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Efficient, High-Yield Route to Long, Functionalized *p*-Phenylene Oligomers Containing Perfluorinated Segments, and Their Cyclodimerizations by Zirconocene Coupling

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Abstract: Linear oligophenylene diynes containing 6, 9, and 12 phenylene rings were synthesized in high yields using the nucleophilic aromatic substitution (S_NAr) of perfluoroarenes by aryllithium reagents as the key carbon−carbon bond-forming reaction. This reaction was demonstrated to proceed readily at low temperatures with sterically hindered substrates and in the presence of base-sensitive silylalkynyl groups. Diynes synthesized by this methodology were readily zirconocene-coupled into large dimeric macrocycles using the zirconocene reagent $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$.

Introduction

Oligo(*p*-phenylenes) have been the subject of many recent investigations, as well-defined models for poly(*p*-phenylene)[1−3] and as new materials with chemically tailored properties.[4,5] In addition, oligo(*p*-phenylenes) have been extensively employed as rigid-rod components in supramolecular chemistry. For example, they can mediate excitation energy transfer between chromophores that they hold several nanometers apart.[6−9] As linkers, oligophenylenes have also been observed to couple electronic properties between distant metal centers, as indicated by changes in redox potentials.[10,11] Functionalized oligophenylenes have found use as synthetic ionophores, which facilitate ion migration through lipid bilayers.[12−15] As monomer units employed in copolymerizations, oligophenylenes have been used to tailor polymeric properties such as crystallinity, fluorescence behavior, and stability.[16−18] Finally, oligophenylene building blocks have been employed in the synthesis of large, rigid macrocycles,[19−22] including a cyclotetraicosophenylene with a diameter of ∼3 nm.[23]

Macrocyclizations via zirconocene-coupling methods allow the cyclization of diynes possessing various geometries and functional groups.[24−33] This synthetic approach to macrocycles offers many advantages over traditional methods, which typically involve high-dilution techniques, lengthy separations, and relatively low yields.[34] The zirconocene-coupling approach to macrocycles provides very high yields of a single product and is based on the reversibility of carbon−carbon bond formation

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in the coupling of silyl-substituted alkynes.[28] Given the potential of this method, and the widespread interest in macrocycles, we have explored its application in the construction of very large (nanometer-scaled) rings, which are difficult to obtain via traditional coupling procedures.[23,35]

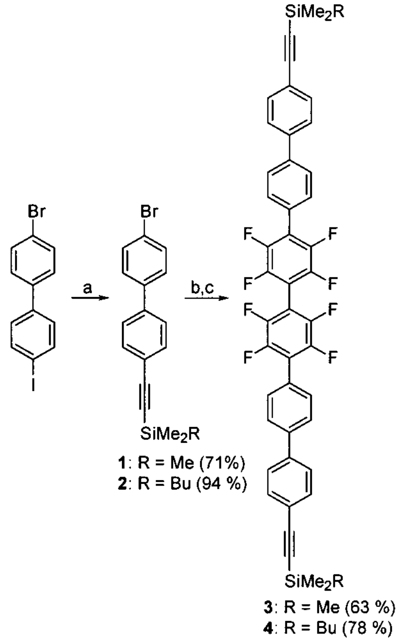
Investigation of the size limitations of the zirconocene-coupling method requires long, rigid diynes as precursors. Previously, we have shown this macrocyclization reaction to provide high-yielding routes to large, triangular macrocycles via coupling of the tetraphenylene diyne $Me_3SiC{\equiv}C(C_6H_4)_4C{\equiv}CSiMe_3$[27] and the isostructural 2,2′-bipyridine $Me_3SiC{\equiv}C(C_6H_4)(C_5H_4N)(C_5H_4N)(C_6H_4)C{\equiv}CSiMe_3$.[24] However, obtaining significant quantities of diynes with longer spacer groups has proven difficult, given the inherently low solubility of oligophenylenes and the low cumulative yields associated with multistep coupling reactions. Thus, the use of zirconocene coupling in the synthesis of nanoscaled macrocycles requires development of large-scale, efficient synthetic routes to rigid, oligomeric diynes.

In this contribution, we describe convergent, high-yielding synthetic routes to long, terminally derivatized oligophenylenes. Linear oligophenylenes containing 12 phenylene units have been synthesized, and longer oligomers should be readily accessible by analogous methods. The four oligophenylenes described here are terminated by trialkylsilylalkynyl groups and are efficiently cyclized via zirconocene coupling to dimeric products. These macrocycles are readily demetalated to give very large, air-stable cyclophanes.

Our synthetic strategy is based on nucleophilic aromatic substitution of perfluorinated arenes by aryllithium nucleophiles. Perfluoroarenes are excellent electrophiles, undergoing nucleophilic substitution readily under mild conditions, and many perfluoroarene substrates exhibit very high regioselectivities.[36] The ease with which fluorinated arenes undergo nucleophilic aromatic substitution (reactions are often rapid below 0 °C)[37] translates into tolerance of many functional groups. Hindered nucleophiles also react readily, allowing the incorporation of synthons bearing bulky, solubility-enhancing substituents.

Oligophenylenes containing perfluorinated segments have found recent use as electron-transport materials in organic light-emitting diodes,[38,39] sensitizers for the photoactivation of water,[40] and elements in the rational design of liquid crystals.[41] Supramolecular chemistry involving phenyl−perfluorophenyl interactions is also a topic of growing interest,[42−45] and molecules containing both phenyl and perfluorophenyl groups are important in this area. Macrocycles containing perfluorinated phenylene segments are likewise of interest as supramolecular building blocks, as the macrocyclic effect can greatly enhance the attractive interactions between electron-poor perfluoroarenes and electron-rich arenes,[42,45,46] facilitating their use in supramolecular construction.

Scheme 1. Synthesis of Hexaphenylene Diynes **3** and **4**[a]



[a] Conditions: (a) $Pd(PPh_3)_4$/CuI, $HC{\equiv}CSiMe_2R$; (b) 2 equiv of *t*-BuLi; (c) 0.5 equiv of decafluorobiphenyl.

Results

The carbanion precursors **1** and **2** used in the nucleophilic aromatic substitution reactions were synthesized from 4-bromo-4′-iodobiphenyl[47] by means of the Sonogashira reaction[48] (Scheme 1). The reaction of 2 equiv of *t*-BuLi with these bromoarenes at −78 °C produced solutions of the desired aryllithium reagents. Addition of 0.5 equiv of decafluorobiphenyl to these in situ-generated carbanions gave hexaphenylene diynes **3** and **4** (Scheme 1). This reaction proceeded at an appreciable rate at −78 °C, as evidenced by the precipitation of a colorless solid (**3** and LiF) within minutes of the start of addition. As expected, the butyl groups of **4** make it significantly more soluble than **3** in organic solvents.

The reaction of 1 equiv of lithiated **2** with a slight excess (1.2 equiv) of decafluorobiphenyl gave an excellent yield (98%) of the monosubstitution product **5** (Scheme 2). This product precipitated out of the reaction mixture, which prevented further conversion to the disubstituted product **4**. Reaction of 2 equiv of **5** with 1,4-dilithio-2,5-diisopropylbenzene, prepared in situ from 1,4-diiodo-2,5-diisopropylbenzene, gave nonaphenylene **6** in 79% yield (Scheme 2).

Monolithiation of 1,4-dibromo-2,5-diisopropylbenzene, followed by reaction with 0.5 equiv of decafluorobiphenyl, gave dibromoquaterphenyl **7** (Scheme 3) in 93% yield. Quaterphenyl **7** may then be dilithiated; the resulting dianion then reacted with 2 equiv of **5** to give dodecaphenylene **8** in 95% yield (Scheme 3).

