Zirconocene-Mediated, High-Yielding Macrocyclizations of Silyl-Terminated Diynes

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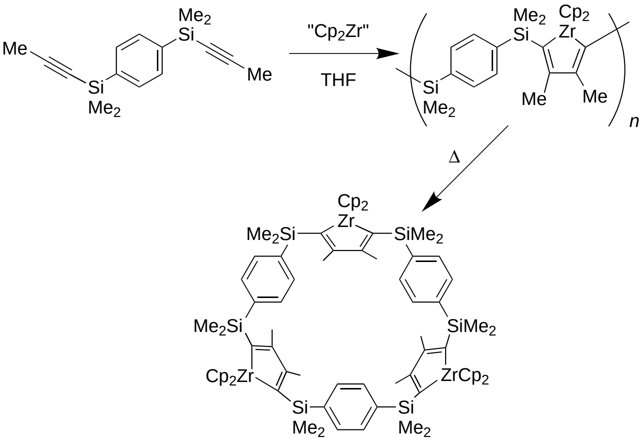
Abstract: A series of silyl-terminated diynes of varying lengths and substitution patterns have been prepared. These diynes undergo zirconocene coupling with selective formation of trimeric macrocycles from linear alkynes, while nonlinear diynes give cyclodimeric products. The length of the linear diynes can be increased for the preparation of macrocycles with large nanoscale cavities. Reaction of the zirconium-containing macrocycles with acid results in the synthesis of metal-free cyclophanes. All of these macrocycles were prepared in multigram quantities, in the absence of high-dilution conditions, to give products in >75% yield that are easily purified as crystalline solids.

Keywords: alkynes · cyclodimerization · cyclophanes · cyclotrimerization · macrocycles

Introduction

Macrocycles are important synthetic targets with applications in a wide range of fields including host–guest chemistry,[1] molecular sensors,[2] supramolecular chemistry,[3] and ion separation.[4] These cyclic molecules are typically prepared using high dilution and/or metal templates to promote macrocycle formation and reduce the amount of unwanted oligomeric by-products.[5] However, such strategies often result in low yields and are not amenable to large-scale preparations. Furthermore, isolation of the macrocyclic products often requires laborious separations of complex product mixtures. To address these challenges, previous reports from our laboratories have described zirconocene coupling as an efficient strategy in the assembly of C–C bonded macrocyclic compounds in high yields,[6] however the potential of this synthetic route remains to be fully exploited.

Negishi has described a simple procedure for the generation of zirconocene, stabilized as a 1-butene adduct, by addition of two equivalents of *n*-butyllithium to a solution of $[Zr(Cp)_2Cl_2]$ in THF at −78 °C.[7] The coupling of alkynes with zirconocene generated by this method produces zirconacyclopentadienes in high yields. We have utilized this powerful carbon–carbon bond-forming reaction in the construction of macromolecules with novel structures.[8] The coupling of diynes bearing silyl substituents allows for controlled regiochemistry, as it is known that alkynyl silanes are coupled exclusively to α-silyl-substituted zirconacyclopentadienes.[9] It is also known that the zirconocene coupling of silyl-substituted alkynes is readily reversible.[9] Thus, use of silyl-substituted bis-alkynes allows the preparation of oligomeric and macrocyclic products upon zirconocene coupling [Eq. (1)].[6a] Furthermore, the reversibility of alkyne coupling provides a low-energy pathway for the conversion of oligomeric products to the thermodynamic product, which is the smallest strain-free ring that can form.



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For the efficient preparation of macrocycles we have shown that both internally[6a, c] and terminally[6b] substituted silyl

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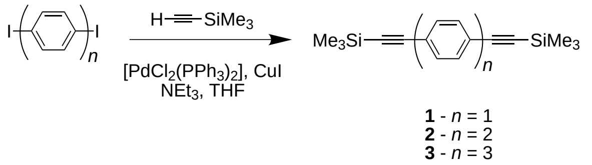
diynes can be used. In the case of internally substituted silyl bis-alkynes, cyclophanes were isolated in excellent yields, in cases where small diynes were employed. However, this synthetic strategy was not useful for the preparation of macrocycles with large cavities.[6c] In contrast, preliminary investigations revealed that terminally substituted silyl diynes have a greater tendency to form macrocyclic (vs. polymeric) structures.[6b] Given the demonstrated potential of the zirconocene coupling of silyl-terminated bis-alkynes to produce new macrocycles in a highly efficient manner, we have embarked upon a systematic study to explore the synthetic possibilities and limitations of this method. This study has involved the preparation of a series of silyl-terminated bis-alkynes of varying lengths and alkyne substitution geometries. Upon zirconocene coupling, the various diyne spacers allowed the selective preparation of trimeric and dimeric macrocyclic products in high yields. Here we discuss a variety of cyclophane targets easily accessed with this efficient synthetic strategy.

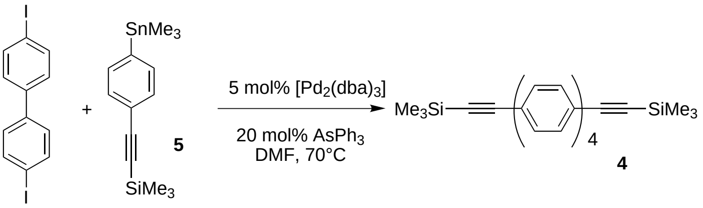
Results

Syntheses of linear diynes: Linear diynes of various lengths were desirable starting materials to probe the size of macrocycles that could be prepared. These diynes (**1**–**3**) were synthesized using the general Pd-catalyzed coupling route outlined in Scheme 1. The monophenylene diyne, 1,4-bis(trimethylsilylethynyl)benzene (**1**)[10] and the biphenylene diyne, 4,4′-bis(trimethylsilylethynyl)biphenyl (**2**),[10] have been previously reported. In a similar fashion, 4,4″-bis(trimethylsilylethynyl)terphenyl (**3**, $n = 3$) was prepared using a modified Sonogashira–Hagahara route to couple sparingly soluble 4,4″-diiodoterphenyl[11] with trimethylsilylacetylene. The final product was more soluble than the iodinated starting material and could be purified and isolated by recrystallization from hot toluene in 86% yield.



Scheme 1. Synthesis of diynes **1**–**3** by the general Pd-catalyzed coupling route.

As the length of the phenylene spacer was increased, the decreased solubility of the halogenated phenylene starting material in the general approach outlined in Scheme 1 became problematic. Therefore, for preparation of the tetraphenylene diyne (**4**), the modified synthetic route given in Scheme 2 was employed. Here, 4,4′-diiodobiphenyl was coupled using a modified Stille protocol[12] with 1-(trimethylstannyl)-4-(trimethylsilylethynyl)benzene (**5**)[13] in dry DMF at 70 °C for 4 days to give the desired tetraphenylene diyne **4**. The crude material could be purified by recrystallization from hot toluene to give a white solid in 50% yield.

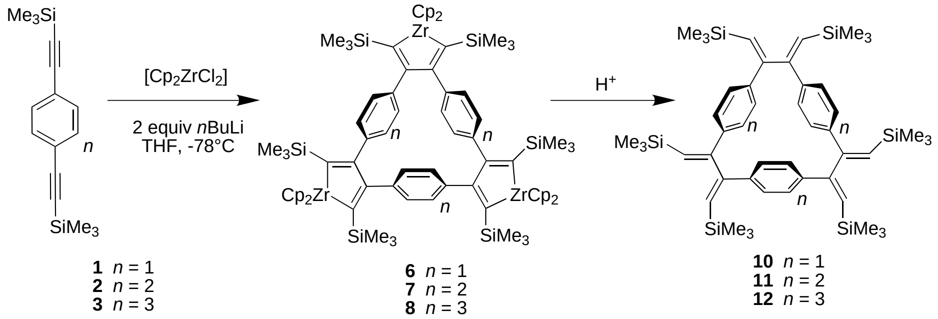


Scheme 2. The preparation of tetraphenylene diyne **4**.

