Bipyridine-Containing Cyclophanes via Zirconocene Coupling

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Zirconocene-coupling reactions of 6,6′-bis[(trimethylsilyl)ethynyl]-2,2′-bipyridine and 5,5′-bis-[(trimethylsilyl)ethynyl]-2,2′-bipyridine give trimeric, zirconocene-containing macrocycles (**3** and **4**, respectively) in high yield. Molecules of **3** in the solid state are chiral about their crystallographic C_2 axis of symmetry, with each bipyridine unit in an anti conformation. Compound **4** exists in solution as a mixture of diastereomers (with D_3 and C_2 symmetries) that could not be distinguished in the solid state by X-ray crystallography. Compounds **3** and **4** are cleanly converted to the corresponding 1,4-bis(trimethylsilyl)butadiene derivatives **5** and **6**, respectively, via demetalation with acetic acid. The latter cyclophanes are less conformationally rigid, as determined by variable-temperature NMR experiments.

Introduction

Bipyridine-containing cyclophanes have a number of potential applications in the fields of molecular recognition and supramolecular chemistry. For example, such compounds may function as complexing agents for cationic,[1–4] neutral,[5] and anionic[6] guests. Coordination polymers have been synthesized by complexation of metal cations by bipyridine-containing cyclophanes,[7] and phenanthroline-based cyclophanes have been used to construct a rich array of supramolecular structures, including Sauvage's catenanes and knots[8] and Lehn's rotaxanes.[9] We have recently employed the zirconocene coupling of diynes in the preparation of zirconium-containing macrocycles and cyclophanes.[10,11] This method provides simple, high-yield routes to metal-containing macrocycles that can vary considerably in size and shape.[12] The resulting zirconacyclopentadiene groups then offer versatile sites for further derivatization of the macrocycles. In this contribution, we describe extensions of this chemistry to the development of synthetic routes to macrocycles containing bipyridines.

Results and Discussion

The zirconium-containing macrocycles **3** and **4** were prepared in good yields by the method outlined in Scheme 1. Initial attempts to couple diynes **1** and **2** were based on conditions we have previously described for the cyclization of 1,4-Me₃SiC≡CC₆H₄C₆H₄C≡CSiMe₃,[10] involving addition of *n*-BuLi to a solution of Cp₂ZrCl₂ and the diyne at −78 °C. However, this method was unsuc-

cessful in that it gave deeply colored reaction mixtures from which only traces of the desired product could be isolated. Good yields of the products were obtained by allowing the zirconocene reagent to form initially, via the reaction of Cp₂ZrCl₂ and *n*-BuLi, before addition of the diyne.

Formation of the trimeric structure **3** is particularly interesting, since zirconocene coupling of the corresponding biphenyl derivative, 3,3′-bis[(trimethylsilyl)ethynyl]-biphenyl, gives a dimer under similar conditions.[13] This difference may be attributed to the greater preference of the bipyridyl diyne for adopting an *anti*-geometry.[14] An ORTEP view of **3** (Figure 1) shows that the molecule possesses C_2 (rather than D_3) symmetry, and this observation was confirmed by NMR spectroscopy. Macrocycle **3** is chiral about its C_2 axis of symmetry, and in crystals of this compound the enantiomers are related by a crystallographic center of symmetry. Interestingly, the bipyridyl unit bisected by the C_2 axis (the horizontal one at the bottom of Figure 1) is buckled toward the center of the ring and has a pyridine–pyridine torsion angle (158°) that is somewhat less than those observed for the molecule's other bipyridine units (165°) and substantially less than the preferred angle of 180°.[14] These distortions are probably related to the rigid conformational requirements of the zirconacyclopentadiene rings. A geometric analysis of the cavity of **3** (considering van der Waals radii for the pyridyl carbon atoms[15]) revealed that spheres with radii up to 0.82 Å may be accommodated.

The ¹H NMR spectrum of **3** in benzene-d_6 exhibits nine distinct pyridyl resonances, indicating that molecules in solution also possess C_2 symmetry. On heating **3** to 115 °C in toluene-d_8, some broadening of the ¹H resonances was noted, but coalescence behavior was not observed. Thus, this ring is conformationally locked into a rigid configuration, such that the barrier to pyridyl ring rotation is greater than 20 kcal/mol.