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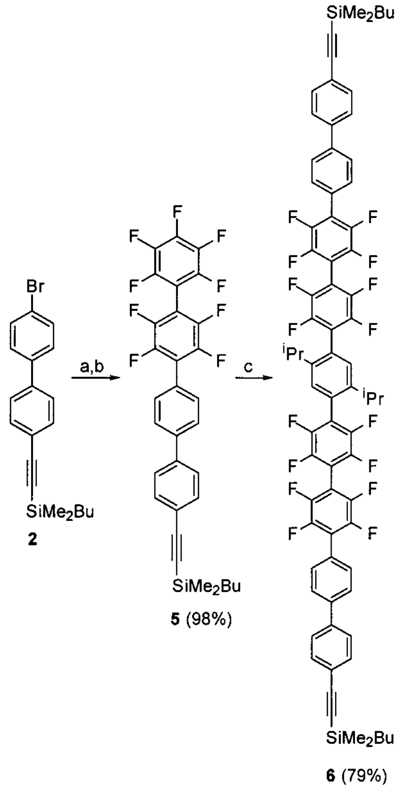
Scheme 2. Synthesis of Monosubstituted Alkyne **5** and Nonaphenylene Diyne **6**[a]



[a] Conditions: (a) 2 equiv of *t*-BuLi; (b) 1.2 equiv of decafluorobiphenyl; (c) **5** is added to a solution of 0.5 equiv of 1,4- dilithio-2,5-diisopropylbenzene, which is generated in situ from 0.5 equiv of 1,4-diiodo-2,5-diisopropylbenene and 2 equiv of *t*-BuLi.

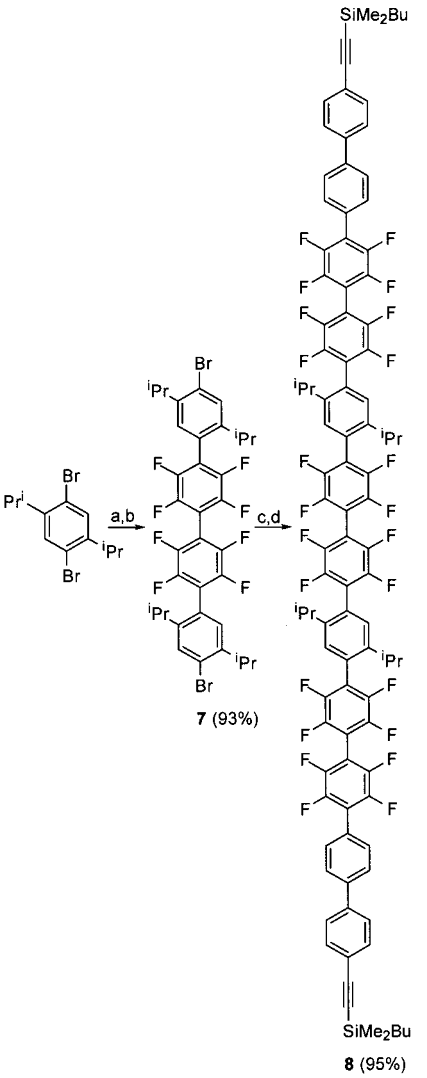
Diynes **3**, **4**, and **6** were cyclodimerized via zirconocene coupling under nearly identical synthetic conditions (Scheme 4). The diynes were suspended in an aromatic solvent (benzene for **3** and **6**, mesitylene for **4**), and a solution of $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$ was then added in the same solvent. Sonication of these suspensions yielded clear orange solutions, and over 24 h at 40 °C, crystalline (**9**) or microcrystalline (**10** and **11**) product precipitated from solution.

Dodecaphenylene zirconacycles **9** and **10** are soluble in benzene, which allowed their characterization by NMR spectroscopy. Octadecaphenylene **11** was highly insoluble in toluene and benzene, however, and decomposed in dichloromethane and THF solution at room temperature, which rendered infeasible its characterization by NMR spectroscopy. The successful synthesis of **11** may be inferred, however, from the full characterization of its derivative **14** (see below).

The crystal structure of **9** was determined from a crystal formed during the course of its synthesis. Selected crystal data are presented in Table 1, and a detailed account of the structure determination is presented in the Supporting Information. An ORTEP view of the structure is shown in Figure 1.

The reaction of **10** with benzoic acid in benzene solution resulted in bleaching of the yellow color of the zirconacycle over several hours. The material isolated from this reaction exhibited three distinct vinyl ^1H NMR resonances, which suggests that the macrocycle had been cleaved. Reactions of **9**, **10**, and **11** with trifluoroacetic acid in benzene, however, rapidly produced the desired cyclophanes **12**−**14** (Scheme 5). Compound **12** was even less soluble than its precursor **9**, and attempts to characterize it by NMR spectroscopy and mass spectrometry were not successful. Its characterization is therefore based solely on elemental analysis. However, the clean demetalations of **10** and **11** to give fully characterized **13** and **14**, respectively, suggest that **9** was demetalated to give **12** in identical fashion.

Scheme 3. Synthesis of Dibromoquaterphenyl **7** and Dodecaphenylene Diyne **8**[a]



[a] Conditions: (a) 1 equiv of *t*-BuLi; (b) 0.5 equiv of decafluorobiphenyl; (c) 2 equiv of *t*-BuLi; (d) 2 equiv of **5**.

Dodecaphenylene diyne **8** also reacted with $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$, giving an orange solution, which subsequently produced a yellow precipitate. This precipitate was insoluble in benzene, toluene, THF, and dichloromethane. A suspension of this product in benzene reacted with trifluoroacetic acid to give a white material that was also highly insoluble. Elemental analysis of the zirconocene-coupled product gave results consistent with a macrocycle, but the extremely low solubilities of the presumed zirconocycle and its demetalated derivative precluded further characterization by NMR spectroscopy or mass spectrometry.

Discussion

As noted earlier, a primary goal of this research was the synthesis of silyl-terminated oligophenylene diynes of nanometer dimension for use in zirconocene-coupling macrocycle syntheses.[24−33] The high-yielding macrocyclizations of quaterphenyl diynes[27] and isostructural bipyridine-containing diynes[25] suggested that even longer diynes might be efficiently cyclized

Scheme 4. Synthesis of Zirconocene-Coupled Dimers **9**, **10**, and **11**

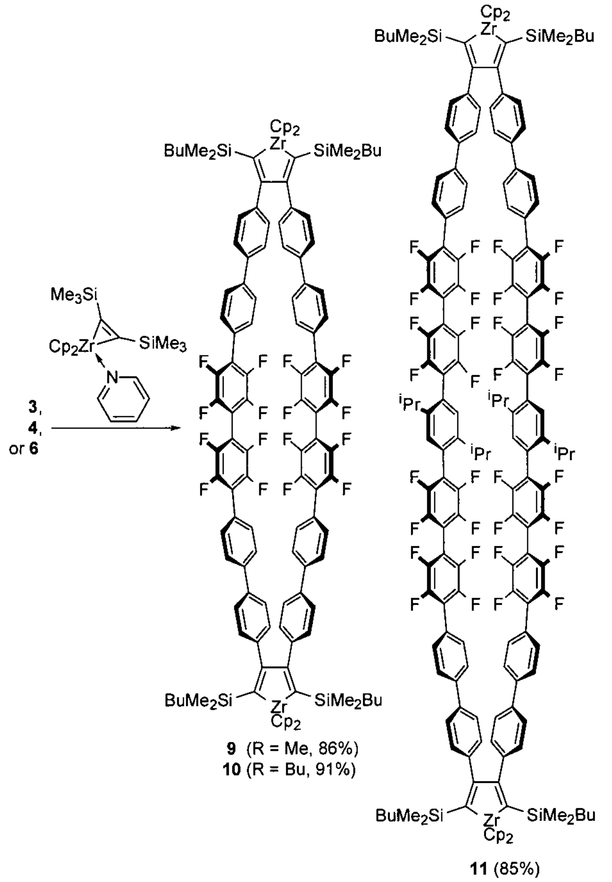


Table 1. Crystallographic Data for Dimeric Macrocycle **9**

empirical formula	$C_{124}H_{100}F_{16}Si_4Zr_2$
formula weight	2188.91
crystal system	triclinic
space group	$P\bar{1}$(No. 2)
crystal color, habit	yellow, blocks
a (Å)	12.0173(3)
b (Å)	16.0939(4)
c (Å)	16.5390(4)
α (deg)	85.785(1)
β (deg)	71.949(1)
γ (deg)	88.627(1)
cell volume (Å³)	3033.1(1)
temp (K)	161 ± 1
Z	1
R, *R*w	0.045, 0.054
goodness of fit	1.64