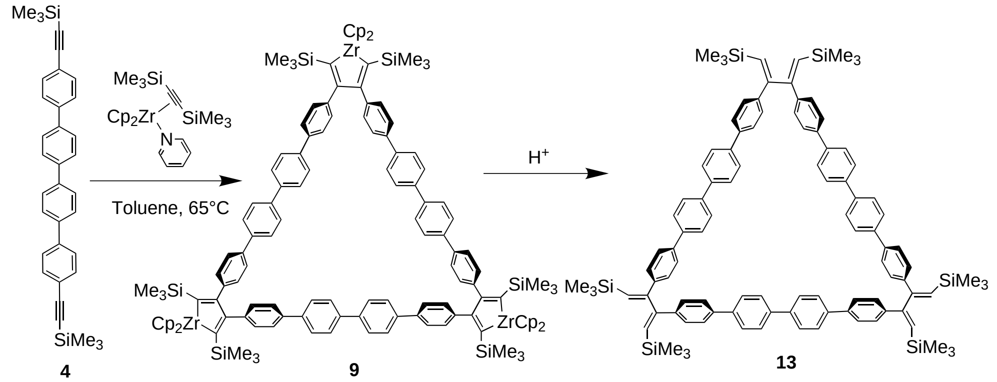
Zirconocene coupling of linear diynes: Diynes **1**–**3** were used in a general zirconocene coupling protocol for the high-yield preparations of zirconocene-containing macrocycles (Scheme 3).[6] The zirconocene reagent was generated in situ using the Negishi protocol.[7a] This procedure employs a 1:1 stoichiometry of the requisite diyne and Negishi zirconocene in THF at −78 °C, with subsequent warming to room temperature and further heating at 65 °C to generate the corresponding metal-containing macrocycles. Diyne **4** was coupled successfully using an alternative $[Zr^{II}(Cp)_2]$ reagent[14] (Scheme 4). In all cases, the resultant macrocycles could be effectively demetallated by reaction with a mild acid (such as acetic acid or benzoic acid) to give the metal-free macrocycles (e.g., Scheme 3).

In the case of the linear, rigid diynes **1**–**4**, the macrocyclic products **6**–**9** are due to cyclotrimerization. With ^{1}H NMR spectroscopy, the formation of macrocyclic products is displayed as a characteristic upfield shift of the trimethylsilyl peak due to a shielding effect of the nearby phenyl rings. For example, in $[D_6]$benzene the SiMe$_3$ peak of diyne **2** at $\delta = 0.27$ shifts to $\delta = -0.26$ in macrocycle **7**. Also, the new Cp peak at approximately $\delta = 6$ integrates to 10H, while the trimethylsilyl peak integrates to 18H, and the peaks confirm the incorporation of zirconocene in a 1:1 ratio with the spacer unit. The fact that we obtained macrocyclic products due to trimerization was established using a combination of mass spectrometry analyses and X-ray crystallography (vide infra).[6]

Isolated macrocycle **6** was treated with acetic acid in THF at room temperature over 12 h to give the metal-free macro-



Scheme 3. Use of diynes **1**–**3** for the preparation of **10**–**12**.



Scheme 4. Coupling of diyne **4** by an alternative $[Zr^{II}(Cp)_2]$ reagent and preparation of **13**.

cycle **10** in 92% yield as a colorless crystalline solid. X-ray quality crystals of **10** were grown from toluene, and the resulting molecular structure confirmed the trimeric nature of the macrocycle (Figure 1). Upon demetallation the bulk material no longer has a Cp peak in the ^{1}H NMR spectrum, but a new signal appears, which is indicative of a vinylic proton at $\delta = 6.42$ (2H). The trimeric nature of the bulk material was further confirmed by electron-impact mass spectrometry, in which case the molecular ion at 816 $[M]^+$ was clearly identified. Thus, by inference the trimeric nature of macrocycle **10** indicates the formation of the trimeric zirconocene-containing macrocycle **6**.

Macrocycle **10** is prepared in 78% overall yield as a crystalline material from the commercially available 1,4-bis(trimethylsilylethynyl)-benzene. This product strongly resembles the interesting and commercially available [2,2,2]-paracyclophane that has been shown to be of interest for cation complexation, both in the interior cavity and on the external faces of the arene rings.[15] Note that [2,2,2]-paracyclophane is prepared in one step from commercially available 1,4-α,α'-dibromobenzene to give a mixture of cyclic products in <20% yield.[16]

Macrocycles **7** and **11** have been fully characterized and discussed in a preliminary communication.[6b] Macrocycles **8** and **9** were characterized by ^{1}H NMR spectroscopy and elemental analysis. The data were consistent with the formation of macrocycles, and further characterization of **12** (demetallated **8**) by mass spectrometry confirmed its cyclotrimeric structure (1274, $[MH]^+$). Treatment of **9** with benzoic acid resulted in poorly soluble material that is consistent with the formation of **13** (by ^{1}H NMR spectroscopy and mass spectrometry), however we did not further pursue its isolation and purification.

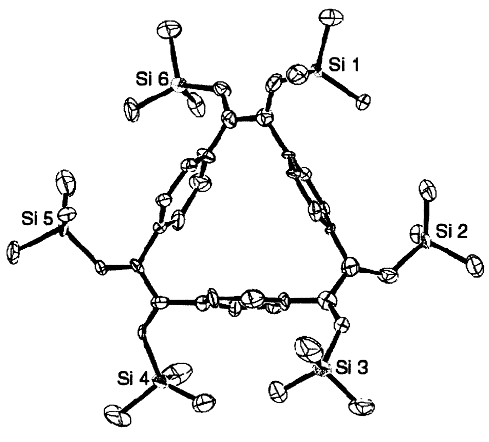
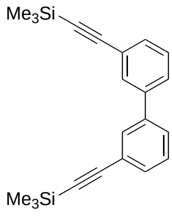


Figure 1. ORTEP depiction of the solid-state molecular structure of **10**.

Synthesis of nonlinear diynes: In addition to varying the length of the phenylene spacer, we were interested in probing the effect of the geometry of the diyne unit to give macrocycles of different shapes. Thus, an alternative biphenyl diyne **14** was prepared from 3,3′-dibromobiphenyl[17] and trimethylsilylacetylene using a Pd^0 catalyst in toluene at 80°C for 14 h. The crude product was purified by silica gel column chromatography using hexanes as an eluent to give the desired compound **14** in good yield as a white crystalline solid. This investigation was extended to include the preparation of an alternative terphenyl diyne **15** using the same Stille coupling protocol outlined in the preparation of compound **4**. Pale yellow crystalline **15** was isolated in 74% yield by removing solvent under reduced pressure and washing the resultant material with minimal pentane.



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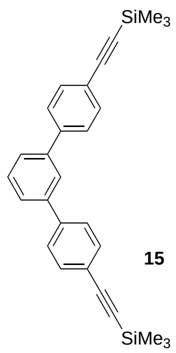

15

Another strategy for varying the geometry of the diyne included the incorporation of an sp^3 hybridized center as shown in Equation (2). Diyne **16** was prepared using a lithium/halogen exchange reaction of 1-bromo-4-trimethylsilylethynylbenzene[18] in a 1:1 mixture of THF/Et$_2$O with dropwise addition of 1.6 M *n*-butyllithium at −78°C. After

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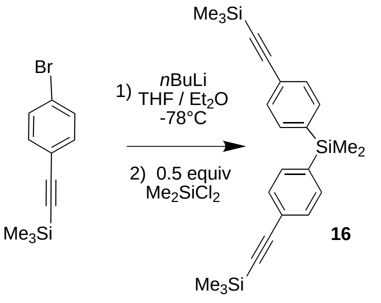
stirring this mixture for 30 minutes, the resulting anion was quenched with dichlorodimethylsilane, and the reaction solution was warmed to room temperature over 6 h. The crude material was isolated by removal of all volatile materials and extraction into a 1:1 mixture of dichloromethane/hexanes. This solution was reduced in volume, and the desired product was purified by silica gel column chromatography to give **16** in excellent yield as a white crystalline material.