On hydrolysis of **3** with acetic acid in toluene, cyclophane **5** was obtained in high yield. This procedure is superior to that involving hydrochloric acid, which gives much lower yields. Cyclophane **5** appears to be considerably less rigid than the parent zirconacycle, since NMR spectra recorded at room-temperature reflect time-aver-

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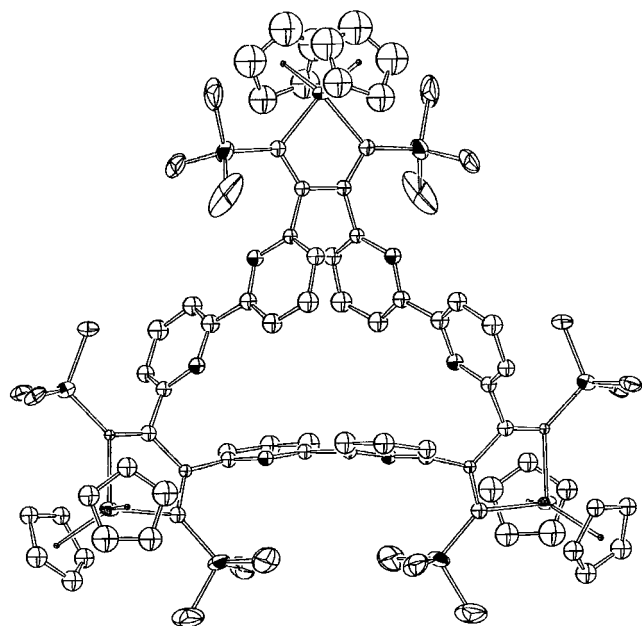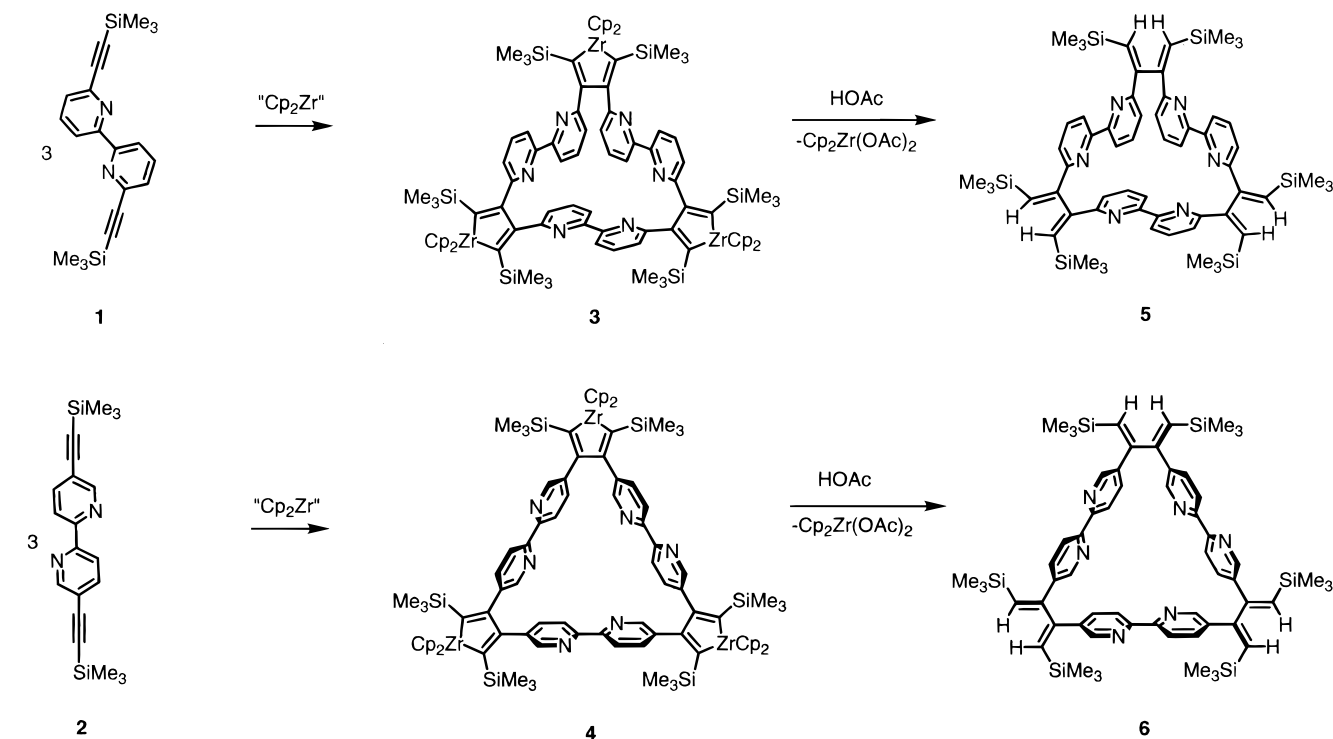(11) Tilley, T. D.; Mao, S. S. H. *J. Am. Chem. Soc.* **1995**, *117*, 5365.