via zirconocene-coupling methodology. Initial attempts to obtain hexaphenylene diynes, based on a Suzuki-coupling strategy,[49] were hindered by the insolubility of the hexaphenylene derivatives. Furthermore, attempts to introduce solubility-enhancing alkyl groups *ortho* to the site of coupling greatly lowered yields of the final product. Thus, numerous chromatographic separations were required to isolate pure products, which were therefore difficult to obtain in large quantities. Moreover, silylalkynes did not survive the harsh, basic conditions of Suzuki coupling, limiting the flexibility of this synthetic approach.

In contrast, nucleophilic aromatic substitutions with perfluoroarenes proceed under much milder conditions[37] than those typically employed for palladium-catalyzed carbon−carbon bond-forming reactions.[50] The terminal 4 and 4′ fluorine atoms of decafluorobiphenyl and analogous compounds such as **5** are regiospecifically substituted by aryllithium reagents.[36] Sterically encumbered aryllithiums worked well in this reaction, as demonstrated by the high-yielding syntheses of **6**, **7**, and **8**. The mild reaction conditions also allow for the presence of base-

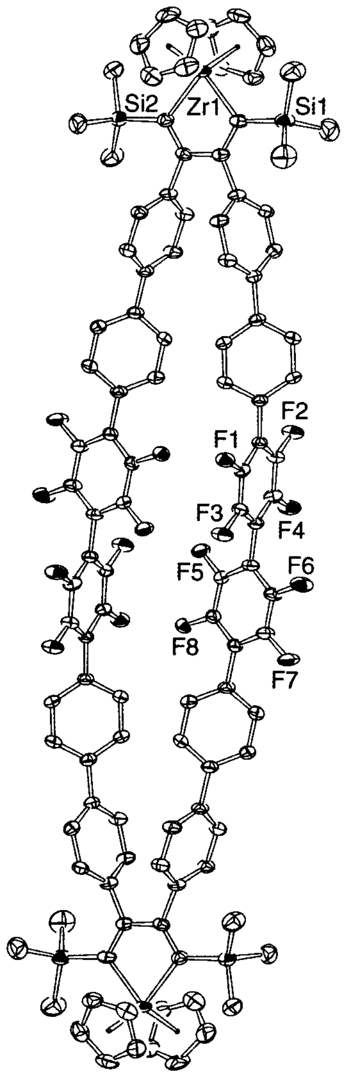
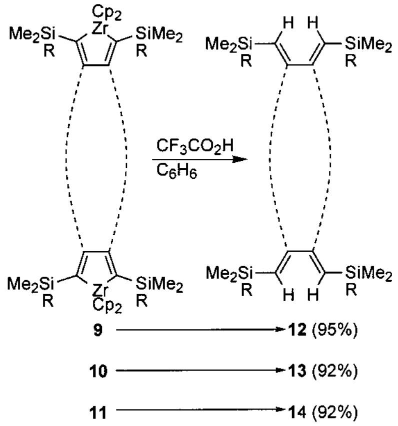


Figure 1. ORTEP diagram of macrocycle **9**. Heteroatoms of the asymmetric unit are labeled. The closest F···F distance across the center of the macrocycle is 2.69 Å.

Scheme 5. Demetalation of **9**−**11** To Give **12**−**14**



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sensitive silylalkynes, which would have been rapidly desilylated by extremely basic aryllithium reagents at room temperature. The higher yields obtained through this procedure also greatly facilitated the isolation and purification of products, eliminating the need for chromatography.

The successful syntheses of hexaphenylenes **3** and **4** (Scheme 1) demonstrates the feasibility of this method for producing oligophenylenes. These reactions cleanly converted the two starting materials, each containing two aromatic rings, into a product containing six aromatic rings. To investigate the possibility of synthesizing longer oligophenylenes by this convergent "length-tripling" methodology, a version of this reaction (Scheme 2) was developed in which the asymmetric substitution product **5** was exclusively formed. The synthesis of **5** is facilitated by the low solubility of the product in the pentane/diethyl ether reaction mixture. Monosubstituted **5** precipitates from solution as it forms, which prevents further conversion to disubstituted **4**. This solubility effect allowed only a slight excess of decafluorobiphenyl to be used while giving a 98% yield of **5**. The possibility of asymmetric substitution lends additional flexibility to this methodology. The synthesis of nonaphenylene **6** from **5** and dilithiodiisopropylbenzene (Scheme 2) demonstrates the feasibility of a slightly different approach involving a difunctional aryllithium reagent and 2 equiv of a monofunctional fluoroarene.

The synthesis of **7** (Scheme 3) demonstrates the addition of a bromolithioarene to a perfluoroarene, such that further lithium−halogen exchange via S_NAr steps could be carried out in the stepwise construction of an oligoarene chain. Thus, the reaction of dilithiated **7** with **5** gives the dodecaphenylene **8** in 95% yield. Significantly, then, an oligoarene may be synthesized from a dilithioarene containing perfluorinated segments. Oligophenylenes may therefore be synthesized in an iterative fashion, without side reactions involving attack on internal perfluorophenylene segments. The successful synthesis of dodecaphenylene **8** suggests that an iterative divergent/convergent approach similar to that described by Tour et al.[51,52] may be employed for oligophenylene synthesis via the synthetic methods described here. A notable advantage of the method described here, however, is that molecular weight and length are tripled (rather than doubled) with each iteration.

The macrocyclization protocol described above is effectively identical to that employed[25,26] to synthesize dimers and trimers from bipyridine-containing diynes using Rosenthal's $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$.[53] Yields are again consistently high, with exclusive formation of a single product. The product in all cases, however, is not the expected trimer but instead a dimer. To close into a dimeric macrocycle, a linear diyne must bend, and there is an energetic cost to this bending which must be compensated for if a dimer is to be the thermodynamic product. Entropy clearly favors the formation of dimers over trimers; three dimers could be formed from two trimers, and trimers also include substantial void spaces that are not present in the more compact dimers. Inclusion of solvent molecules[25] in these cavities would further reduce the entropy. In addition to solution thermodynamics, crystallization may also perturb dimer−trimer equilibria by trapping out less soluble kinetic products.

The structure of macrocycle **9** provides insight into the nature of the bending of the oligophenylene spacer groups. Figure 2 provides a minimal view of the structure of **9**. The solid lines in this figure are phenyl−phenyl C−C bonds, and the dashed lines represent vectors connecting the *para* carbon atoms of each phenyl ring. The angles between these bonds and vectors, given in Figure 2, describe the bending of the hexaphenylene chain. Much of the bending is seen to be concentrated at one end of this chain. This appears to facilitate packing of the two oligophenylene chains, to give a compact, centrosymmetric structure that excludes solvent of crystallization from the center of the macrocycle. Attempts to obtain X-ray quality crystals of macrocycles **10**−**14** did not prove successful, but mass spectrometry clearly showed the demetalated macrocycles **13** and **14** to be dimeric.