(2)

Zirconocene coupling of nonlinear diynes: In the case of nonlinear diynes (**14**–**16**) the observed macrocyclic products (**17**–**19**) were dimeric. As in the previous cases, the dimeric nature of the resulting macrocyclic products was confirmed by both mass spectrometry and X-ray crystallography of either the Zr-containing cyclophanes or their demetallated analogues.

Once again, an upfield shift of the ^{1}H NMR resonance for the trimethylsilyl peak to $\delta = -0.05$ indicated formation of a macrocycle (**17**). This macrocycle displays solution-phase behavior consistent with molecular C_2 (rather than D_2) symmetry. In the ^{1}H NMR spectrum there are two inequivalent Cp peaks at $\delta = 6.19$ and 6.14, each integrating to 5H. These inequivalent signals are proposed to arise from a conformationally constrained, boatlike structure that has one Cp in a pseudoequatorial orientation and the other in a pseudoaxial position. Usually the zirconacyclopentadiene units are coplanar in the resultant macrocycles, however in this case, the 3,3′-alkyne substitution pattern of diyne **14** precludes this possibility. The dimeric nature of this macrocycle was suggested by FAB mass spectrometry with the observation of a peak corresponding to the molecular ion at 1136 *m*/*z*. The demetallated macrocycle **20** was isolated in 75% yield after treating **17** with benzoic acid in toluene at room temperature for 16 h. X-ray quality crystals were grown by slow evaporation from a solution in benzene, and the crystals thereby confirmed a dimeric structure (Figure 2).

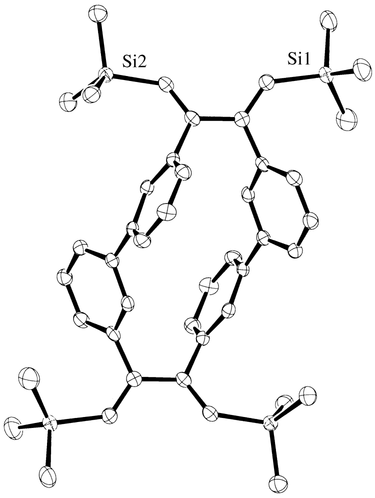
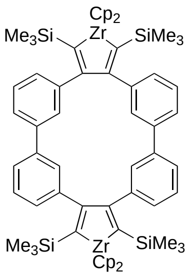


Figure 2. ORTEP depiction of the solid-state molecular structure of **20**.



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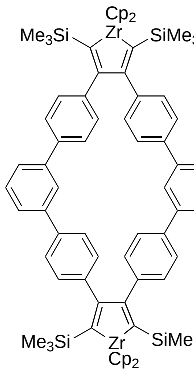

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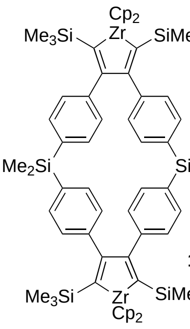

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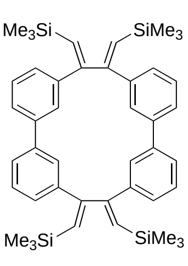

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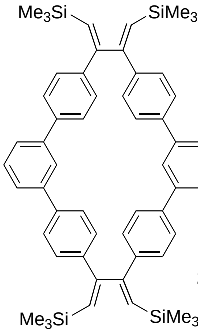

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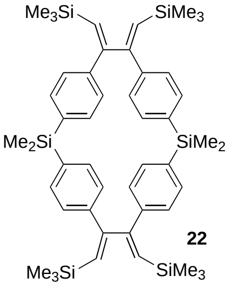


22

Macrocycle **18** was prepared using Negishi zirconocene coupling conditions to give the anticipated dimeric macrocycle in good yield as a pale yellow powder. The ^{1}H NMR spectrum displayed a Cp signal at $\delta = 6.21$, and the $SiMe_3$ signal was observed at $\delta = 0.01$. Yellow X-ray quality crystals of this compound were grown by slow evaporation from a solution in benzene (Figure 3). The demetallated macrocycle was prepared by reaction of **18** with benzoic acid in toluene to give macrocycle **21** in excellent yield. The preparation of a dimeric metal-free macrocycle was confirmed by NMR spectroscopy (loss of the Cp peak and appearance of a singlet in the vinylic region) and electron-impact mass spectrometry,

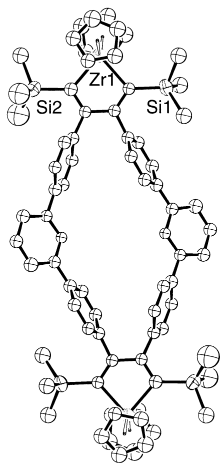


Figure 3. ORTEP depiction of the solid-state molecular structure of **18**.

in which case the major peak was that corresponding to the molecular ion at 848 *m*/*z*.

Finally, macrocycle **19**, which was prepared from the diyne with an sp^3 hybridized center, was shown to be the product of cyclodimerization. In this case, the zirconocene-containing macrocycle **19**, which was prepared in the standard fashion, was not isolated and characterized, but rather was treated in situ with HCl (6 M) to give macrocycle **22** as a white solid in 94 % yield. This macrocycle was shown to be dimeric by electron-impact mass spectrometry, which allowed observation of a molecular ion at 814 *m*/*z*.

Discussion

Previous results from these laboratories have demonstrated the usefulness of terminally substituted diynes as building blocks for the preparation of macrocyclic products in exceptionally high yields.[6b] Here, we discuss the utility of terminally substituted diynes for the preparation of macrocycles of various sizes. We have also investigated the effect of precursor diyne geometry on the shape of the resulting macrocyclic products.

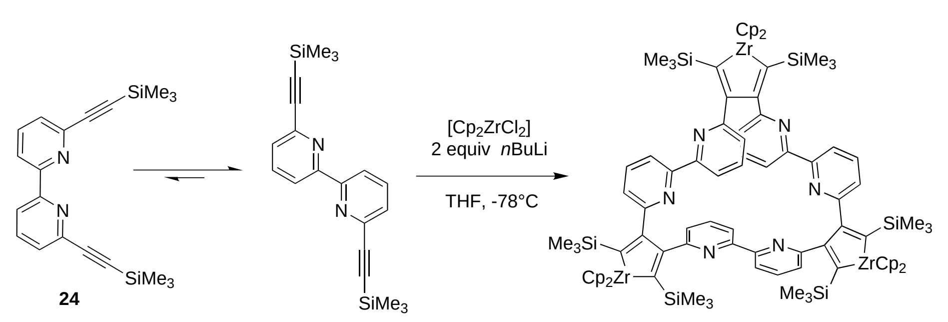
The use of linear, rigid-rod spacers allows the preparation of trimeric macrocycles of variable size. In contrast to previously published work on internally substituted silyl alkynes,[6c] the application of this strategy toward the synthesis of increasingly larger trimeric macrocycles by increasing the length of the precursor diyne works efficiently, and the synthetic protocol has proven to be very general. Consequently, zirconocene coupling of diynes **1**–**4** resulted only in cyclotrimerization products (**6**–**13**). We have investigated a range of spacer lengths from 6 to 19 Å,[19] and were able to consistently prepare the resulting macrocycles in excellent yield ($\geq 80\,\%$) with no modification of the experimental procedure. In contrast, for the internally substituted cases, as the spacer became larger, an equilibrium between oligomeric and macrocylic structures was observed, in which case dilute solutions favored the preparation of macrocycles.[6c]

Here, the range of spacer lengths has allowed the preparation of macrocycles with variable cavity sizes. For example, the tetraphenyl spacer permits the preparation of macrocycles with a cavity of nanoscale dimensions in which the distance from the center of the molecular cavity to the tetraphenylene spacer group is estimated to be approximately 7 Å.[20]

As the length of the rigid-rod spacer increases, the solubility of both the diyne precursor and resultant macrocycle decreases significantly. Thus, as in the case of diyne **4**, the Negishi zirconocene reagent[7] was not useful, since removal of the desirable organic products from the LiCl by-product became problematic. This difficulty was overcome by using an alternative zirconocene reagent (Scheme 4).[14] In this case, the inorganic salt by-products and the solubility problems associated with the requisite low temperatures (−78 °C) for Negishi zirconocene were avoided. Even with this alternative zirconocene coupling reagent, the larger macrocycle was isolated in a somewhat smaller yield, undoubtedly due to isolation and purification challenges associated with reduced solubility of the resultant macrocyclic product **9**. We are currently exploring the synthesis of very large macrocycles from even longer spacers.[21] In these cases, the synthetic challenge is the preparation of soluble oligophenylene diyne precursors for use in subsequent zirconocene-mediated macrocyclizations.