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Scheme 1

Figure 1. ORTEP diagram of **3**, with thermal ellipsoids drawn at 50% probability. Note that the "hatched" ellipsoids correspond to heteroatoms.

aged D_3 symmetry for the molecule (one set of pyridyl, vinyl, and trimethylsilyl NMR resonances). On lowering the temperature to −40 °C (in toluene-d_8), the pyridyl, vinyl, and trimethylsilyl ¹H resonances decoalesce, and at −65 °C, the macrocycle appears to adopt a C_2-symmetric conformation, similar to that observed for the room-temperature structure of the parent zirconacycle (three sets of pyridyl, vinyl, and trimethylsilyl NMR resonances). The variable-temperature NMR spectra reflect a rotational barrier of approximately 11 kcal/mol.[16] The greater flexibility of this ring compared to **3** may be
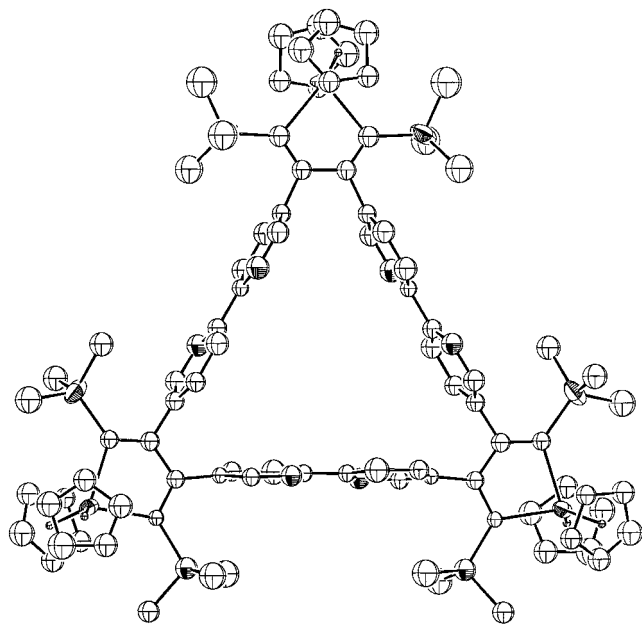
attributed to wider torsion angles at the butadiene "corners", which allow the pyridyl rings to rotate more freely.

In contrast to **3**, macrocycle **4** exhibits a number of conformations (or rotamers), which are expected to have comparable energies. Assuming that the bipyridyl units adopt an *anti*-planar configuration (the experimental energy minimum[14]), each bipyridyl group would have one of two distinct orientations with respect to the rest of the ring, as illustrated in Chart 1. With two possible bipyridyl orientations for each of the three ring positions, there are four unique isomers that correspond to a diastereomeric pair of enantiomers with C_2 and D_3 symmetries (Chart 1).