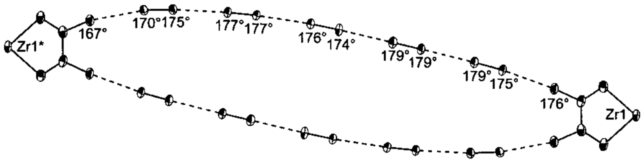

Figure 2. Angles between para carbon atoms of the hexaphenylene chain of **9**. The closest F···F distance across the center of the macrocycle is 2.69 Å.

The failure of benzoic acid as a demetalation reagent is noteworthy in light of this reagent's utility in demetalating trimeric macrocycles.[25] The observation that it reacts more slowly than trifluoroacetic acid suggests that rapidity of demetalation is crucial; a mono-demetalated macrocycle may be substantially more strained than its precursor Zr_2 macrocycle and thus more prone to ring opening.

Concluding Remarks

The methodology outlined herein provides a straightforward, high-yielding, and versatile route to oligophenylenes containing perfluorinated segments. These oligophenylenes contain base-sensitive silylacetylene groups, and we believe that these coupling reactions will also tolerate other functional groups as a consequence of the very low barrier to the S_NAr reaction. The zirconocene-mediated macrocyclization of these oligophenylene diynes was also demonstrated to proceed readily and in high yield. The size limits for macrocycles obtained by this method have not yet been reached, as indicated by the high synthetic yields observed. Note that the crystallographic Zr−Zr distance of **9** is 32.4 Å, and models suggest that the Zr−Zr distance in **11** is 44 Å. If dodecaphenylene **8** forms a zirconocene-coupled dimeric structure analogous to **9**, **10**, and **11**, this macrocycle will have a Zr−Zr distance of ~57 Å. This macrocycle would be the second cyclotetraicosaphenylene to be synthesized, although it would have a geometry that is quite different from that of the hexagon reported by Hensel and Schlüter.[23]

The oligophenylenes and macrocycles described here may be of interest as electronic materials. The incorporation of perfluorophenylene segments into these macrocycles allow for their use in arene−perfluoroarene supramolecular systems, opening the door to host−guest chemistry and molecular recognition with nanometer-scale substrates. Investigations of these, and other, implications of this chemistry are currently underway.

Experimental Section

General Information. All reactions involving air-sensitive compounds were carried out under nitrogen or argon using standard Schlenk techniques and dry, oxygen-free solvents. Pentane, diethyl ether, benzene, and tetrahydrofuran were distilled under nitrogen from sodium

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benzophenone ketyl. Toluene, toluene-d_8, and benzene-d_6 were distilled under nitrogen from Na/K. Dichloromethane-d_2 was vacuum transferred from CaH_2. Respectively, *n*-BuLi and *t*-BuLi were used as a 1.6 M solution in hexanes and a 1.7 M solution in pentane. Literature methods were followed to prepare 4-bromo-4′-iodobiphenyl.[47]

All NMR spectra were recorded at room temperature. ^1H and ^{13}C chemical shifts were referenced to the residual proton or carbon resonance of the deuterated solvent. ^{19}F chemical shifts were referenced to α,α,α-trifluorotoluene (0 ppm) in a sealed capillary. All mass spectra and combustion analyses were obtained at the Micro-Mass Facility of the University of California, Berkeley.

4-Bromo-4′-(trimethylsilyl)alkynylbiphenyl (1). 4-Bromo-4′-iodobiphenyl (10.4 g, 29.0 mmol), $Pd(PPh_3)_4$ (0.168 g, 0.145 mmol), and CuI (0.0552 g, 0.290 mmol) were loaded into a 500-mL Schlenk flask with a Teflon stopper in the drybox, and dry benzene (250 mL) was added on the Schlenk line. Stirring this suspension resulted in bleaching of the yellow color of the $Pd(PPh_3)_4$ within minutes as it dissolved. Diisopropylamine (50 mL) and then trimethylsilylacetylene (4.10 mL, 29.0 mmol) were added via syringe, and the Teflon stopcock was sealed. The reaction solution warmed notably, and a large amount of diisopropylammonium iodide was deposited as the color changed from colorless to pale yellow. After 1 h, the reaction solution was again colorless and no longer warm to the touch. The volatile materials were removed after another 2 h under dynamic vacuum, and the reaction mixture was suspended in pentane (500 mL). This pentane suspension was filtered through a plug of silica (50 mL), and the pentane was then removed under dynamic vacuum. The crude product was recrystallized from 95% ethanol. The yield of white needles was 6.80 g, 71%: ^1H NMR (500 MHz, benzene-d_6) δ 0.27 (s, 9 H, $Si(CH_3)_3$), 6.86 (d, $J = 6.5$ Hz, 2 H, phenylene), 7.01 (d, $J = 6.5$ Hz, 2 H, phenylene), 7.25 (d, $J = 6.5$ Hz, 2 H, phenylene), 7.49 (d, $J = 6.5$ Hz, 2 H, phenylene); $^{13}C\{^1H\}$ NMR (125 MHz, benzene-d_6) δ 0.4 ($Si(CH_3)_3$), 95.8 (alkynyl), 106.1 (alkynyl), 122.6 (phenylene), 123.3 (phenylene), 127.4 (phenylene), 129.2 (phenylene), 132.4 (phenylene), 133.1 (phenylene), 139.6 (phenylene), 140.5 (phenylene); EI-MS *m/z* 330 (Br doublet, M^+), 315 (Br doublet, $M^+ - Me$). Anal. Calcd for $C_{17}H_{17}BrSi$: C, 62.00; H, 5.20. Found: C, 62.00; H, 5.18.

4-Bromo-4′-(butyldimethylsilyl)alkynylbiphenyl (2). 4-Bromo-4′-iodobiphenyl (10.0 g, 27.9 mmol), $Pd(PPh_3)_4$ (0.322 g, 0.279 mmol), and CuI (0.106 g, 0.557 mmol) were loaded into a 500-mL Schlenk flask with a Teflon stopper in the drybox, and dry benzene (250 mL) was added on the Schlenk line. Stirring caused rapid bleaching of the yellow color of $Pd(PPh_3)_4$ as it dissolved. Diisopropylamine (50 mL) and then butyldimethylsilylacetylene (3.91 g, 27.9 mmol) were added via syringe, and the Teflon stopcock was sealed. The reaction solution warmed notably and turned pale yellow, and diisopropylammonium iodide precipitated. After stirring for 1 h, the reaction solution was again colorless and no longer warm to the touch. The volatile materials were removed after another 2 h under dynamic vacuum, and the reaction mixture was suspended in pentane (500 mL). This pentane suspension was filtered through a plug of silica (50 mL), and the pentane was removed under dynamic vacuum. The yield of white microcrystals was 9.76 g, 94%: ^1H NMR (500 MHz, benzene-d_6) δ 0.29 (s, 6 H, $SiMe_2Bu$), 0.74 (t, $J = 8.5$ Hz, 2 H, $SiMe_2CH_2CH_2CH_2CH_3$), 0.92 (t, $J = 7$ Hz, 3 H, $SiMe_2CH_2CH_2CH_2CH_3$), 1.39 (q, $J = 7$ Hz, 2 H, $SiMe_2CH_2CH_2CH_2CH_3$), 1.51 (m, 2 H, $SiMe_2CH_2CH_2CH_2CH_3$), 6.86 (d, $J = 6.5$ Hz, 2 H, phenylene), 7.01 (d, $J = 6.5$ Hz, 2 H, phenylene), 7.25 (d, $J = 6.5$ Hz, 2 H, phenylene), 7.50 (d, $J = 6.5$ Hz, 2 H, phenylene); $^{13}C\{^1H\}$ NMR (125 MHz, benzene-d_6) δ −1.1 ($SiMe_2Bu$), 14.4 ($SiMe_2Bu$), 16.6 ($SiMe_2Bu$), 26.9 ($SiMe_2Bu$), 27.1 ($SiMe_2Bu$), 95.3 (alkynyl), 106.5 (alkynyl), 122.6 (phenylene), 123.4 (phenylene), 127.4 (phenylene), 129.2 (phenylene), 132.4 (phenylene), 133.1 (phenylene), 139.6 (phenylene), 140.5 (phenylene); GC−MS *m/z* 372 (Br doublet, M^+), 357 (Br doublet, $M^+ - Me$). Anal. Calcd for $C_{20}H_{23}BrSi$: C, 64.68; H, 6.24. Found: C, 64.60; H, 6.35.

