10345

New Zirconocene-Coupling Route to Large, Functionalized Macrocycles

Jonathan R. Nitschke, Stefan Zürcher, and T. Don Tilley*

Contribution from the Department of Chemistry, University of California, Berkeley, Berkeley, California 94720-1460 and the Chemical Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720

Abstract: The development of a new macrocyclization reagent, Rosenthal's $Cp_2Zr(pyr)(Me_3SiC≡CSiMe_3)$, has allowed the preparation of two large, functionalized macrocycles. The diyne 5,5′-bis(4-trimethylsilylphenyl)-2,2′-bipyridine was trimerized to the bipyridine-containing macrocycle **5**, and 1,4-bis(4-(trimethylsilyl)ethynyl-phenyl)-2,3-diphenyl-1,4-diazabuta-1,3-diene was dimerized to macrocycle **6**. Both zirconocene-containing macrocycles were characterized by single-crystal X-ray diffraction. Macrocycle **5**, which is cleanly converted to air-stable cyclophane **7** with benzoic acid, has a cavity of van der Waals radius 6.03 Å. In general, the $Cp_2Zr(pyr)(Me_3SiC≡CSiMe_3)$ reagent gives higher yields of macrocycles via the coupling of diynes than does the reagent generated by addition of *n*-BuLi to Cp_2ZrCl_2.

We recently demonstrated the utility of zirconocene-coupling methods for the high-yield synthesis of macrocycles from readily available diynes.[1−6] This synthetic approach to macrocycles offers a number of advantages over more traditional methods, which typically provide relatively low yields and often require conditions of high dilution and lengthy separations from oligomeric byproducts.[7,8] More recently, we attempted to expand the scope of zirconocene-based macrocyclization methods by developing synthetic modifications which lead to macrocycles and cages of various shapes, sizes, and functionalization.[2−6] The use of zirconocene coupling in the synthesis of functionalized macrocycles has proven particularly challenging because derivatives of zirconocene are highly reactive toward a wide range of functional groups, especially those containing heteroatoms.[9,10]

Macrocycles containing pyridine or bipyridine units are of interest as ligands for transition metals and as supramolecular building blocks. We recently reported the use of Negishi's in situ-generated zirconocene reagent synthesized from Cp_2ZrCl_2 and *n*-BuLi, believed to be $Cp_2Zr(THF)$-(1-butene),[11] in the syntheses of macrocycles **1** and **2**.[5] These syntheses were possible only after allowing the zirconocene reagent to form initially at low temperature, before addition of the diyne. A notable feature of **1** is its extremely rigid structure, with the pyridyl rings locked into an orthogonal conformation with respect to the overall plane of the macrocycle by steric constraints at the triangle's "corners".

In this contribution, we describe modifications of the zirconocene-coupling procedure which allow (1) the synthesis of larger, bipyridine-containing macrocycles, which greatly expand the potential for host−guest chemistry and supramolecular chemistry for macrocycles obtained by such coupling methods, and (2) the synthesis of less rigid diimine-containing macrocycles. The trimeric macrocycle **5** (Scheme 1) possesses a cavity which is significantly larger than those of **1** and **2**, such that host−guest interactions involving molecular guests should be possible. In addition, **5** would be expected to have a highly rigid triangular geometry, but with bipyridyl groups which are free to rotate about the pyridyl-phenylene bonds; the phenyl−phenyl bond in biphenyl has a barrier to rotation of only 1.4 kcal/mol.[12] This rotational freedom should allow (for example) the linking of macrocycles via coordination chemistry. In the case of macrocycle **6**, the incorporation of diimine ligands into a macrocyclic framework is expected to create novel ligand environments for transition metal diimine complexes, which have recently been associated with interesting transition-metal-based transformations including the efficient polymerization of olefins.[13,14]

In our previous research on macrocycle syntheses via the coupling of diynes, we exclusively employed the Negishi zirconocene reagent, which gives good results for phenylene-bridged diynes[1] and (under specific reaction conditions) in the syntheses of **1** and **2**.[5] However, we have found that this reagent fails to produce macrocycles from many functionalized diynes.

(1) Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995,** *117,* 7031.

(2) Liu, F. Q.; Harder, G.; Tilley, T. D. *J. Am. Chem. Soc.* **1998,** *120,* 3271.

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

(4) Mao, S. S. H.; Liu, F. Q.; Tilley, T. D. *J. Am. Chem. Soc.* **1998,** *120,* 1193.

(5) Nitschke, J. R.; Tilley, T. D. *J. Org. Chem.* **1998,** *63,* 3673.

(6) Mao, S. S. H.; Nitschke, J. R.; Liu, F.-Q.; Clouston, L. C.; Harder, G. H. manuscript in preparation.