The molecular structure of **4** (Figure 2) is very similar (within experimental error) to that of the carbocyclic analogue,[10] as might be expected given the structural similarity of phenyl and pyridyl rings. The X-ray scattering factors for CH and N are so similar that it proved impossible to distinguish these sites in the structure. The largest sphere that could be accommodated in the cavity of **4** would have a van der Waals radius of 1.85 Å, suggesting that **4** and **6** might function as good hosts for small molecules or ions in host−guest complexes ($r_{vdW} =$ 1.81 Å for Cl⁻; 1.95 Å for Br⁻).[15]
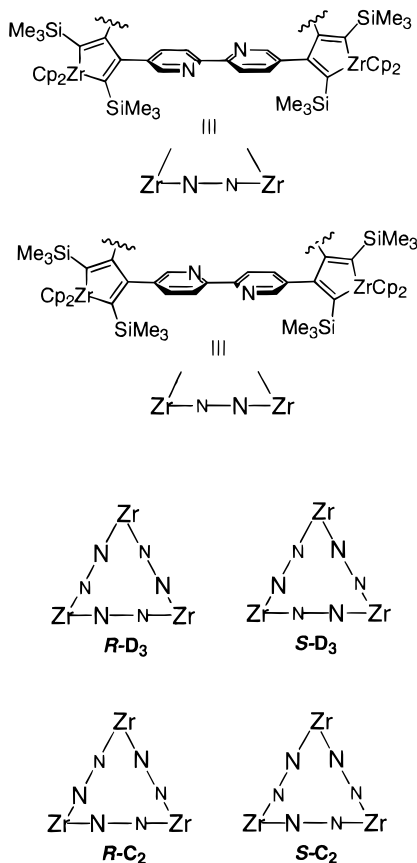
Given a purely statistical distribution of the *anti*-bipyridine group orientations, the expected $D_3:C_2$ ratio of isomers for **4** is 1:3. However, the NMR spectra of **4** in benzene-d_6 indicate that these rotamers are present in an approximate $D_3:C_2$ ratio of 1:6. The pyridyl region contains 12 ¹H resonances, with nine of these having approximately twice the integrated intensity of the other three. A TOCSY spectrum allowed assignment of the three less intense resonances to the single unique pyridyl ring of the D_3 isomer. The remaining nine resonances group into three spin systems, which correspond to the unique pyridyl rings of the C_2-symmetric isomer. When heated to 115 °C in toluene-d_8, the pyridyl resonances

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Figure 2. ORTEP diagram of **4**, with thermal ellipsoids drawn at 50% probability. Note that the "hatched" ellipsoids correspond to heteroatoms.
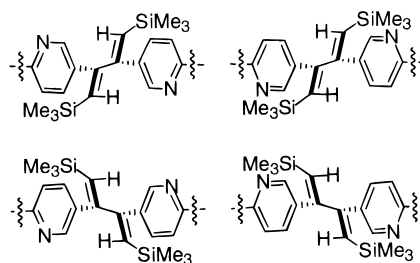
Chart 1

Chart 2

ring has time-averaged D_3 symmetry at room temperature in solution, since only three pyridyl resonances are observed. The pyridyl resonances broaden and decoalesce ($T_c = -40$ °C; $\Delta G^{\ddagger} \approx 10$ kcal/mol) to a number of broader, overlapping resonances at -80 °C, while the trimethylsilyl and vinyl ^{1}H NMR resonances decoalesce at a significantly lower temperature (-60 °C). Due to the broadness of the peaks at the lowest temperature examined (-90 °C), it is not possible to assign a detailed molecular structure at the low-temperature limit, but the different temperatures for the coalescence of the pyridyl and vinyl/trimethylsilyl resonances suggest two independent motions for the molecule. Note that the syn diene corners of the cyclophane are expected to have a twist (as they do in the crystallographically characterized carbocyclic analog),[10] which provides another set of stereocenters. We suggest that the twist of the diene corners is independent of the pyridyl ring conformations, resulting in a number of interconverting conformational isomers at room temperature. Four distinct conformations of the diene subunits are illustrated in Chart 2.

Future work will include investigations of the host–guest properties of the new cyclophanes described here and cationic pyridinium species derived therefrom. We are also exploring modifications of this procedure to produce heteroaromatic cyclophanes of various sizes and shapes.

Experimental Section

General Methods. All reactions involving air-sensitive compounds were carried out under nitrogen using standard Schlenk techniques and dry, oxygen-free solvents. Pentane, diethyl ether, benzene, and tetrahydrofuran were distilled under nitrogen from sodium benzophenone ketyl. Toluene, toluene-d_8, and benzene-d_6 were distilled under nitrogen from Na/K. *n*-BuLi was used as a 2.6 M solution in *n*-hexane. Compound **1**, 6,6′-bis[(trimethylsilyl)ethynyl]-2,2′-bipyridine, and compound **2**, 5,5′-bis[(trimethylsilyl)ethynyl]-2,2′-bipyridine, were prepared according to literature methods.[17] The zirconocene reagent was generated by the method of Negishi.[18]

All NMR spectra were recorded at room temperature, unless otherwise noted. Chemical shifts are referenced to the residual proton or carbon resonance of the deuterated solvent. In some cases, DEPT[19] was used to assign carbon resonances. All mass spectra were obtained at the Mass Spectrometry Facility of the University of California, Berkeley. Combustion analyses were provided by E + R Microanalytical Laboratory.