Hexaphenylene Diyne 3. Alkyne **1** (3.11 g, 9.43 mmol) was loaded into a 500-mL Schlenk flask with a Teflon stopper in the drybox and then dissolved in dry toluene (175 mL) on the Schlenk line. Dry diethyl ether (50 mL) was added to this solution, which was then chilled to −78 °C in a dry ice/acetone bath. *tert*-Butyllithium (11.4 mL, 19.3 mmol) was then added dropwise with a syringe, to give a clear yellow solution. This solution was allowed to stir at −78 °C for 30 min. Decafluorobiphenyl (1.50 g, 4.49 mmol) was loaded into a 50-mL Schlenk flask, which was then purged with dry nitrogen for 30 min. Addition of dry toluene (40 mL) gave a clear solution with stirring. This solution was then added dropwise by cannula to the first flask at −78 °C. Cloudiness was observed in the reaction flask when the addition was nearly complete. On completion of addition, the Teflon stopper of the reaction flask was sealed, and the reaction was allowed to warm slowly to room temperature over 6 h, as the dry ice evaporated from the cold bath. The reaction mixture, thick with white precipitate, was then washed with water (2 × 100 mL) in a separatory funnel and the white, finely divided product was isolated on a medium frit. The product was then washed with water (2 × 25 mL) and diethyl ether (2 × 25 mL) and dried under dynamic vacuum. The yield of white microcrystalline product was 2.26 g, 63%: ^1H NMR (500 MHz, benzene-d_6) δ 0.30 (s, 9 H, $Si(CH_3)_3$), 7.20 (d, $J = 8$ Hz, 2 H, phenylene), 7.24 (d, $J = 8$ Hz, 2 H, phenylene), 7.29 (d, $J = 8$ Hz, 2 H, phenylene), 7.57 (d, $J = 8$ Hz, 2 H, phenylene); ^{19}F NMR (470.6 MHz, benzene-d_6) δ −78.9 (m, 4 F), −75.2 (m, 4 F); EI-MS *m/z* 794 (M^+), 779 ($M^+ - Me$); λ_{max} (CH_2Cl_2) 306 nm. Anal. Calcd for $C_{46}H_{34}F_8Si_2$: C, 69.50; H, 4.31. Found: C, 69.52; H, 4.24.

Hexaphenylene Diyne 4. Alkyne **2** (3.11 g, 9.43 mmol) was loaded into a 500-mL Schlenk flask with a Teflon stopper in the drybox and then dissolved in dry hexanes (100 mL) on the Schlenk line. Dry diethyl ether (50 mL) was added to this solution, and it was chilled to −85 °C in a liquid nitrogen/methanol bath, giving a white suspension. *tert*-Butyllithium (7.6 mL, 12.9 mmol) was then added dropwise with a syringe, which did not change the appearance of the reaction mixture. The reaction mixture was allowed to warm to −60 °C to give a clear, light amber solution. Decafluorobiphenyl (1.00 g, 2.99 mmol) was loaded into a 100-mL Schlenk flask, which was then purged with dry nitrogen for 30 min. Dry hexanes (40 mL) were then added, and this mixture was stirred until a colorless solution was obtained. This solution was added to the first flask dropwise by cannula, at −80 °C. Cloudiness was observed in the reaction flask once the addition was nearly complete. On completion of addition, the Teflon stopper of the reaction flask was sealed, and the reaction was allowed to warm slowly to room temperature over 3 h. The reaction mixture, containing white precipitate, was then diluted with dichloromethane (500 mL). Insoluble salts were first removed by filtering the suspension through filter paper and then the product solution was passed through a plug of silica (50 mL). Solvents were then removed under dynamic vacuum, and the product was washed with hexanes (250 mL). The yield of white microcrystalline product was 2.03 g, 78%: ^1H NMR (500 MHz, benzene-d_6) δ 0.32 (s, 6 H, $SiMe_2Bu$), 0.76 (t, $J = 8.5$ Hz, 2 H, $SiMe_2CH_2CH_2CH_2CH_3$), 0.94 (t, $J = 7$ Hz, 3 H, $SiMe_2CH_2CH_2CH_2CH_3$), 1.41 (q, $J = 7.5$ Hz, 2 H, $SiMe_2CH_2CH_2CH_2CH_3$), 1.53 (m, 2 H, $SiMe_2CH_2CH_2CH_2CH_3$), 7.21 (d, $J = 8$ Hz, 2 H, phenylene), 7.24 (d, $J = 8$ Hz, 2 H, phenylene), 7.29 (d, $J = 6.5$ Hz, 2 H, phenylene), 7.58 (d, $J = 6.5$ Hz, 2 H, phenylene); $^{13}C\{^1H\}$ NMR (125 MHz, benzene-d_6, not all resonances observed due to poor solubility) δ −1.1 ($SiMe_2Bu$), 14.4 ($SiMe_2Bu$), 16.6 ($SiMe_2Bu$), 26.9 ($SiMe_2Bu$), 27.1 ($SiMe_2Bu$), 127.7 (phenylene), 127.8 (phenylene), 128.9 (phenylene), 131.2 (phenylene), 133.2 (phenylene), 140.6 (phenylene); ^{19}F NMR (470.6 MHz, benzene-d_6) δ −78.9 (m, 4 F), −75.2 (m, 4 F); FAB-MS *m/z* 878 (M^+), 821 ($M^+ - Bu$); λ_{max} (CH_2Cl_2) 306 nm. Anal. Calcd for $C_{52}H_{46}F_8Si_2$: C, 71.05; H, 5.27. Found: C, 71.14; H, 5.21.

