 7.24. Found: C, 78.98; H, 7.19.

**Macrocycle 11.** Terphenyl**9** (0.15 g, 0.34 mmol) and Cp<sub>2</sub>Zr(py)(η<sup>2</sup>-Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>) (0.16 g, 0.34 mmol) were loaded into separate flasks. The diyne was dissolved in diethyl ether (15 mL), and a solution of the Cp<sub>2</sub>Zr(py)(η<sup>2</sup>-Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>) in diethyl ether (5 mL) was added via cannula. This was stirred at ambient

temperature for 16 h, during which time an orange precipitate formed. The solvent was removed by cannula filtration, and the crude solid was dried under vacuum. This solid was suspended in THF (15 mL), and to this was added TFA (0.10 mL, 1.3 mmol). This was stirred at ambient temperature for 1 h, during which time the solid dissolved into solution. The solvent and excess acid were removed under vacuum, and the resulting yellow solid was purified by column chromatography (silica gel, hexanes/toluene) to give a light yellow solid in 23% yield (0.035 g, 0.039 mmol): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.11 (s, 8H), 6.76 (s, 8H), 6.26 (t, *J* = 7.0 Hz, 4H), 2.13 (s, 24H), 2.03 (dt, *J* = 7.3 Hz, 8H), 1.50 (tt, *J* = 7.6 Hz, 8H), 1.38 (tq, *J* = 7.2 Hz, 8H), 0.86 (t, *J* = 7.2 Hz, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>) δ 140.3 (two overlapping peaks), 139.5, 137.3, 136.2, 128.1, 127.5, 125.6, 32.1, 30.2, 23.0, 20.8, 14.4; MALDI-TOF *m/z* = 896 (M<sup>+</sup>). Anal. Calcd for C<sub>68</sub>H<sub>80</sub>: C, 91.01; H, 8.99. Found: C, 90.63; H, 9.10.

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**Supporting Information Available:** General experimental methods, copies of <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, tables of bond lengths and angles, and the X-ray crystallographic data for compound **10** in the form of CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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