Macrocycles 3 and 4. These compounds were prepared according to the same procedure. In the drybox, a PTFE-stoppered Schlenk flask was loaded with Cp$_2$ZrCl$_2$ (0.167 g, 0.574 mmol), and a Schlenk flask was loaded with **1** or **2** (0.200 g, 0.574 mmol). The contents of each flask were dissolved in

broaden considerably, suggesting that coalescence is just above this temperature. We can therefore estimate the kinetic barrier to ring rotation (and rotamer interconversion) as ≥ 19 kcal/mol, in keeping with a highly constrained geometry at the zirconacyclopentadiene "vertices".

Demetalation of **4** with acetic acid in toluene gives the corresponding cyclophane **6** in high yield. Like **5**, this

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approximately 5 mL of dry THF. The Cp$_2$ZrCl$_2$-containing flask was chilled to −78 °C in dry ice/acetone, and *n*-BuLi (0.645 mL, 1.03 mmol) was added dropwise via syringe with rapid stirring, causing the solution to take on a light gold color. The solution of the diyne was then added slowly via syringe down the side of the chilled flask, allowing it to precool before reacting. The solution initially turned from a gold color to colorless and then slowly turned to a deep red-amber (in the case of **1**) or deep green (in the case of **2**) as the flask warmed to room temperature over 5 h. The mixture was then heated to 60 °C for 12 h (to allow oligomeric species to reassemble into macrocycles), and the solvent was then removed under vacuum.

Ten milliliters of dry diethyl ether was then added with stirring, yielding a dark suspension. After 5 min, 10 mL of water that had been deoxygenated by 2 freeze−pump−thaw cycles was added. The solid product was then separated by filtration in air, washed with 10 mL of water and 10 mL of pentane, and then recrystallized from dry toluene under N$_2$. The material was then collected and dried in vacuo. The solid macrocycles are air-stable for days at room temperature, but solutions decompose within hours.

Macrocycle **3**: yield 82%; yellow blocks; ^{1}H NMR (500 MHz, C$_6$D$_6$) δ −0.12 (s, 36 H), −0.05 (s, 18 H), 6.15 (s, 10 H), 6.16 (s, 10 H), 6.20 (s, 10 H), 6.23 (d, 2 H, *J* = 7.59 Hz), 6.57 (t, 2 H, *J* = 7.74 Hz), 6.71 (d, 2 H, *J* = 7.53 Hz), 6.88 (d, 2 H, *J* = 7.52 Hz), 6.92 (t, 2 H, *J* = 7.72 Hz), 7.20 (t, 2 H, *J* = 7.74 Hz), 7.87 (d, 2H, *J* = 7.81 Hz), 8.15 (d, 2H, *J* = 7.85 Hz), 8.24 (d, 2 H, *J* = 7.75 Hz); ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$) δ 2.4 (CH$_3$), 2.7 (CH$_3$), 111.1 (CH), 111.2 (CH), 111.5 (CH), 116.7 (CH), 118.1 (CH), 118.3 (CH), 120.4 (CH), 124.1 (CH), 125.2 (CH), 134.3 (CH), 134.5 (CH), 136.6 (CH), 145.7 (C), 147.4 (C), 147.6 (C), 153.6 (C) 155.9 (C), 157.1 (C), 161.2 (C), 163.3 (C), 163.6 (C), 201.7 (C), 203.9 (C), 207.2 (C); FAB MS (FAB was carried out in a sulfolane matrix, using Cs atom bombardment): *m/z* 1269 ([^{2}/$_3$M]·Cs$^+$), 1139 (^{2}/$_3$MH$^+$), 919 (^{2}/$_3$MH$^+$ − Cp$_2$Zr), 789 (^{2}/$_3$MH$^+$ − **5**), 569 (^{1}/$_3$MH$^+$). Anal. Calcd for C$_{90}$H$_{102}$Si$_6$N$_6$Zr$_3$: C, 63.22; H, 6.01; N, 4.91. Found: C, 63.00; H, 6.28; N, 4.91.