The ORTEP diagram presented in Figure 1 shows the key features associated with these cyclotrimerized products. The phenyl substituents are not conjugated with the diene units of the demetallated macrocycles, as they are perpendicular to the diene moiety as a result of steric factors. The diene units of the demetallated species are not coplanar; instead they display a torsion angle about the C–C single bond that averages 25°. This torsion is necessary to accommodate both the vinyl protons and bulky trimethylsilyl groups. These features are observed for all trimeric macrocycles of this type.[6]

In contrast to the use of precursor diynes with linear alkynyl substituents, it was observed that nonlinear diynes (**14**–**16**) enabled the isolation of products due to cyclodimerization (**17**–**22**). The macrocycles that formed from diynes **14** and **15**, were isolated in somewhat reduced yields (75–80 %) with the other by-products being due to complex mixtures of oligomers. However, because of the crystalline nature of macrocycles **17** and **18**, we were able to easily obtain the purified products of cyclodimerization. In the solid-state molecular structure of **20**, the macrocycle adopts a twisted conformation, with the biphenyl units having a dihedral angle of approximately 47°, while the C–C single bond of the diene unit displays a torsion angle of approximately 25°. The distance across the cavity of this small macrocycle is approximately 4.3 Å (as measured from the C–C single bond connecting the phenyl units of one spacer to the C–C single bond connecting the phenyl units of the opposite side). In the solid state, **20** possesses crystallographically imposed C_2 molecular symmetry, like that observed in the solution phase of its zirconium-containing precursor (**17**). However, the ^{1}H NMR data for **20** are consistent with solution-phase C_{2v} symmetry (as seen in the vinyl region of the spectrum, in which only one signal at $\delta = 6.55$ is observed), which suggests enhanced conformational mobility in this compound relative to its progenitor, **17**. The zirconium-containing dimeric macrocycle **17** also displayed increased air and moisture sensitivity in comparison with the cyclotrimeric macrocycles. These observations and the somewhat reduced synthetic yield for **17** suggest the presence of more ring strain compared with the cyclotrimeric macrocycles previously discussed.

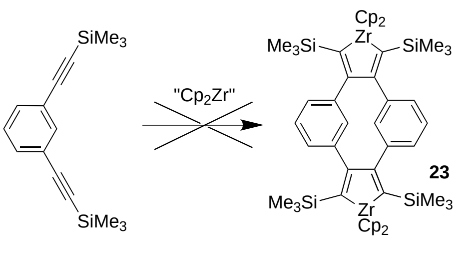


Scheme 5. Cyclotrimerization with diyne **24**.

The effect of nonlinear diynes on the shape of the resultant macrocycle was also noted in the coupling of bis-alkyne **15**; as predicted, crystalline dimeric macrocycles were obtained upon zirconocene coupling (Figure 3). The distance across the cavity of this macrocycle is 5.6 Å with the two protons that are pointing toward the center of the cavity being slightly out of the plane of the zirconacyclopentadiene groups.

In the case of diyne **8**, in which an sp^3 hybridized Si center was incorporated into the spacer to give a modified angle between the nonlinear alkynyl substituents, the yields were much improved (94%) for the isolation of macrocycle **22**. In this case demetallation was achieved with HCl (6 M). These reaction conditions are not general for demetallation, and in particular, dimeric macrocycles **20** and **21** are known to decompose under these harsh reaction conditions. Thus, the observed higher yields and chemical robustness of this system are believed to be due to the reduced ring strain of this cyclodimeric product.

The effect of ring strain on macrocycle formation was further noted in our attempt to prepare monophenylene *meta*-substituted macrocycle **23** [Eq. (3)]. Here, the ^1H NMR spectra obtained for isolated products from use of both zirconocene reagents were consistent with complex mixtures of oligomeric materials. In the case of the *ortho*-substituted substrate it has been reported that an alkyne π-complex of zirconocene is the isolable product.[22] However, with a methylene spacer unit the cyclodimeric macrocycle was obtained in low yield.[23]



(3)

All the results presented are consistent with the fact that the shape and size of the resultant macrocycle can be predicted based on the geometry of the precursor diyne, given that these reaction conditions favor formation of the smallest strain-free ring that can form. However, it should be noted that functionality can be an important factor in determining the structure of the macrocyclic products.[24] In contrast to the cyclodimeric product formed upon zirconocene coupling of diyne **6**, its bipyridine analogue (**24**) yields the product of cyclotrimerization (Scheme 5).[24] This difference may be attributed to the preference of the bipyridyl diyne for adopting an *anti*-geometry, and the alkyne units are placed in the requisite linear arrangement for cyclotrimerization to take place. This example represents a case, in which the energy gained from the entropically favored formation of the smallest macrocyclic ring is not sufficient to overcome the preferred *anti*-conformation of the diyne precursor.

These new zirconium-containing macrocycles are also attractive intermediates in the synthesis of a range of functionalized macrocycles through substitution chemistry at the zirconocene site of the zirconacyclopentadiene units.[25] However, such substitution chemistry has proven difficult in the presence of the α-silyl substituents of the zirconacyclopentadienes. Current investigations are focusing on development of general reagents to effect these desirable transformations.

Conclusion

We have prepared a range of new cyclophanes from various terminally substituted silyl bis-alkynes. The geometry of the initial diyne has been shown to determine the shape of the resultant macrocyclic product in a predictable fashion. Thus, it is possible to selectively prepare cyclotrimeric products from linear, rigid spacers, while cyclodimeric materials are accessed with nonlinear spacers. The size of the spacer can be increased to access large cyclophanes with nanoscale cavities. The application of this strategy in the preparation of very large macrocycles has been shown to proceed with no appreciable loss in yield for the larger substrates. The product yields for this synthetic methodology are remarkably high in all the cases presented, with a slight reduction in yield being observed when the resultant macrocyclic products are somewhat strained. The Negishi protocol for generating zirconocene[7] in situ is preferred for the preparation of these unfunctionalized macrocycles as a result of the ease of generation of the zirconocene. However, in cases, in which substrate and/or product solubility is low, the alternative zirconocene reagent (Rosenthal's complex) has proven to be the reagent of choice.[14]

All of these macrocycles can be prepared on a multigram scale, in the absence of high dilution conditions, and are isolated and purified as crystalline solids. Consequently, this synthetic method provides a simple and versatile method for the preparation of cyclophanes of different sizes and shapes by simple, strategic modifications of the diyne precursor.