(7) Dietrich, B.; Viout, P.; Lehn, J.-M. *Macrocyclic Chemistry: Aspects of Organic and Inorganic Supramolecular Chemistry*; VCH: New York, 1993.

(8) Parker, D. *Macrocycle Synthesis: a Practical Approach*; Oxford University Press: Oxford, 1996.

(9) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994,** *116,* 1880.

(10) Fisher, R. A.; Buchwald, S. L. *Organometallics* **1990,** *9,* 871.

(11) Negishi, E. I.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986,** *27,* 2829.

(12) Almenningen, A.; Bastiansen, O.; Fernholt, L. *J. Mol. Struct.* **1985,** *128,* 59.

(13) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995,** *117,* 6414.

(14) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998,** 849.
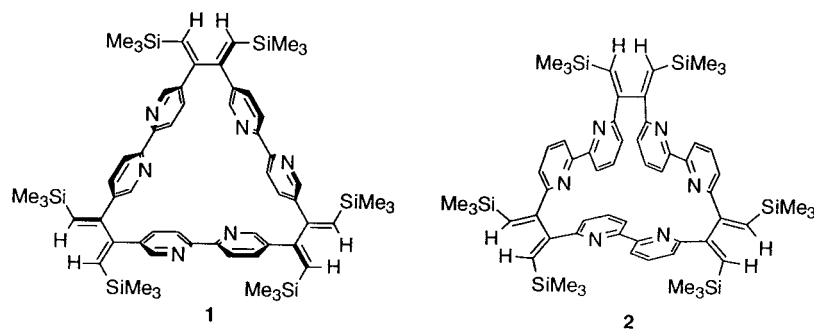
As reported here, these problems can be overcome through the use of a different zirconocene macrocyclization reagent, the alkyne complex Cp$_2$Zr(pyr)(Me$_3$SiC≡CSiMe$_3$) that was reported by Rosenthal.[15]

Results and Discussion

Syntheses of Diynes. The precursor diyne 5,5′-bis[4-(trimethylsilylethynyl)phenyl]-2,2′-bipyridine (**3**) was synthesized according to the procedure outlined in Scheme 1. The broadly useful synthon *p*-Me$_3$SnC$_6$H$_4$SiMe$_3$ has been described previously,[16] but we obtained this compound by a simplified procedure, directly from 1,4-dibromobenzene in 95% isolated yield. Initial attempts to employ Stille coupling conditions in the reaction of this reagent with 5,5′-dibromo-2,2′-bipyridine, using Pd(PPh$_3$)$_4$ catalyst at 110 °C, were unsuccessful. This failure appeared to result from decomposition of the catalyst to

palladium metal before reaction of the deactivated C−Br bond at the 5-position of the pyridyl ring[17] could take place. The desired product 5,5′-bis(4-trimethylsilylphenyl)-2,2′-bipyridine was obtained in 93% isolated yield using the catalyst Pd-(AsPh$_3$)$_2$Cl$_2$ in DMF, which has been shown to be more stable and more active for Stille couplings.[18] The following reaction, involving cleavage of the C−Si bonds with ICl, was accomplished in 82% yield. The resulting diiodide was then converted to the desired compound **3** (79% isolated yield) via reaction with trimethylsilylacetylene under Sonogashira conditions.[19]

The diyne 1,4-bis[4-(trimethylsilyl)ethynylphenyl]-2,3-diphenyl-1,4-diazabuta-1,3-diene (**4**) was obtained in 74% yield by the condensation of 4-(trimethylsilyl)ethynyl-aniline[20] with benzil, using titanium tetrachloride/triethylamine as the dehydrating agent (eq 1).