X-ray Crystallographic Study of 3. Crystals were grown by slow diffusion of pentane into a THF solution of **3**. The crystal studied measured 0.2 × 0.2 × 0.1 mm and belonged to space group *C*2/*c* with *a* = 32.4164(6) Å, *b* = 19.3169(4) Å, *c* = 15.5474(3) Å, *β* = 92.54(3)°, *V* = 9725.9(4) Å^3, *Z* = 4 (the molecule lies on a crystallographic *C*$_2$ axis), and *D*$_{calcd}$ = 1.266 g/cm^3. Graphite-monochromated Mo Kα radiation was employed to collect 6073 unique reflections, 2131 with *I* > 3.00σ(*I*). For the 299 refined parameters, *R* = 6.6%, *R*$_w$ = 6.9%, and GOF = 1.92.

Macrocycle **4**: yield 76%; yellow blocks; ^{1}H NMR (500 MHz, C$_6$D$_6$) δ −0.36, −0.37 (overlapping s, 31.5 H), 5.98, 5.99, 6.00 (overlapping s, 17.5 H), 6.59 (dd, 1 H, *J* = 2,8 Hz), 6.78 (dd, 1 H, *J* = 2, 6.5 Hz), 6.79 (dd, 1 H, *J* = 2.5, 7 Hz), 6.92 (dd, 0.5 H, *J* = 2.5, 8 Hz), 7.95 (d, 1 H, *J* = 8 Hz), 8.18 (d, 0.5 H, *J* = 2.5 Hz), 8.25 (d, 1 H, *J* = 7.5 Hz), 8.25 (s, 1 H), 8.35 (s, 0.5 H), 8.37 (d, 1 H, *J* = 1 Hz), 8.43 (d, 1 H, *J* = 1.5 Hz), 8.55 (d, 1 H, *J* = 8.5 Hz); (300 MHz, toluene-*d*$_8$) pyridyl peaks (δ = 8.16, 8.33) separated by 50 Hz at 298 K are nearly coalesced at 388 K, giving a barrier to pyridyl rotation > 19 kcal/mol, using the following formula:[16]

$$\Delta G_c^{\ddagger} = (4.58 \times 10^{-3})\left(9.97 + \log\left(\frac{T}{\delta v}\right)\right)T \, \text{kcal/mol}$$

^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$) δ 3.15 (CH$_3$), 3.18 (CH$_3$), 111.98 (CH), 119.96 (CH), 120.29 (CH), 120.69 (CH), 137.54 (CH), 137.58 (CH), 137.68 (CH), 141.28 (C), 141.37 (C), 141.48 (C), 149.38 (CH), 149.57 (CH), 149.76 (CH), 153.29 (C), 153.45 (C), 153.49 (C) 209.78 (C), 209.87 (C), 209.98 (C); FAB MS (FAB was carried out in a sulfolane matrix, using Cs atom bombardment) *m/z* 1269 ([^{2}/$_3$M]·Cs$^+$), 1139 (^{2}/$_3$MH$^+$), 919 (^{2}/$_3$MH$^+$ − Cp$_2$-Zr), 789 (^{2}/$_3$MH$^+$ − **5**), 569 (^{1}/$_3$MH$^+$). Anal. Calcd for C$_{90}$H$_{102}$Si$_6$N$_6$Zr$_3$: C, 63.22; H, 6.01; N, 4.91. Found: C, 63.03; H, 6.02; N, 4.91.

X-ray Crystallographic Study of 4. Crystals were grown by slow diffusion of pentane into a THF solution of **4**. The crystal studied measured 0.2 × 0.2 × 0.1 mm and belonged to space group *C*2/*c* with *a* = 20.3658(2) Å, *b* = 20.2638(1) Å, *c* = 29.1380(4) Å, *β* = 110.270(1)°, *V* = 11280.2(2) Å^3, *Z* = 4 (the molecule lies on a crystallographic *C*$_2$ axis), and *D*$_{calcd}$ = 2.165 g/cm^3. Graphite-monochromated Mo Kα radiation was employed to collect 8335 unique reflections, 3534 with *I* > 3.00σ-(*I*). For the 328 refined parameters, *R* = 11.0%, *R*$_w$ = 13.0%, and GOF = 2.71.

Macrocycles 5 and 6. Both isomeric cyclophanes were prepared by the same procedure. The zirconium-containing compounds **3** and **4** (0.100 g) were dissolved in 5 mL of dry toluene under nitrogen, and ca. 10 equiv (0.15 mL) of glacial acetic acid was added via syringe. Twelve hours later, the yellow color of the starting material had completely faded, giving a colorless, slightly cloudy solution. Toluene and excess acetic acid were removed over 5 h at 60 °C in vacuo, and the resulting residue was taken up in 5 mL of toluene. This solution was then filtered through 0.5 mL of neutral silica in a pipet. Solvent was again removed, giving the desired product.