Alkyne 5. Alkyne **2** (9.29 g, 25.0 mmol) was loaded into a 1-L Schlenk flask with a Teflon stopper and then dissolved in dry pentane (250 mL). Dry diethyl ether (100 mL) was added to this solution, and it was chilled to −78 °C in a dry ice/acetone bath, giving a white suspension. *tert*-Butyllithium (30.9 mL, 52.5 mmol) was then added dropwise with a syringe. The reaction mixture was allowed to warm to the point where all solids redissolved, giving a clear yellow solution, and then cooled once more to −78 °C. Decafluorobiphenyl (10.0 g, 30.0 mmol) was loaded into a 250-mL Schlenk flask, which was then purged with dry nitrogen for 30 min. Dry pentane (125 mL) was added, and stirring was continued until a clear solution was obtained. This solution was added dropwise by cannula to the first flask, at −78 °C. A thin precipitate formed on addition, which thickened as the addition progressed. On completion of addition, the Teflon stopper of the reaction flask was sealed, and the reaction was allowed to warm slowly to room temperature over 6 h as the dry ice evaporated. The reaction mixture, containing white precipitate, was washed with water (3 × 250 mL) in a separatory funnel. The organic phase was reduced in volume by one-third under dynamic vacuum, and the solid product was isolated on a medium frit. The product was then washed with water (3 × 50 mL) and pentane (3 × 25 mL). The yield of white microcrystalline product was 14.8 g, 98%: ^{1}H NMR (500 MHz, benzene-d_6) δ 0.31 (s, 6 H, SiMe_2Bu), 0.76 (t, $J = 8.5$ Hz, 2 H, SiMe$_2$CH_2CH$_2$CH$_2$CH$_3$), 0.94 (t, $J = 7$ Hz, 3 H, SiMe$_2$CH$_2$CH$_2$CH$_2$CH_3), 1.41 (q, $J = 7.5$ Hz, 2 H, SiMe$_2$CH$_2$CH_2CH$_2$CH$_3$), 1.53 (m, 2 H, SiMe$_2$CH$_2$CH$_2$CH_2CH$_3$), 7.20 (m, 4 H, phenylene), 7.27 (d, $J = 8$ Hz, 2 H, phenylene), 7.57 (d, $J = 8$ Hz, 2 H, phenylene); ^{13}C{^{1}H} NMR (125 MHz, dichloromethane-d_2, not all resonances observed) δ −1.7 (SiMe_2Bu), 14.0 (SiMe$_2$$Bu$), 16.2 (SiMe$_2$$Bu$), 26.4 (SiMe$_2$$Bu$), 26.7 (SiMe$_2$$Bu$), 95.3 (alkynyl), 105.25 (alkynyl), 123.2 (phenylene), 127.4 (phenylene), 127.4 (phenylene), 127.6 (phenylene), 131.0 (phenylene), 132.8 (phenylene), 140.3 (phenylene), 141.87 (phenylene); ^{19}F NMR (470.6 MHz, benzene-d_6) δ −96.9 (m, 2 F), −86.4 (m, 1 F), −78.8 (m, 2 F), −75.3 (m, 2 F), −75.1 (m, 2 F); EI-MS m/z 606 (M$^+$), 591 (M$^+$ − Me), 578 (M$^+$ − Bu). Anal. Calcd for $C_{52}H_{46}F_8Si_2$: C, 63.36; H, 3.82. Found: C, 63.14; H, 3.75.

Nonaphenylene Diyne 6. Into a 500-mL Schlenk flask was loaded 1,4-diiodo-2,5-diisopropylbenzene (0.162 g, 0.393 mmol). This flask was then purged with nitrogen for 30 min, and dry toluene (100 mL) was added to give a clear solution. Dry diethyl ether (50 mL) was then added, and the solution was cooled to −78 °C in a dry ice/acetone bath. *tert*-Butyllithium (0.99 mL, 1.69 mmol) was added dropwise via syringe, giving an orange, slightly cloudy solution. This solution was stirred at −78 °C for 30 min. Alkyne **5** (0.500 g, 0.842 mmol) in toluene (75 mL) was then added dropwise by cannula at −78 °C, which produced a precipitate. On completion of addition, the reaction flask was sealed, and the reaction was allowed to warm slowly to room temperature over 6 h as the dry ice evaporated. The reaction mixture, containing white precipitate, was then washed with water (3 × 100 mL) in a separatory funnel. The organic phase was separated and reduced in volume by one-third under dynamic vacuum, and the solid product was isolated on a medium frit. The product was then washed with water (3 × 50 mL) and pentane (3 × 25 mL). The yield of white microcrystalline product was 0.412 g, 79%: ^{1}H NMR (500 MHz, dichloromethane-d_2) δ 0.24 (s, 6 H, SiMe_2Bu), 0.73 (t, $J = 8.5$ Hz, 2 H, SiMe$_2$CH_2CH$_2$CH$_2$CH$_3$), 0.93 (t, $J = 7$ Hz, 3 H, SiMe$_2$CH$_2$CH$_2$CH$_2$CH_3), 1.25 (d, $J = 6.5$ Hz, 6 H, isopropyl), 1.43 (m, 4 H, SiMe$_2$CH$_2$CH_2CH_2CH$_3$), 2.84 (m, $J = 6.5$ Hz, 1 H, isopropyl), 7.38 (s, 1 H, central phenylene), 7.58 (d, $J = 8$ Hz, 2 H, phenylene), 7.66 (m, 4 H, phenylene), 7.82 (d, $J = 8$ Hz, 2 H, phenylene); ^{19}F NMR (470.6 MHz, benzene-d_6) δ −78.8 (m, 2 F), −75.0 (m, 4 F), −74.2 (m, 2 F); FAB-MS m/z 1334 (M$^+$), 1279 (M$^+$ − Bu); $\lambda_{\max}$ (CH$_2$Cl$_2$) 300 nm. Anal. Calcd for $C_{76}H_{62}F_{16}Si_2$: C, 68.35; H, 4.68. Found: C, 68.40; H, 4.60.

Dibromoquaterphenyl 7. Into a 500-mL Schlenk flask was loaded 1,4-dibromo-2,5-diisopropylbenzene (10.0 g, 31.2 mmol), toluene (200 mL), and diethyl ether (50 mL), and the resulting solution was cooled to −78 °C in a dry ice/acetone bath. *tert*-Butyllithium (18.4 mL, 31.2 mmol) was then added dropwise via syringe. The reaction solution first turned pale yellow and then colorless. This solution was stirred at −78 °C for 10 min. Decafluorobiphenyl (4.97 g, 14.9 mmol) in toluene (50 mL) was then added dropwise by cannula at −78 °C. On completion of the addition, the reaction flask was sealed, and the reaction was allowed to warm slowly to room temperature over 6 h as the dry ice evaporated. The reaction mixture developed a brown color, while remaining free of precipitate over this time. The reaction mixture was stripped of solvents under dynamic vacuum. Hexanes (500 mL) were added, and the resulting tan suspension was filtered through a plug of silica (20 mL). The solvents were removed under dynamic vacuum. The slightly yellow product was then suspended in methanol (250 mL), stirred vigorously for 12 h, and isolated on a fine frit. The yield of white microcrystalline product was 10.7 g, 93%: ^{1}H NMR (500 MHz, benzene-d_6) δ 0.87 (d, $J = 7$ Hz, 6 H, CH(CH_3)$_2$), 1.05 (d, $J = 7$ Hz, 6 H, CH(CH_3)$_2$), 2.57 (m, $J = 7$ Hz, 1 H, CH(CH$_3$)$_2$), 3.34 (m, $J = 7$ Hz, 1 H, CH(CH$_3$)$_2$), 7.03 (s, 1 H, phenyl), 7.67 (s, 1 H, phenyl); ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6, not all resonances observed) δ 23.0 (^{i}Pr), 23.9 (^{i}Pr), 31.6 (^{i}Pr), 33.3 (^{i}Pr),123.2 (phenylene), 123.4 (phenylene), 125.1 (phenylene), 127.7 (phenylene), 129.1 (phenylene), 131.5 (phenylene), 144.1 (fluorophenylene), 146.0 (fluorophenylene), 146.3 (phenylene), 148.1 (phenylene); ^{19}F NMR (470.6 MHz, benzene-d_6) δ −75.3 (m, 4 F), −74.3 (m, 2 F), −74.1 (m, 2 F); FAB-MS m/z 776 (M$^+$), 761 (M$^+$ − Me). Anal. Calcd for $C_{57}H_{32}Br_2F_8$: C, 55.69; H, 4.15. Found: C, 55.50; H, 4.16.