Scheme 1

$$(1)$$
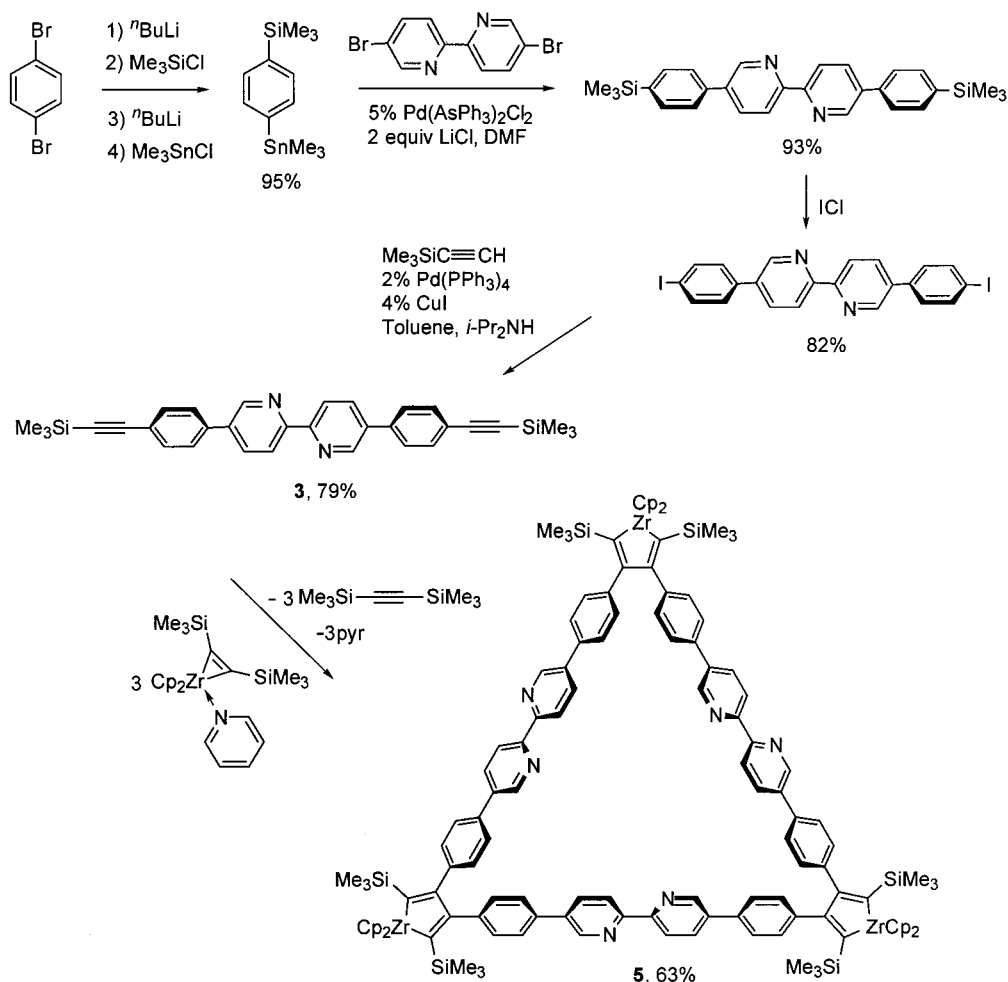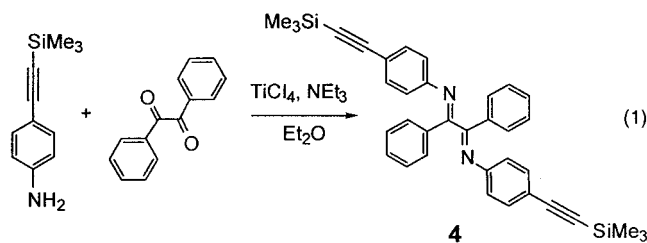
Syntheses of Diimine-Containing Macrocycles. Attempts to synthesize macrocycle **5** (Scheme 1) via reaction of diyne **3** with Cp_2ZrCl_2/*n*-BuLi, using our previously described procedure,[5] produced only complex reaction mixtures. Heating such mixtures to 80 °C for 12 h increases the abundance of one product, as indicated by the development of a purple color and the increase of a resonance in the ^1H NMR spectrum at δ 5.37. This shift is nearly identical to that exhibited by the Cp ligands of deep-purple $Cp_2Zr(2,2'\text{-bipyridine})$,[21] which suggests that formation of a bipyridine complex competes with generation of the desired macrocycle. Similarly, macrocycle **6** (eq 3) was not formed upon reaction of Cp_2ZrCl_2/*n*-BuLi with **4** in tetrahydrofuran. Instead, this reaction produced a complex mixture which did not contain the desired product **6** (by ^1H NMR spectroscopy).

The zirconocene reagent generated from Cp_2ZrCl_2 and *n*-BuLi presents several practical difficulties in the coupling of functionalized diynes. We have observed variations in the yields of alkyne-coupling reactions that seem to reflect changes in the quality of commercial *n*-BuLi. The highly reactive nature of the Negishi zirconocene reagent is reflected both in its decomposition at room temperature and in its indiscriminate reactivity toward multifunctional molecules such as **3** and **4**. To overcome these difficulties, a more stable and selective zirconocene reagent was sought. Several stable $Cp_2Zr(II)$ derivatives are known, for example $Cp_2Zr[Ph_2P(CH_2)_3CH{=}CH_2]$[23] and $Cp_2Zr(CO)_2$,[24] but these have not been developed into generally useful alkyne-coupling reagents. A more attractive candidate appeared to be Rosenthal's recently reported $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$. This compound is stable and isolable, and was reported to exhibit certain reactivity patterns analogous to those for the putative $Cp_2Zr(THF)(1\text{-butene})$.[11] We speculated that the greater stability of $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ might reflect a greater selectivity in its reactions toward functionalized diynes, allowing the synthesis of macrocycles containing chelating diimine units.