Experimental Section

All manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or a Vacuum Atmospheres glove box. Dry, oxygen-free solvents were employed throughout. All solvents were distilled from sodium/benzophenone ketyl. [D$_6$]Benzene was purified by vacuum distillation from Na/K alloy. Elemental analyses were performed by the UCB Microanalytical Laboratory or Desert Analytics. NMR spectra were recorded on a Bruker AMX (300 MHz), a Varian Bruker-AMX (400 MHz), or a Bruker DRX (500 MHz) spectrometer at 25 °C and referenced to residual solvent resonances. ^{13}C spectra were proton decoupled. Mass spectrometry was carried out on a VG ProSpec or a VG ZAB using electron-impact or FAB sources. Zirconocene dichloride (Strem), *n*-butyllithium solution (Aldrich), 4,4′-dibromobiphenyl (Aldrich), 4,4′-diiodobiphenyl (Aldrich), and trimethylsilylacetylene (GFS) were used as received. The compounds 1,4-bis(trimethylsilylethynyl)benzene **1**,[10] 4,4′-bis(trimethylsilylethynyl)biphenyl **2**,[10] 1-bromo-4-(trimethylsilylethynyl)benzene,[13] 4,4″-diiodoterphenyl,[12] 4-(trimethylsilylethynyl)-1-(trimethylstannyl)benzene **5**,[13] and 3,3′-dibromobiphenyl[17] were prepared by literature procedures.

4,4″-Bis(trimethylsilylethynyl)terphenyl (3): A PTFE-stoppered Schlenk flask (1 L) was charged with 1,4″-diiodoterphenyl[12] (30.0 g, 62.2 mmol), [Pd(PPh$_3$)$_4$] (0.180 g, 0.156 mmol), and CuI (0.0593 g, 0.311 mmol). *i*Pr$_2$NH (100 mL) and dry THF (400 mL) were added to these reagents, followed by trimethylsilylacetylene (17.0 mL, 131 mmol). The reaction was stirred overnight at 50 °C, and the solvents were removed in vacuo. The product mixture was suspended in toluene (2 L), filtered on a Buchner funnel, and passed through a plug of silica (100 mL) that was washed with additional toluene (200 mL). The resulting light yellow solution was reduced in volume to 100 mL, and the cream-colored solid was collected by filtration. The crude product was recrystallized from hot toluene to give white crystals (22.5 g, 86 % yield).

^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 7.68$ (s, 2H; ArH), 7.59 (d, J(H,H) = 8.5 Hz, 2H; ArH), 7.56 (d, J(H,H) = 8.5 Hz, 2H; ArH), 0.29 (s, 9H; Si(CH$_3$)$_3$); ^{13}C NMR (125 MHz, CDCl$_3$): $\delta = 140.7$, 139.8, 132.7, 127.6, 126.9, 122.4 (ArC), 105.1, 95.3 (C≡C), 0.2 (SiCH$_3$); elemental analysis calcd (%) for $C_{28}H_{30}Si_2$ (422.2): C 79.56, H 7.15; found: C 79.76, H 7.06.

4,4‴-Bis(trimethylsilylethynyl)tetraphenyl (4): In a Schlenk flask (100 mL) equipped with a stir bar, [Pd$_2$(dba)$_3$] (0.340 g, 0.371 mmol) and AsPh$_2$ (0.454 g, 1.48 mmol) were loaded in the glove box. In a separate Schlenk flask (100 mL) Me$_3$SnC$_6$H$_4$C≡CSiMe$_3$ **5**[13] (2.50 g, 7.42 mmol) and 4,4′-diiodobiphenyl (1.00 g, 2.46 mmol) were loaded. This Schlenk flask was evacuated and backfilled before suspending the organics in dry DMF (30 mL). This mixture was transferred by cannula to the reaction flask containing the catalyst mixture. The flask with the organic reagents was washed with dry DMF (20 mL), and this solution was transferred to the reaction flask as well. This flask was then sealed and heated to 70 °C with stirring for 4 days, and a dark gray suspension of white precipitate resulted. The precipitate was collected by vacuum filtration on a Buchner funnel and redissolved into boiling toluene (600 mL). The solution was then filtered hot, and the collected precipitate was washed with hot toluene (2 × 100 mL). The resulting yellow solution was concentrated to 600 mL, at which point a hazy solution developed. The heating was stopped, and the product was permitted to crystallize overnight. The resulting white waxy, flaky material was collected by filtration (0.600 g, 50 % yield). This compound required no further purification.

^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.74-7.67$ (m, 8H; ArH), 7.62–7.54 (m, 8H; ArH), 2.72 (s, 18H; SiCH$_3$); No ^{13}C data could be collected because of poor solubility; MS (70 eV): *m/z* (%): 498 $[M]^+$, 483 $[M - CH_3]^+$; elemental analysis calcd (%) for $C_{34}H_{34}Si_2$ (498.2): C 81.87, H 6.87; found: C 81.74, H 6.74.

Trimeric macrocycle (6): A PTFE-stoppered Schlenk flask (100 mL) was charged with [Zr(Cp)$_2$Cl$_2$] (2.16 g, 7.39 mmol) and dissolved in dry THF (20 mL). A separate Schlenk flask (100 mL) was loaded with 1,4-bis(trimethylsilylethynyl)benzene (**1**) (2.00 g, 7.39 mmol), to which THF (20 mL) was added. The [Zr(Cp)$_2$Cl$_2$] flask was cooled to −78 °C, and a solution of *n*BuLi in hexane (2.46 M, 6.0 mL, 14.78 mmol) was added dropwise. The reaction was stirred at −78 °C for 20 min, and then the 1,4-bis(trimethylsilylethynyl)benzene solution was added dropwise. The reaction mixture was warmed to room temperature and heated to 60 °C for 12 h. The THF was then removed in vacuo, and distilled water (90 mL) was added to dissolve the by-product LiCl. The yellow suspension was stirred vigorously for 1 h. The solid product was collected using a Hirsch funnel. The water wash was repeated, and the (highly insoluble) product was then washed similarly with Et$_2$O (90 mL) and toluene (90 mL). Care was taken to ensure that the isolated product was finely divided, as chunks of material can occlude H$_2$O. The yellow microcrystalline product was dried under vacuum to give of the desired material (3.05 g, 85 % yield).

^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta = 6.54$ (s, 2H; C$_4$H$_4$), 6.19 (s, 5H; C$_5$H$_5$), −0.06 (s, 9H; Si(CH$_3$)$_3$); elemental analysis calcd (%) for $C_{78}H_{96}Si_6Zr_3$ (1474.2): C 63.48, H 6.56; found: C 63.42, H 6.18.

Trimeric macrocycle (7): A round-bottom flask (250 mL) was charged with [Zr(Cp)$_2$Cl$_2$] (2.3 g, 8.0 mmol), 4,4′-bis(trimethylsilylethynyl)biphenyl (**2**) (2.8 g, 8.0 mmol), and THF (150 mL). The flask was cooled to −78 °C, and a solution of *n*BuLi in hexanes (1.6 M, 10 mL, 16 mmol) was added dropwise. The reaction mixture was warmed to room temperature then stirred for 16 h, and then heated to reflux for a further 24 h. All volatile materials were removed in vacuo, and the residue was washed with hexanes (3 × 40 mL). The hexane-insoluble residue was then extracted with hot toluene (5 × 40 mL), and the toluene extracts were combined and cooled to −40 °C to afford **7** as yellow crystals (4.1 g, 90 %).

^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta = 7.16$ (d, J(H,H) = 8.1 Hz, 4H; ArH), 6.71 (d, J(H,H) = 8.1 Hz, 4H; ArH), 6.13 (s, 10H; C$_5$H$_5$), −0.26 (s, 18H; SiCH$_3$); ^{13}C NMR (100.6 MHz, C$_6$D$_6$): $\delta = 206.1$ (ZrC$_4$(Si(CH$_3$)$_3$)$_2$), 149.4 (ZrC$_4$(Si(CH$_3$)$_3$)$_2$), 142.7, 134.2, 128.6, 128.2 (ArC), 111.4 (C$_5$H$_5$), 3.00 (SiCH$_3$); elemental analysis calcd (%) for $C_{96}H_{108}Si_6Zr_3$ (1702.2): C 67.66, H 6.39; found: C 66.93, H 6.36.