Dodecaphenylene Diyne 8. Into a 500-mL Schlenk flask was loaded **7** (1.00 g, 1.29 mmol), and the flask was fitted with a 125-mL pressure-equalizing addition funnel. The flask and funnel were then purged with nitrogen for 30 min, and dry toluene (200 mL) was added, giving a clear, colorless solution. Dry diethyl ether (50 mL) was added, and the solution was cooled to −78 °C in a dry ice/acetone bath. *tert*-Butyllithium (1.59 mL, 2.71 mmol) was added dropwise via syringe, causing a pale yellow color to develop. This solution was stirred at −78 °C for 10 min. Alkyne **5** (1.56 g, 2.58 mmol) in toluene (100 mL) was then transferred by cannula into the addition funnel. Addition was carried out rapidly (∼3 drops/s) at −78 °C. A white precipitate developed in the reaction flask as the addition progressed, which became very thick within 15 min. On completion of addition, the reaction flask was sealed, and the reaction was allowed to warm slowly to room temperature over 6 h as the dry ice evaporated. The precipitate redissolved during this time, with only a slight haze remaining at room temperature. The reaction mixture was then filtered through a plug of silica (30 mL). Solvents were removed under dynamic vacuum. The slightly yellow product was suspended in methanol (250 mL), stirred vigorously for 12 h, and isolated on a fine frit. The yield of white microcrystalline product was 2.19 g, 95%: ^{1}H NMR (500 MHz, dichloromethane-d_2) δ 0.24 (s, 6 H, SiMe_2Bu), 0.73 (t, $J = 7.5$ Hz, 2 H, SiMe$_2$CH_2CH$_2$CH$_2$CH$_3$), 0.94 (t, $J = 7.5$ Hz, 3 H, SiMe$_2$CH$_2$CH$_2$CH$_2$CH_3), 1.26 (br d, 12 H, CH(CH_3)$_2$), 1.44 (m, 4 H, SiMe$_2$CH$_2$CH_2CH_2CH$_3$), 2.86 (m, 2 H, CH(CH$_3$)$_2$), 7.40 (br s, 2 H, diisopropylphenylene) 7.58 (d, $J = 8.5$ Hz, 2 H, phenylene), 7.66 (m, 4 H, phenylene), 7.81 (d, $J = 8.5$ Hz, 2 H, phenylene); ^{13}C{^{1}H} NMR (125 MHz, dichloromethane-d_2, not all resonances observed) δ −1.7 (SiMe_2Bu), 14.0 (SiMe$_2$$Bu$), 16.2 (SiMe$_2$$Bu$), 24.12 (CH($CH_3$)$_2$), 26.4 (SiMe$_2$$Bu$), 26.7 (SiMe$_2$$Bu$), 31.2 ($C$H(CH$_3$)$_2$), 95.2 (alkynyl), 105.3 (alkynyl), 107.0 (phenylene-F), 122.6 (phenylene-F), 123.2 (phenylene), 126.6 (phenylene), 127.4 (phenylene), 127.7 (phenylene), 128.6 (phenylene), 131.0 (phenylene), 132.8 (phenylene), 140.4 (phenylene), 141.8 (phenylene), 143.6 (phenylene-F), 145.6 (phenylene-F), 146.4 (phenylene); ^{19}F NMR (470.6 MHz, dichloromethane-d_2) δ −80.5 (m, 2 F), −77.1 (m, 4 F), −76.4 (m, 1 F), −76.3 (m, 1 F), −76.1 (m, 3 F), −76.0 (m, 1 F); FAB-MS m/z 1791 (M$^+$), 1736 (M$^+$ − Bu); $\lambda_{\max}$ (CH$_2$Cl$_2$) 298 nm. Anal. Calcd for $C_{100}H_{78}F_{24}Si_2$: C, 67.03; H, 4.39. Found: C, 66.93; H, 4.41.

Dimeric Macrocycles 9−11. These macrocycles were synthesized through very similar procedures; differences are noted below. Diyne **3** (0.100 g, 0.126 mmol), **4** (0.100 g, 0.114 mmol), or **6** (0.100 g, 0.0749 mmol) was loaded into a Teflon-stoppered 100-mL Schlenk flask and suspended in dry benzene (50 mL, used with **3** and **6**) or dry mesitylene (50 mL, used with **4**) in a glovebox. A solution of Cp$_2$Zr(py)(Me$_3$SiC≡CSiMe$_3$) (0.0593 g, 0.126 mmol (for **3**); 0.0536 g, 0.114 mmol (for **4**); 0.0353 g, 0.0749 mmol (for **6**)) in the same solvent was then added with a pipet, and the flask was sealed and brought out of the glovebox. The reaction mixture was sonicated to render it a homogeneous light brown solution (5−20 min) and placed in a 40 °C water bath for 48 h. During this time, the product deposited as yellow microcrystals (**10** and **11**) or macroscopic crystals (**9**) on the walls of the flask. The solvent was removed by cannula filtration, and the product was dried under dynamic vacuum. Yields were as follows: **9**, 0.110 g, 86%; **10**, 0.114 g, 91%; **11**, 0.099 g, 85%. Macrocycle **9** (from diyne **3**): ^{1}H NMR (500 MHz, benzene-d_6) δ 0.03 (s, 9 H, Si(CH_3)$_3$), 6.22 (s, 5 H, Cp) 6.68 (d, $J = 8$ Hz, 2 H, phenylene), 7.04 (d, $J = 8$ Hz, 2 H, phenylene), 7.23 (d, $J = 8$ Hz, 2 H, phenylene), 7.32 (d, obscured by ^{13}C satellite of solvent, 2 H, phenylene); ^{19}F NMR (470.6 MHz, benzene-d_6) δ −78.9 (m, 4 F), −75.2 (m, 4 F). Anal. Calcd for $C_{112}H_{88}F_{16}Si_4Zr_2 \cdot C_6H_6$: C, 67.14; H, 4.49. Found: C, 67.40; H, 4.66. Macrocycle **10** (from diyne **4**): ^{1}H NMR (500 MHz, benzene-d_6) δ 0.08 (s, 6 H, Si(CH_3)$_2$Bu), 0.34 (t, $J = 8.5$ Hz, 2 H, Si(CH$_3$)$_2$CH_2CH$_2$CH$_2$CH$_3$), 0.96 (t, $J = 7$ Hz, 3 H, Si(CH$_3$)$_2$CH$_2$CH$_2$CH$_2$CH_3), 1.37 (m, 4 H, $Si(CH_3)_2CH_2CH_2CH_2CH_3$), 6.25 (s, 5 H, cyclopentadienyl) 6.70 (d, $J = 8$ Hz, 2 H, phenylene), 7.04 (d, $J = 8$ Hz, 2 H, phenylene), 7.23 (d, $J = 8$ Hz, 2 H, phenylene), 7.32 (d, $J = 8$ Hz, 2 H, phenylene); $^{13}C\{^1H\}$ NMR (125 MHz, benzene-d_6) δ 1.8 ($SiMe_2Bu$), 14.5 ($SiMe_2Bu$), 18.6 ($SiMe_2Bu$), 21.7 ($SiMe_2Bu$), 27.4 ($SiMe_2Bu$), 112.0 (cyclopentadienyl), 123.6 (phenylene), 125.85 (phenylene), 126.1 (phenylene), 127.7 (phenylene), 131.1 (phenylene), 131.4 (phenylene), 137.5 (phenylene), 138.0 (phenylene), 143.2 (phenylene), 146.0 (phenylene), 149.9 (phenylene), 203.1 (Zr-*C*); ^{19}F NMR (470.6 MHz, benzene-d_6) δ −79.6 (m, 4 F), −75.3 (m, 4 F). Anal. Calcd for $C_{124}H_{112}F_{16}Si_4Zr_2\cdot 2\ C_9H_{12}$: C, 69.86; H, 5.61. Found: C, 69.6; H, 5.34. Macrocycle **11** (from diyne **6**): Attempts at characterization by NMR spectroscopy were unsuccessful due to low solubility. Anal. Calcd for $C_{124}H_{112}F_{16}Si_4Zr_2\cdot 5\ C_6H_6$: C, 69.23; H, 5.00. Found: C, 69.16; H, 5.00.