The reported synthesis of $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ involves the generation and purification of $Cp_2Zr(THF)(Me_3\text{-}SiC{\equiv}CSiMe_3)$, followed by reaction with pyridine.[15] The intermediate THF adduct is somewhat unstable; it loses THF under vacuum or in pentane solution to yield a product in which C−H activation of the cyclopentadienyl rings has occurred.[22] We, therefore, developed a simplified synthetic procedure for this compound (Scheme 2) which avoids isolation of the THF adduct and gives an improved yield (85% from Cp_2ZrCl_2, as compared to the literature yield of 49%[15,22]). This synthesis involves generation of the Negishi zirconocene reagent in the
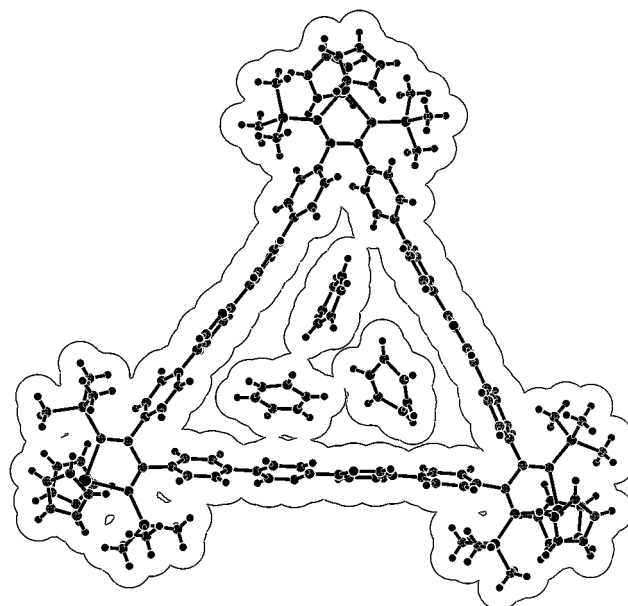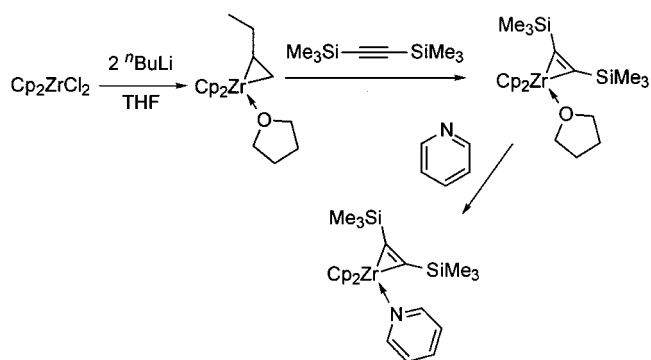

Figure 1. CHARON diagram of **5** showing three benzene guests and van der Waals surfaces.

Scheme 2

presence of $Me_3SiC{\equiv}CSiMe_3$, followed by the in situ displacement of the THF ligand by pyridine.

When equimolar amounts of $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ and **3** are mixed in benzene, crystals of **5** are observed to precipitate within hours. Heating to 40 °C enables nearly quantitative formation (91% isolated yield) of the macrocycle within 24 h. Thus, the efficient conversion to **5** may be assisted by its low solubility in benzene. The greater stability of $Cp_2\text{-}Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ seems to result in a higher selectivity for this reagent, as the deep purple zirconocene bipyridine complex observed with use of the Cp_2ZrCl_2/*n*-BuLi reagent does not form (visually or by NMR spectroscopy) under the new protocol. However, heating a toluene solution of **5** in a sealed NMR tube to 100 °C for 2 h resulted in the development of a purple color, and a ^1H NMR resonance at δ 5.37 appeared. The selective formation of zirconacyclopentadiene functionalities with use of the $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ reagent is, therefore, under kinetic control.

From a crystal grown during the course of the reaction, the X-ray crystal structure of **5** was determined (Figure 1). The

(15) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A. *Z. Anorg. Allg. Chem.* **1995**, *621*, 77.

(16) Cook, M. A.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1970**, *23*, 85.

(17) Mitchell, T. N. *Synthesis* **1992**, 803.

(18) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585.

(19) Ziessel, R.; Suffert, J.; Youinou, M.-T. *J. Org. Chem.* **1996**, *61*, 6535.

(20) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, *1980*, 627.

(21) Bishop, L. A.; Turner, M. A.; Kool, L. B. *J. Organomet. Chem.* **1998**, *553*, 53.