Trimeric macrocycle (8): A PTFE-stoppered Schlenk flask (100 mL) was charged with [Zr(Cp)$_2$Cl$_2$] (0.692 g, 2.37 mmol) that was dissolved in dry THF (20 mL). A separate Schlenk flask (100 mL) was loaded with 4,4″-bis(trimethylsilylethynyl)terphenyl (**3**) (1.00 g, 2.37 mmol), to which was added THF (50 mL). The [Zr(Cp)$_2$Cl$_2$] flask was cooled to −78 °C, and a solution of *n*BuLi in hexane (1.6 M, 2.96 mL, 4.73 mmol) was added dropwise. The reaction was stirred at −78 °C for 20 min, and then the 4,4″-bis(trimethylsilylethynyl)terphenyl solution was added dropwise by cannula. The reaction mixture was warmed to room temperature, and heated to 60 °C for 12 h. The THF was then removed in vacuo, and distilled water (90 mL) was added to dissolve the by-product LiCl. The yellow suspension was stirred vigorously for 1 h. Then the solid product was collected using a Hirsch funnel. The water wash was then repeated, and the (highly insoluble) product was washed similarly with Et$_2$O (50 mL), and toluene (50 mL). Care was taken to ensure that the isolated product was finely divided, as chunks of material can occlude H$_2$O. The product was dried under vacuum to give yellow microcrystalline material (1.39 g, 91 %).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.55$ (s, 2H; ArH), 7.22 (d, J(H,H) = 8.5 Hz, 2H; ArH), 6.76 (d, J(H,H) = 8.5 Hz, 2H; ArH), 6.39 (s, 10H; C$_5$H$_5$), −0.29 (s, 9H; Si(CH$_3$)$_3$); No ^{13}C NMR data were obtained because of poor solubility; elemental analysis calcd (%) for $C_{114}H_{120}Si_6Zr_3$ (1930.2): C 70.86, H 6.26; found: C 70.72, H 6.04.

Trimeric macrocycle (9): A Schlenk flask (50 mL), equipped with stir bar, was charged with crystalline [Zr(Cp)$_2$(pyr)(Me$_3$SiC≡CSiMe$_3$)][14] (94 mg, 0.20 mmol) and diyne **4** (100 mg, 0.200 mmol). The mixture was suspended in toluene (15 mL). This solution was heated to 65 °C for 36 h to give a pale yellow solution. The solvent was removed under vacuum to give a dark yellow powder that was further purified by recrystallization from benzene, and this afforded pale yellow crystals (119 mg, 82 % yield).

^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta = 7.36$ (m, 12H; ArH), 6.93 (d, J(H,H) = 8 Hz, 4H; ArH), 6.23 (s, 10H; C$_5$H$_5$), −0.06 (s, 18H; SiCH$_3$); No ^{13}C NMR data were obtained because of poor solubility; elemental analysis calcd (%) for $C_{132}H_{132}Si_6Zr_3$ (2160.8): C 73.31, H 6.11; found: C 73.70, H 6.47.

Trimeric cyclophane (10): A Schlenk flask (100 mL) was charged with monophenylene trimer (**6**) (0.500 g, 1.02 mmol), and it was then suspended in dry THF (50 mL). Glacial acetic acid (1.16 mL, 20.3 mmol) was added to this yellow suspension, and the mixture was stirred for 12 h at room temperature. Over this time, the color gradually became white, and all solids dissolved. The THF and excess acetic acid were removed in vacuo, and the residue was dissolved in toluene (100 mL). The slightly hazy, colorless solution was passed through a plug of silica (20 mL) and washed through with toluene (40 mL). The toluene was removed in vacuo, and the product was washed with hexanes (20 mL). The yield of tiny colorless crystals was 0.255 g, 92 %.

^{1}H NMR (500 MHz, C_6D_6): $\delta = 6.81$ (s, 2H; ArH), 6.42 (s, 1H; HC=C), 0.09 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 164.4$, 140.7, 130.6, 129.4, (ArC and C=C), 1.1 ($Si(CH_3)_3$); MS (70 eV): m/z (%): 816 $[M]^+$, 801 $[M - CH_3]^+$, 743 $[M - Si(CH_3)_3]^+$; elemental analysis calcd (%) for $C_{48}H_{72}Si_6$ (816.5): C 70.51, H 8.88; found: C 70.47, H 9.00.

Trimeric cyclophane (11): A round-bottom flask (100 mL) was charged with macrocycle **7** (0.95 g, 1.9 mmol) and THF (20 mL). An aqueous HCl solution (6 M, 20 mL) was added to the flask, and the resulting mixture was stirred for 2 h at room temperature. The reaction mixture was poured into methanol (200 mL), and the white powder **11** was collected (0.52 g, 98 %). Crystals were obtained by cooling of a saturated solution (ca. 0.5 g/50 mL) in toluene/acetonitrile (ca. 3:1) to −10 °C.

^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.05$ (s, 8H; ArH), 6.54 (s, 2H; $C_4(SiMe_3)H_2$), 0.03 (s, 18H; $SiCH_3$); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 162.6$ ($C_4(SiMe_3)_2H_2$), 140.8 ($C_4(SiMe_3)_2H_2$), 138.0, 130.5, 130.0, 125.9 (ArC), 111.4 (C_5H_5), 0.43 ($SiCH_3$); MS (70 eV): m/z (%): 1045 $[M]^+$; elemental analysis calcd (%) for $C_{66}H_{84}Si_6$ (1044.5): C 74.79, H 8.10; found: C 73.52, H 8.43.

Trimeric cyclophane (12): A Schlenk flask (100 mL) was charged with trimeric macrocycle **8** (0.236 g, 0.366 mmol) and dry benzene (50 mL). Glacial acetic acid (0.2 mL, 3.6 mmol) was added to this yellow suspension, and the mixture was vigorously stirred for 24 h at room temperature. Over this time the yellow suspension gradually became white. The benzene and excess acetic acid were removed in vacuo, and the residue was dissolved in toluene (100 mL). The slightly hazy colorless solution was passed through a plug of silica (10 mL) and washed through with toluene (100 mL). The toluene was removed in vacuo, and the product was washed with methanol (20 mL) to give colorless microcrystals (0.14 g, 90 %).

^{1}H NMR (500 MHz, C_6D_6): $\delta = 7.29$ (d, J(H,H) = 8.5 Hz, 2H; ArH), 7.28 (s, 2H; ArH), 7.22 (d, J(H,H) = 8.5 Hz, 2H; ArH), 6.59 (s, 1H; HC=C), 0.09 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 163.5$, 141.3, 139.7, 130.6, 129.7, 128.9, 127.7, 126.4 (ArC and C=C), 0.8 ($Si(CH_3)_3$); MS (70 eV): m/z (%): 1274 $[MH]^+$, 1260 $[M - CH_3]^+$, 1202 $[M - Si(CH_3)_3]^+$; elemental analysis calcd (%) for $C_{84}H_{96}Si_6$ (1272.5): C 79.18, H 7.59; found: C 78.96, H 7.39.