X-ray Crystal Structure of 9. From the crystals formed during the course of reaction, a yellow blocky crystal of dimensions 0.18 × 0.32 × 0.15 mm was selected. Data from this crystal were collected on a Siemens SMART diffractometer with a CCD detector at 161 K using Mo Kα radiation. Frames corresponding to an arbitrary hemisphere of data were taken using ω scans of 0.3° counted for 30 s. Of the 13 710 reflections collected, 9672 were unique, and of these, 6418 were observed with $I > 3\sigma(I)$. All non-hydrogen atoms were refined anisotropically (739 parameters total); hydrogen atoms were included at calculated positions but not refined. Details are included in the Supporting Information.

Demetalated Macrocycles 12−14. Identical procedures were followed, except where noted. Zirconacycle **9** (0.0500 g, 0.0246 mmol), **10** (0.0500 g, 0.0227 mmol), or **11** (0.0500 g, 0.0161 mmol) was loaded into a Teflon-stoppered 100-mL Schlenk flask in a glovebox. On the Schlenk line, dry benzene (50 mL) was added, and the mixture was sonicated for 20 min to give a homogeneous, finely divided suspension. Trifluoroacetic acid (19 μL, 0.25 mmol (for **9**); 17 μL, 0.23 mmol (for **10**); 12 μL, 0.16 mmol (for **11**)) was then added via syringe with rapid stirring, which caused the suspensions to bleach colorless within minutes. After stirring for 1 h, the solvent and excess trifluoroacetic acid were removed under dynamic vacuum. Highly insoluble macrocycle **12** (from zirconacycle **9**) was suspended in dry benzene (50 mL), sonicated for 30 min, and then isolated by filtration on a fine frit. Macrocycles **13** and **14** were dissolved in dry dichloromethane (100 mL) and passed through a plug of silica (3 mL) in a glovebox. The dichloromethane was then removed under dynamic vacuum, and the product was washed with dry diethyl ether (2 × 10 mL) and isolated on a fine frit. Yields were as follows: **12**, 0.037 g, 95%; **13**, 0.040 g, 92%; **14**, 0.040 g, 92%. Macrocycle **12** (from zirconacycle **9**): Attempts at characterization by NMR spectroscopy and mass spectrometry were unsuccessful due to low solubility**.** Anal. Calcd for $C_{92}H_{72}F_{16}Si_4$: C, 69.33; H, 4.55. Found: C, 69.10; H, 4.44. Macrocycle **13** (from zirconacycle **10**): ^1H NMR (500 MHz, benzene-d_6) δ 0.18 (s, 6 H, $Si(CH_3)_2Bu$), 0.67 (t, $J = 8.5$ Hz, 2 H, $Si(CH_3)_2CH_2CH_2CH_2CH_3$), 0.94 (t, $J = 7$ Hz, 3 H, $Si(CH_3)_2CH_2CH_2CH_2CH_3$), 1.38 (m, 4 H, $Si(CH_3)_2CH_2CH_2CH_2CH_3$), 6.90 (s, 1 H, vinyl) 6.98 (d, $J = 8$ Hz, 2 H, phenylene), 7.06 (d, $J = 8$ Hz, 2 H, phenylene), 7.19 (d, $J = 8$ Hz, 2 H, phenylene), 7.28 (d, $J = 8$ Hz, 2 H, phenylene); $^{13}C\{^1H\}$ NMR (125 MHz, benzene-d_6, not all resonances observed) δ −0.7 ($SiMe_2Bu$), 14.4 ($SiMe_2Bu$), 17.2 ($SiMe_2Bu$), 27.1 ($SiMe_2Bu$), 27.4 ($SiMe_2Bu$), 126.7 (phenylene), 128.0 (phenylene), 128.9 (phenylene), 131.1 (phenylene), 131.5 (phenylene), 139.0 (phenylene), 142.4 (phenylene), 142.8 (phenylene), 160.7 (phenylene); ^{19}F NMR (470.6 MHz, benzene-d_6) δ −79.4 (m, 4 F), −75.2 (m, 4 F); FAB-MS *m*/*z* 1761.8 (M^+), 1705.7 ($M^+ - Bu$). Anal. Calcd for $C_{104}H_{96}F_{16}Si_4$: C, 70.88; H, 5.49. Found: C, 70.59; H, 5.35. Macrocycle **14** (from zirconacycle **11**): ^1H NMR (500 MHz, dichloromethane-d_2) δ −0.02 (s, 6 H, $SiMe_2Bu$), 0.54 (t, $J = 8.5$ Hz, 2 H, $SiMe_2CH_2CH_2CH_2CH_3$), 0.85 (t, $J = 7$ Hz, 3 H, $SiMe_2CH_2CH_2CH_2CH_3$), 1.15 (d, $J = 6.5$ Hz, 6 H, isopropyl), 1.31 (m, 4 H, $SiMe_2CH_2CH_2CH_2CH_3$), 2.77 (m, $J = 6.5$ Hz, 1 H, isopropyl), 6.47 (s, 1 H, vinyl), 6.99 (d,), 7.30 (m, 3 H, phenylene), 7.52 (d, $J = 8$ Hz, 2 H, phenylene), 7.56 (d, $J = 8$ Hz, 2 H, phenylene); ^{19}F NMR (470.6 MHz, benzene-d_6) δ −80.0 (m, 2 F), −76.5 (m, 4 F), −75.6 (m, 2 F); FAB-MS *m*/*z* 2674 (M^+), 2618 ($M^+ - Bu$). Anal. Calcd for $C_{76}H_{62}F_{16}Si_2$: C, 68.25; H, 4.82. Found: C, 68.32; H, 4.92.

Reaction of 8 with $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$. Dodecaphenylene diyne **8** (0.100 g, 0.056 mmol) was loaded into a Teflon-stoppered 100-mL Schlenk flask and suspended in dry toluene (50 mL). A solution of $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$ (0.026 g, 0.056 mmol) in toluene (10 mL) was then added with a pipet, and the flask was sealed and brought out of the glovebox. The reaction mixture was sonicated to render it a homogeneous light brown solution (5 min) and placed in a 40 °C water bath for 48 h. During this time, yellow product precipitated from solution. The solvent was removed by cannula filtration and the product dried under dynamic vacuum. The yield of product was 0.101 g, 84%, if it is a zirconocene-coupled macrocycle with three molecules of toluene. Attempts at characterization by NMR spectroscopy were unsuccessful due to low solubility. Anal. Calcd for $C_{220}H_{176}F_{48}Si_4Zr_2\cdot 3\ C_7H_8$: C, 67.27; H, 4.68. Found: C, 67.39; H, 4.49. Dry benzene (50 mL) was added to the product of this reaction (0.050 g), and the mixture was sonicated for 20 min to obtain a homogeneous finely divided suspension. Trifluoroacetic acid (12 μL, 0.16 mmol) was then added via syringe with rapid stirring, which caused the suspension to bleach colorless within minutes. After stirring for 1 h, the solvent and excess trifluoroacetic acid were removed under dynamic vacuum. The product was washed with benzene (2 × 10 mL) and dichloromethane (2 × 10 mL) and dried under dynamic vacuum. Attempts at characterization by NMR spectroscopy and mass spectrometry were again unsuccessful due to low solubility.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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