Macrocycle **5**: yield 95%; white crystals; ^{1}H NMR (400 MHz, benzene-*d*$_6$) δ 0.04 (s, 9 H), 6.84 (s, 1 H), 6.99 (s, 2 H), 8.24 (d, 1 H, *J* = 5.5 Hz); (300 MHz, toluene-*d*$_8$, 188 K) δ 0.06 (s, 9 H), 0.09 (s, 9 H), 0.25 (s, 9 H), 6.55 (t, 1 H, *J* = 7.5 Hz), 6.65 (d, 1 H, *J* = 7 Hz), 6.74 (t, 1 H, *J* = 8 Hz), 6.9, 7.0,[20] 7.0,[20] 7.1,[20] 7.2,[20] 7.31 (d, 1 H, *J* = 7 Hz), 8.17 (d, 1 H, *J* = 7 Hz), 8.32 (d, 1 H, *J* = 7 Hz), 8.47 (d, 1 H, *J* = 8 Hz); (300 MHz, toluene-*d*$_8$, 298 K) 0.06 (s, 9 H), 6.80 (s, 1 H), 6.9,[20] 7.1,[20] 8.17 (dd, 1 H, *J* = 1.5, 7 Hz); pyridyl peaks (δ = 8.17, 8.47) separated by 90 Hz at 188 K are coalesced at 233 K, giving a barrier to pyridyl rotation of approximately 11 kcal/mol; ^{13}C{^{1}H} NMR (100 MHz, benzene-*d*$_6$) δ 0.2 (CH$_3$), 119.4 (CH), 124.9 (CH), 132.7 (CH), 135.8 (CH), 155.4 (C), 159.6 (C), 159.9 (C); EI-MS *m/z* 1051 (MH$^+$), 1036 (MH$^+$ − CH$_3$), 978 (MH$^+$ − Si(CH$_3$)$_3$). Anal. Calcd for C$_{60}$H$_{78}$Si$_6$N$_6$: C, 68.51; H, 7.47; N, 7.99. Found: C, 68.24; H, 7.37; N, 7.99.

Macrocycle **6**: yield 93%; white crystals; ^{1}H NMR (500 MHz, benzene-*d*$_6$) δ −0.09 (s, 9 H), 6.51 (s, 1 H), 7.12 (dd, 1 H, *J* = 2, 8.5 Hz), 8.26 (d, 1 H, *J* = 8.5 Hz), 8.61 (d, 1 H, *J* = 2 Hz); (300 MHz, toluene-*d*$_8$, 183 K) −0.07 (s), −0.06 (s), −0.03 (s), 0.00 (s), 6.54 (broad s), 6.63 (broad d), 6.95 (broad d), 7.1,[20] 7.96 (broad d), 8.29 (broad d), 8.61 (broad m), 8.8 (broad), 9.1 (broad); (300 MHz, toluene-*d*$_8$, 298 K) δ 0.08 (s, 9 H), 6.51 (s, 1 H), 7.15 (dd, 1 H, *J* = 2.5, 8.5 Hz), 8.27 (dd, 1 H, *J* = 0.5, 8.5 Hz), 8.54 (dd, 1 H, *J* = 0.5, 2.5 Hz); broad pyridyl peaks (δ = 7.96, 8.61) separated by 195 Hz at 183 K are coalesced at 233 K, giving a barrier to pyridyl rotation of approximately 11 kcal/mol; ^{13}C{^{1}H} NMR (125 MHz, benzene-*d*$_6$) δ 0.67, 120.84, 134.20, 137.48, 137.59, 150.02, 155.00, 158.21; EI-MS *m/z* 1051 (MH$^+$), 1036 (MH$^+$ − CH$_3$), 978 (MH$^+$ − Si(CH$_3$)$_3$). Anal. Calcd for C$_{60}$H$_{78}$Si$_6$N$_6$: C, 68.51; H, 7.47; N, 7.99. Found: C, 68.21; H, 7.60; N, 7.55.

Supporting Information Available: Tables of positional and thermal parameters, bond lengths, angles, and torsional angles for the crystal structures, and a TOCSY ^{1}H NMR spectrum of the pyridyl region of **4** (19 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(20) These resonances were obscured by the toluene solvent's residual proton signal.