(22) Rosenthal, U.; Ohff, A.; Michalik, M.; Goerls, H.; Burlakov, V. V.; Shur, V. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1193.
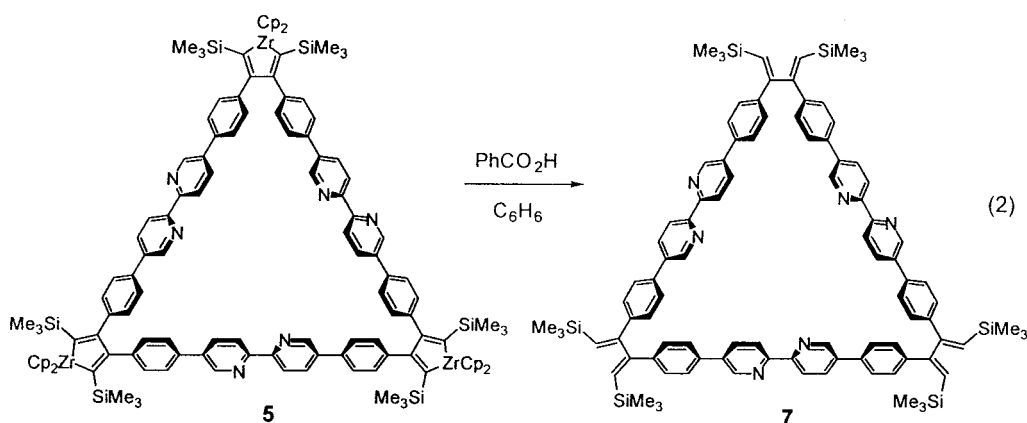
(23) Yamazaki, A.; Nishihara, Y.; Nakajima, K.; Hara, R.; Takahashi, T. *Organometallics* **1999**, *18*, 3015.

(24) Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1976**, *107*, C19.

structure consists of independent macrocycles, each of which contains three molecules of benzene as guests in the macrocycle cavity. The largest sphere that could be accommodated within the central cavity of the macrocycle would have a van der Waals radius of 6.03 Å. This is the length of the shortest vector that may be drawn from the center of the molecular cavity to the van der Waals surface of the bipyridyl groups. The average torsion angle between the phenyl and pyridyl rings is 37°, which is close to the literature value for biphenyl (44°),[25] and substantially greater than the average pyridyl−pyridyl torsion angle of 6°, which is close to the experimental value of 0° for 2,2′-bipyridine.[26]

Macrocycle **5** readily demetalates upon treatment with benzoic acid in benzene solution, yielding colorless cyclophane **7**, as shown in eq 2. Attempts to form porous coordination networks by linking molecules of **7** into a solid-state structure have so far proven unsuccessful. Mixtures of **7** with $CuPF_6$, $Cu(O_3SCF_3)$, $AgPF_6$, $Ag(O_3SCF_3)$, $AgNO_3$, and $Pd(BF_4)_2$ in nitromethane, acetonitrile, acetone, dimethylformamide, and pyridine yielded clear solutions of the same color as $M(bipy)_2$. Vapor or liquid diffusion of Et_2O or C_6H_6 into these solutions, or gels made from these solutions with poly(ethyleneoxide),[27] yield precipitated materials of poor crystallinity. Ongoing efforts along these lines are targeting derivatives of **7** that feature alternative structures that result from zirconocene-transfer reactions.

The zirconocene reagent $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ also allows the clean macrocyclization of diazadiene **4**, but the less rigid character of this diyne results in a dimerization, rather than a trimerization (eq 3). When this reaction was carried out in hexane, the yield was slightly improved to 66% (vs 63% in benzene solution). Highly soluble side products, which were presumed to be a mixture of oligomers and the diazadiene chelate complex of zirconocene, remained in the hexane solution after crystallization of the product. The broad peaks of the macrocycle in the proton NMR spectrum at room temperature in benzene-d_6 suggest a conformational equilibrium which is slow on the NMR time scale. A better spectrum with significantly improved resolution was obtained in dichloromethane-d_2 at room temperature.

Figure 2. (a) ORTEP diagram of one of the two crystallographically independent molecules of **6**, viewed down the pseudo-C_2 axis. Ellipsoids drawn at 50% probability. (b) Line drawing of **6** perpendicular to the pseudo-C_2 axis.

were grown by slow diffusion of pentane into a diethyl ether solution at −10 °C. An ORTEP view of **6** is given in Figure 2. The asymmetric unit contains two crystallographically independent molecules. Both are pseudo-C_2-symmetric and folded about an axis that passes roughly through the two diimine groups (Figure 2b). This folding may be described by the angles between the two ZrN_2 planes, which are 85 and 88° for the two molecules. It is associated with a twisting of the diimine units, which may be described by N−C−C−N torsion angles ranging from 89 to 103°. In this conformation, the C=N double bonds are nearly coplanar with the exocyclic phenyl rings. Two of the four nitrogen atoms point toward the center of the macro-

(2)

Attempts to demetalate macrocycle **6** with benzoic acid resulted in a complex reaction mixture which contained only a minor amount of the desired macrocyclic product (<40% isolated by column chromatography). A side product isolated from the same reaction was the diazadiene **4**, which indicates that benzoic acid acts to cleave the macrocycle.