3,3′-Bis(trimethylsilylethynyl)biphenyl (14): A PTFE-stoppered Schlenk flask (500 mL) was charged with copper(I) iodide (26.0 mg, 0.135 mmol) and $[Pd(PPh_3)_4]$ (104 mg, 0.0898 mmol) in the glove box. In a separate Schlenk flask 3,3′-dibromobiphenyl[17] (1.4 g, 4.49 mmol) was dissolved in toluene (20 mL) and transferred by cannula to the reaction flask containing the catalyst mixture. Degassed diisopropylamine (15 mL) was added by cannula to this suspension. The reaction mixture was stirred for 15 minutes, after which it was transparent. Finally, trimethylsilylacetylene (3.20 mL, 2.20 g, 22.4 mmol) was added by syringe. The reaction mixture was stirred for 14 h at 80 °C. The resulting mixture was cooled and filtered by gravity before removal of the volatile material under vacuum. The resulting solid was suspended in hexanes (60 mL) and filtered through a silica plug. The silica plug was washed with hexanes (3 × 30 mL), and the combined filtrates were dried under vacuum and purified by silica gel column chromatography using hexanes as a eluent. The resulting white crystalline material was isolated in 70 % yield (1.1 g).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.70$ (s, 2H; ArH), 7.54 (m, 2H; ArH), 7.41 (m, 2H; ArH), 7.30 (m, 2H; ArH), 0.28 (s, 18H; $Si(CH_3)_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 140.4$, 131.0, 130.7, 128.8, 127.3, 123.7 (ArC), 104.9, 94.5 (C≡C), −0.1 ($Si(CH_3)_3$); MS (70 eV) m/z (%): 346 $[M]^+$, 331 $[M - CH_3]^+$; elemental analysis calcd (%) for $C_{22}H_{26}Si_2$ (346.2): C 76.23, H 7.56; found: C 75.96, H 7.22.

Diyne (15): A Schlenk flask (100 mL), equipped with stir bar, was charged with $[Pd_2(dba)_3]$ (0.124 g, 0.135 mmol) and $AsPh_3$ (0.165 g, 0.540 mmol) in the glove box. In a separate Schlenk flask (100 mL), 4-(trimethylsilylethynyl)-1-(trimethylstannyl)benzene (1.00 g, 2.97 mmol) was loaded. The compound 1,3-dibromobenzene (0.163 mL, 0.318 g, 1.35 mmol) was added to this Schlenk flask by syringe. This mixture of organic compounds was evacuated and backfilled with N_2 three times before being dissolved in dry DMF (20 mL). This solution of organic reagents was added to the Schlenk flask containing the Pd catalyst by cannula. The Schlenk flask containing the organic reagents was rinsed with dry DMF (15 mL) and added to the catalyst suspension. The dark suspension was stirred at 65 °C for 3 days, and this resulted in a greenish/yellow suspension. The reaction mixture was cooled and diluted with toluene (50 mL). The organic fraction was washed with $NaCO_3$ (1 M, 50 mL), followed by water (3 × 50 mL), and finally brine (50 mL). The solvents were removed in vacuo, and the resultant light brown oil was redissolved in hexanes (100 mL) and filtered through a silica plug (30 mL). After the removal of hexanes under vacuum a pale yellow crystalline solid was isolated in 74 % yield (0.42 g). This material was then washed with minimal pentane to further purify.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.76$ (s, 1H; ArH), 7.60–7.52 (m, 11H; ArH), 0.26 (s, 18H, $SiCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 141.0$, 140.9, 132.4, 129.4, 126.9, 126.3, 125.8, 122.2 (ArC), 104.9, 95.0 (C≡C), 0.0 ($SiCH_3$); MS (70 eV): m/z (%): 422 $[M]^+$, 407 $[M - CH_3]^+$; elemental analysis calcd (%) for $C_{28}H_{30}Si_2$ (394.1): C 79.56, H 7.15; found: C 79.54, H 7.11.

Diyne (16): A round-bottom flask (250 mL) was charged with 1-bromo-4-(trimethylsilylethynyl)benzene (6.00 g, 23.7 mmol) and a mixture of THF/diethyl ether (1:1, 120 mL). The flask was cooled to −78 °C, and then nBuLi (1.6 M/hexane, 14.8 mL, 23.7 mmol) was added dropwise. The mixture was stirred for 30 min at −78 °C. Me_2SiCl_2 (1.10 mL, 12.0 mmol) was then added dropwise, and the temperature of the flask was raised to room temperature over 6 h. The volatile materials were removed in vacuo, and the residue was extracted with dichloromethane/hexanes (1:1, 120 mL). The solution was concentrated to 20 mL and then passed through a silica gel (15 × 4.2 cm) column using a mixture of dichloromethane/hexane (1:7) as an eluting solvent. The product was obtained as a crystalline solid in 89 % yield (4.30 g) after removal of solvents.

^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.47$ (d, J(H,H) = 8.4 Hz, 4H; ArH), 7.21 (d, J(H,H) = 8.4 Hz, 4H; ArH), 0.27 (s, 6H; $Si(CH_3)_2$), 0.19 (s, 18H; $C{\equiv}CSi(CH_3)_3$); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 136.0$, 135.4, 131.0 (ArC), 125.1, 105.1, 96.7 (C≡C), −0.1 ($C{\equiv}CSi(CH_3)_3$), −2.5 ($SiCH_3$); elemental analysis calcd (%) for $C_{24}H_{32}Si_3$ (404.3): C 71.22, H 7.97; found: C 71.08, H 7.74.

Dimeric macrocycle (17): A Schlenk flask (100 mL), equipped with stir bar, was charged with $[Zr(Cp)_2Cl_2]$ (0.845 g, 2.89 mmol) dissolved in dry THF (20 mL). In a separate Schlenk flask diyne **14** (1.00 g, 2.89 mmol) was dissolved in dry THF (10 mL). The zirconocene dichloride solution was cooled to −78 °C before the addition of a solution of nBuLi in hexane (1.6 M, 3.61 mL, 5.9 mmol). This reaction mixture was stirred at low temperature for 15 minutes before addition of the diyne solution by cannula. The reaction mixture was slowly warmed to room temperature with stirring and then heated to 60 °C for a further 12 h. All volatile materials were removed in vacuo, and the residue was extracted with toluene (30 mL), and the supernatant was removed from the insoluble salts by cannula filter. The solution in toluene was then evaporated to dryness, and the crude material was isolated as a dark yellow solid material. This material was purified by washing with minimum amounts of hexanes (2 × 3 mL) to give a bright yellow solid material (1.2 g, 1.1 mmol) which could be recrystallized from a concentrated solution in toluene (73 % yield).

^{1}H NMR (300 MHz, C_6D_6): $\delta = 6.89$ (t, J(H,H) = 9 Hz, 2H; ArH), 6.82 (s, 2H; ArH), 6.57 (d, J(H,H) = 6 Hz, 2H; ArH), 6.19 (s, 5H; Cp*H*), 6.17 (d, J(H,H) = 3 Hz, 2H; ArH), 6.14 (s, 5H; CpH), −0.05 (s, 18H; $Si(CH_3)_3$); ^{13}C data were not obtained because of low solubility; MS (70 eV): m/z (%): 1136 $[M]^+$; HRMS calcd: 1133.2820; found: 1133.2823; elemental analysis calcd (%) for $C_{64}H_{72}Si_4Zr_2$ (1134.8): C 67.66, H 6.39; found: C 67.66, H 6.63.

Dimeric macrocycle (18): A Schlenk flask (20 mL), equipped with stir bar, was charged with $[Zr(Cp)_2Cl_2]$ (51.9 mg, 0.177 mmol) in the dry box. This material was dissolved in THF (5 mL) and then cooled to −78 °C before the addition of a solution of nBuLi (2.5 M, 0.14 mL, 0.35 mmol) in hexanes. This solution was stirred for 15 minutes at −78 °C, before the cannula addition of a solution of diyne **15** (75 mg, 0.177 mmol) in THF (5 mL) from a separate Schlenk flask. The resulting reaction mixture was stirred for 4 h while slowly warming to room temperature. Then the solution was heated to 65 °C for a further 12 h. The deep orange solution was evaporated to dryness, and the desired product was redissolved in toluene and filtered away from the insoluble material by cannula filtration. This solution was evaporated to dryness to isolate the crude product, which was further purified by washing with dry hexanes to give a pale yellow powder (97 mg, 0.0753 mmol, 85 % yield). X-ray quality crystals were grown by slow evaporation of a solution in benzene.