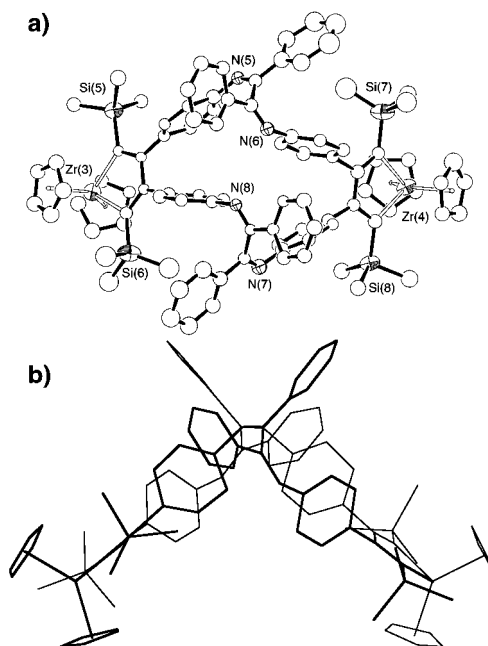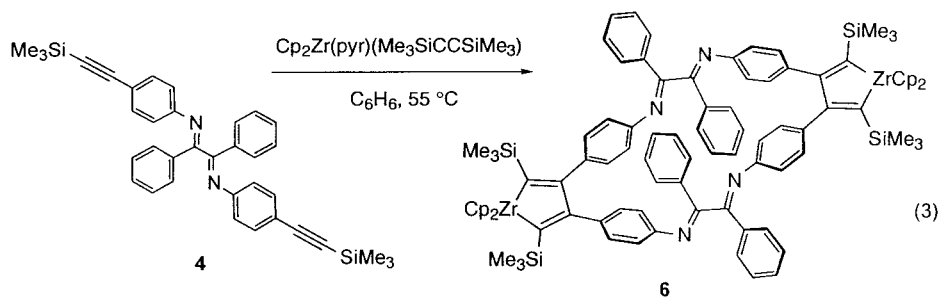Single crystals of macrocycle **6** suitable for an X-ray analysis

cycle and are separated by a distance of 3.6 Å, whereas the other two nitrogen atoms point away from the macrocycle center. The crystal of **6** that was used for data collection also contained substantial regions of electron density, which are undoubtedly due to incorporated solvent (about 32 molecules of diethyl ether or pentane per unit cell). This disordered solvent resulted in a rather poor resolution of the structure ($R = 11\%$).

(25) Almenningen, A.; Bastiansen, O.; Fernholt, L. *J. Mol. Struct.* **1985**, *128*, 59.
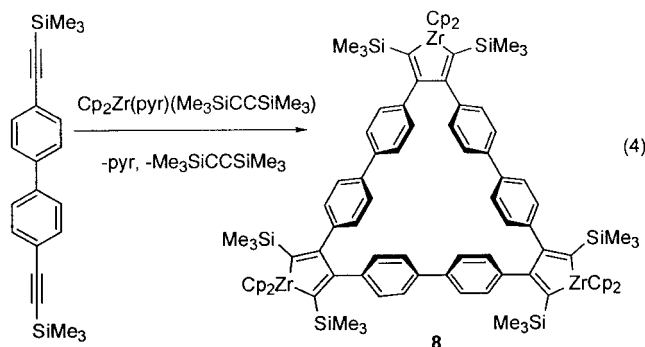
(26) Almenningen, A.; Bastiansen, O.; Gundersen, S.; Samdal, S. *Acta Chem. Scand.* **1989**, *43*, 932.

(27) Yaghi, O. M.; Li, G.; Li, H. *Chem. Mater.* **1997**, *9*, 1074.

Me₃Si—≡— [with 4-C₆H₄, N, Ph groups] **4** $\xrightarrow[\text{C}_6\text{H}_6,\ 55\ ^\circ\text{C}]{\text{Cp}_2\text{Zr(pyr)(Me}_3\text{SiCCSiMe}_3)}$ **6** (3)

Other Coupling Reactions with Cp₂Zr(pyr)(Me₃SiC≡CSiMe₃). To gain more insight into the observed selectivity exhibited by Cp₂Zr(pyr)(Me₃SiC≡CSiMe₃) for alkyne-coupling over bipyridine coordination, its direct reaction with 2,2′-bipyridine was examined. The reaction of 10 mg of the zirconocene reagent with 1 equiv of 2,2′-bipyridine in benzene-d_6 required ca. 24 h at 25 °C and gave a quantitative yield of the known complex Cp₂Zr(2,2′-bipyridine).[21]

The zirconocene reagent Cp₂Zr(pyr)(Me₃SiC≡CSiMe₃) reacts with 1 equiv of 4,4′-bis(trimethylsilylethynyl)biphenyl in benzene to yield a near-quantitative yield of the previously reported macrocycle **8** (eq 4). This observation suggests that the Cp₂Zr(pyr)(Me₃SiC≡CSiMe₃) reagent is superior to Cp₂ZrCl₂/n-BuLi, which yields macrocycle **8** in 90% isolated yield. One problem associated with the use of the latter reagent, which is avoided with the new protocol, is separation of the poorly soluble **8** from the Cp₂ZrCl₂/n-BuLi coproduct LiCl.