^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.33$ (br s, 1H; ArH), 7.20–7.13 (m, obscured by solvent signal, ArH), 7.04 (t, J(H,H) = 8 Hz, 1H; ArH), 6.79 (d, J(H,H) = 8 Hz, 4H; ArH), 6.21 (s, 10H; CpH), 0.01 (s, 18H; $Si(CH_3)_3$); ^{13}C NMR data were not obtained because of poor solubility; repeated attempts to obtain satisfactory analytical data of crystalline material were not successful. The X-ray crystal structure (Figure 3) and further reactivity to compound **21** confirmed its identity.

Dimeric cyclophane (20): In a Schlenk flask (25 mL), equipped with stir bar, macrocycle **17** (200 mg, 0.176 mmol) and benzoic acid (1.00 g, 8.20 mmol) were dissolved in dry toluene (7 mL). The reaction mixture was stirred at room temperature overnight, then diluted with toluene (30 mL) before filtering to remove precipitates. The filtrate was washed with a Na_2CO_3 solution (2 M, 2 × 30 mL) and brine (30 mL). The organic fraction was dried over $MgSO_4$, then evaporated to dryness to give the crude product as a pale yellow powder (90 mg, 76% yield). This material was further purified by recrystallization from a solution in benzene with slow evaporation to give colorless blocklike crystals.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.23$ (s, 2H; ArH), 7.13 (m, signal obscured by solvent peak, ArH), 7.05 (d, J(H,H) = 8 Hz, 2H; ArH), 6.91 (t, J(H,H) = 8 Hz, 2H; ArH), 6.55 (s, 2H; C=CH), 0.05 (s, 18H; $SiCH_3$); ^{13}C NMR data were not obtained because of poor solubility; MS (70 eV): m/z (%): 696 $[M]^+$; elemental analysis calcd (%) for $C_{44}H_{56}Si_4$ (696.3): C 75.79, H 8.10; found: C 75.55, H 8.26.

Dimeric cyclophane (21): In a Schlenk flask (25 mL), equipped with stir bar, macrocycle **18** (75 mg, 0.058 mmol) and benzoic acid (71 mg, 0.58 mmol) were dissolved in dry toluene (5 mL). The reaction mixture was stirred at room temperature overnight, and then diluted with toluene (20 mL) before filtering to remove precipitates. The supernatant was washed with Na_2CO_3 solution (2 M, 2 × 30 mL) and brine (30 mL). The organic fraction was dried over $MgSO_4$, and then evaporated to dryness to give the crude product (40 mg, 80% yield). The product was further purified by recrystallization from a solution in hexanes (5 mL) to give colorless needlelike crystals (30 mg, 61% yield).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.42$ (m, 3H; ArH), 7.21 (d, J(H,H) = 9 Hz, 4H; ArH), 7.19 (s, 1H; ArH), 6.93 (d, J(H,H) = 9 Hz, 4H; ArH), 6.31 (s, 2H; $CHSiMe_3$), −0.06 (s, 18H; $SiCH_3$); MS (70 eV): m/z (%): 848 $[M]^+$; elemental analysis calcd (%) for $C_{56}H_{64}Si_4$ (848.4): C 79.18, H 7.59; found: C 79.94, H 7.64.

Dimeric cyclophane (22): A Schlenk tube (250 mL) was charged with $[Zr(Cp)_2Cl_2]$ (0.68 g, 2.32 mmol), diyne **16** (0.937 g, 2.32 mmol), and THF (80 mL). The flask was cooled to −78 °C, and then nBuLi (1.6 M/hexane, 2.90 mL, 4.64 mmol) was added dropwise. The flask was allowed to warm to room temperature over 7 h and was heated for 1 h at 65 °C. An aqueous HCl solution (6 M, 20 mL) was added to the flask, and then the resulting mixture was stirred for 2 h at room temperature. The reaction mixture was poured into methanol (150 mL), and the white precipitate was collected and purified by silica gel chromatography (eluted with hexane/ether, 100:1) to afford 0.89 g (94%) of **22** as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.12$ (d, J(H,H) = 8 Hz, 8H; ArH), 6.77 (d, J(H,H) = 8 Hz, 8H; ArH), 6.07 (s, 4H; C=CH), 0.46 (s, 12H; $Si(CH_3)_2$), −0.15 (s, 36H; $Si(CH_3)_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 163.6$ (C=CHSi), 141.9, 136.9, 132.9 (ArC), 129.2 (C=C), 128.6 (ArC), 0.37 ($Si(CH_3)_3$), −2.62 ($Si(CH_3)_2$); MS (70 eV): m/z (%): 814 $[M]^+$; elemental analysis calcd (%) for $C_{48}H_{68}Si_6$ (813.1): C 70.86, H 8.42; found: C 70.48, H 8.27.

Crystal data for 10 ($C_{48}H_{72}Si_6$): crystal dimensions 0.20 × 0.10 × 0.22 mm, triclinic, space group $P\bar{1}$, $a = 10.1899(4)$, $b = 15.9734(7)$, $c = 17.6277(7)$ Å, $\beta = 73.955(1)^\circ$; $V = 2616.6(2)$ Å^3, $\rho_{calcd} = 1.038$ g cm^{-3}, $2\theta_{max}$ 51.5°, Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), ω scans, $T = -109.0$ °C, of 11852 measured reflections, 8333 were unique, and 3188 were observed with $[I > 3.00\sigma(I)]$, data corrected for Lorentz and polarization effects, analyzed for agreement and absorption using XPREP with an empirical absorption correction using SADABS ($T_{max} = 0.98$, $T_{min} = 0.68$). The structure was solved by direct methods (SIR92) and developed by least-squares refinement against $|F^2|$. No. of parameters, 487; H atoms were included but not refined; $R = 0.101$ and $R_w = 0.128$; $\Delta\rho_{max} = 0.71$ e$^-$ Å^{-3}.

Crystal data for 18 ($Zr_4Si_4C_{106}H_{95}$): crystal dimensions 0.21 × 0.13 × 0.12 mm, monoclinic, space group $C2/c$, $a = 14.8362(1)$, $b = 27.4645(7)$, $c = 22.5575(3)$ Å, $\beta = 101.107(2)^\circ$; $V = 9019.3(3)$ Å^3, $\rho_{calcd} = 1.225$ g cm^{-3}, $2\theta_{max}$ 44.3°, Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), ω scans, $T = -106 \pm 1$ °C, of 16363 measured reflections, 5790 were unique, and 2509 were observed with $[I > 3.00\sigma(I)]$, data corrected for Lorentz and polarization effects, analyzed for agreement and absorption using XPREP with an empirical absorption correction using SADABS ($T_{max} = 0.96$, $T_{min} = 0.74$). The structure was solved by direct methods (SIR92) and developed by least-squares refinement against $|F^2|$. No. of parameters, 220; H atoms were calculated but not refined; $R = 0.076$ and $R_w = 0.088$; $\Delta\rho_{max} = 0.80$ e$^-$ Å^{-3}.

Crystal data for 20 ($C_{44}H_{56}Si_4$): crystal dimensions 0.10 × 0.25 × 0.35 mm, triclinic, space group $P\bar{1}$, $a = 6.8221(6)$, $b = 11.775(1)$, $c = 14.192(1)$ Å, $\beta = 101.088(1)^\circ$; $V = 10669(1)$ Å^3, $\rho_{calcd} = 1.085$ g cm^{-3}, $2\theta_{max}$ 46.5°, Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), ω scans, $T = -145.0$ °C, of 5118 measured reflections, 3026 were unique, and 2565 were observed with $[I > 3.00\sigma(I)]$, data corrected for Lorentz and polarization effects, analyzed for agreement and absorption using XPREP with an empirical absorption correction using SADABS ($T_{max} = 0.96$, $T_{min} = 0.87$). The structure was solved by direct methods (SIR92) and developed by least-squares refinement against $|F^2|$. No. of parameters, 217; H atoms were included but not refined; $R = 0.035$ and $R_w = 0.050$; $\Delta\rho_{max} = 0.21$ e$^-$ Å^{-3}.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-162175, 162176, and 162177. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: (+44) 1223-336-003; e-mail: deposit@ccdc.cam.ac.uk).

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