[Scheme for eq (4): biphenyl bis(trimethylsilylethynyl) starting material] $\xrightarrow[\text{-pyr, -Me}_3\text{SiCCSiMe}_3]{\text{Cp}_2\text{Zr(pyr)(Me}_3\text{SiCCSiMe}_3)}$ [macrocycle **8**] (4)

Use of Cp₂Zr(pyr)(Me₃SiC≡CSiMe₃) in the coupling of 5,5′-bis(trimethylsilylalkynyl)-2,2′-bipyridine was also investigated. The coupling of this diyne to macrocycle **9**, in 76% yield with Cp₂ZrCl₂/n-BuLi, was reported previously.[5] In benzene-d_6, the reaction of eq 5 proceeded to a 1:3 mixture of the desired macrocycle **9** and what is believed to be the bipyridine complex **10** (by ¹H NMR spectroscopy). However, when pentane was used as the reaction solvent, a 92% isolated yield of macrocycle **9** was obtained. In this case, it appears that the precipitation of **9** from pentane favors formation of the product. Note that the use of the Cp₂ZrCl₂/n-BuLi reagent in pentane under similar conditions is severely limited by the negligible solubility of Cp₂ZrCl₂ in nonpolar solvents at −78 °C.[28]

Concluding Remarks

The diyne macrocyclization chemistry described here was made possible by the identification of a new reagent for alkyne coupling, Rosenthal's Cp₂Zr(pyr)(Me₃SiC≡CSiMe₃). This reagent offers a number of compelling advantages over the widely used Cp₂ZrCl₂/n-BuLi and should significantly expand the scope of zirconocene-based coupling reactions. With the synthetic procedure introduced here, Cp₂Zr(pyr)(Me₃SiC≡CSiMe₃) is readily prepared in large quantities directly from commercially available Cp₂ZrCl₂. Unlike the zirconocene reagent that is generated by adding n-BuLi to Cp₂ZrCl₂, Cp₂Zr(pyr)(Me₃SiC≡CSiMe₃) is stable at room temperature, and can be stored indefinitely under an inert atmosphere. This allows much more precise control over the stoichiometry of reactions, especially because Cp₂Zr(THF)(1-butene) is unstable and may not form quantitatively. The stability of Cp₂Zr(pyr)(Me₃SiC≡CSiMe₃) also allows for coupling reactions that are slower and require elevated temperatures to drive the reactions to completion. The side products from coupling reactions (pyridine and Me₃SiC≡CSiMe₃) are soluble and volatile and, thus, much easier to remove than the LiCl side-product associated with Cp₂ZrCl₂/n-BuLi. A further advantage of this reagent derives from its solubility properties, which allow coupling reactions in a variety of solvents and, in particular, nonpolar solvents such as pentane. In contrast, use of the Cp₂ZrCl₂/n-BuLi reagent is generally limited to tetrahydrofuran solvent. Finally, Cp₂Zr(pyr)(Me₃SiC≡CSiMe₃) exhibits a useful selectivity in the coupling of alkynes in the presence of certain functional groups, such as diimine and pyridine groups. This latter factor has proven beneficial in providing synthetic routes to the functionalized macrocycles reported here.

In earlier reports, we described the use of zirconocene coupling in the high-yield syntheses of macrocycles having various shapes and sizes.[1−6] It is remarkable that in some cases, this method allows convenient, high-yield syntheses of macrocycles having very large molecular dimensions. Macrocycle **5**, which results from the cyclization of a diyne containing a spacer group of four aromatic rings, is similar in size to the macrocycle previously formed by the cyclization of Me₃SiC≡C(C₆H₄)₄C≡CSiMe₃.[6,29] In extending the utility of this method, we have sought to produce functionalized macrocycles that can act as ligands or participate in host−guest interactions. Whereas smaller rings containing bipyridine units have been reported previously, **5** represents the first macrocycle with the potential to display a wide range of binding properties due to its larger cavity. The formation of macrocycle **6** is interesting in that it represents a different kind of structure based on diyne dimerization, which results from the less rigid structure of the spacer group. Future investigations will address not only manipulation of macrocycle structures available via zirconocene-coupling routes, but the use of such derivatized macrocycles in supramolecular chemistry.

Experimental Section

General. 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 benzophen-

(28) Takahashi, T.; Kotora, M.; Fischer, R.; Nishihara, Y.; Nakajima, K. *J. Am. Chem. Soc.* **1995**, *117*, 11039.

(29) Mao, S. S. H. Ph.D. Thesis, the University of California, Berkeley, 1996.
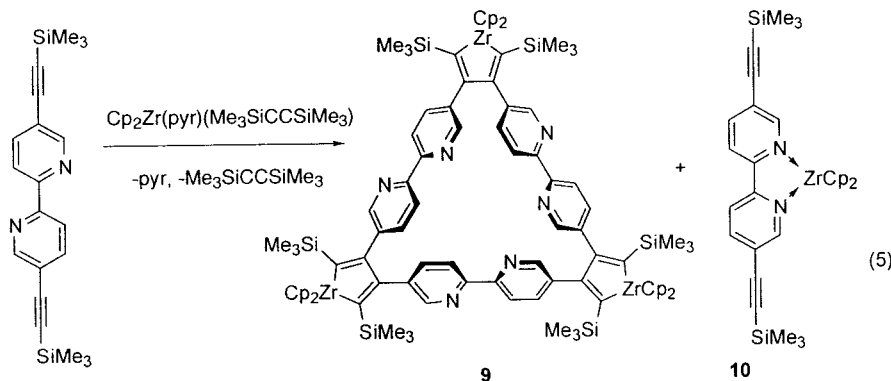
one ketyl. Toluene, toluene-d_8, and benzene-d_6 were distilled under nitrogen from Na/K. Methylene chloride-d_2 was distilled under vacuum from CaH$_2$. *n*-BuLi was used as a 1.6 M solution in hexanes. 4-(Trimethylsilyl)ethynyl-aniline,[20] 5,5′-dibromobipyridine,[30] and 5,5′-bis(trimethylsilylalkynyl)-2,2′-bipyridine[31] were prepared according to literature methods.

All NMR spectra were recorded at room temperature. Chemical shifts are referenced to the residual proton or carbon resonance of the deuterated solvent. In some cases, DEPT[32] 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 Desert Analytics.

An Improved Synthesis of Cp$_2$Zr(pyr)(Me$_3$SiC≡CSiMe$_3$). Cp$_2$-ZrCl$_2$ (5.00 g, 17.10 mmol) and Me$_3$SiC≡CSiMe$_3$ (2.91 g, 17.1 mmol) were loaded into a 400-mL Schlenk flask in the drybox and dissolved in dry THF (100 mL) on the Schlenk line. The clear, colorless solution was chilled to −78 °C in a dry ice/acetone bath, and *n*-BuLi (21.4 mL, 34.2 mmol) was added dropwise via syringe, causing a slow color change to light yellow. The mixture was stirred for 10 min at −78 °C, then the cold bath was removed and the reaction mixture allowed to warm to room temperature over 2 h, over which time it turned deep crimson. Pyridine (1.38 mL, 17.1 mmol) was then added via syringe, which caused the reaction mixture to immediately turn opaque purple. The solvent was then removed under dynamic vacuum until only 20 mL remained, at which point the reaction mixture was triturated with dry pentane (250 mL). The pentane solution was stirred for 30 min, then cannula-filtered into an Ar-purged 500-mL Schlenk flask. The volume of this solution was reduced by half under dynamic vacuum, and the flask was placed in a −80 °C freezer for 24 h, which resulted in the formation of opaque purple crystals. The supernatant was cannula-filtered off and the crystals dried under dynamic vacuum for 1 h. The isolated yield was 6.844 g, 85%. The ^{1}H and ^{13}C spectra of this compound in toluene-d_8 match the literature values.[15] ^{1}H NMR (500 MHz, benzene-d_6) δ 0.32 (br s, 18 H, Si(CH_3)$_3$), 5.46 (s, 10 H, cyclopentadienyl), 6.40 (m, 2 H, pyridine), 6.79 (m, 1 H, pyridine), 8.85 (m, 2 H, pyridine). ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6) δ 2.86 (Si(CH_3)$_3$), 106.71 (cyclopentadienyl), 123.43 (pyridine), 136.85 (pyridine), 154.41 (pyridine).

1-Trimethylsilyl-4-trimethylstannylbenzene. This compound has been reported in the literature.[16] The synthesis described herein requires only one reaction vessel and proceeds in higher yield. Into a 1-L Schlenk flask fitted with a 100 mL pressure-equalizing addition funnel was loaded 1,4-dibromobenzene (23.6 g, 100 mmol) in the drybox. Dry ether (300 mL) was added via cannula. The mixture was stirred until a clear solution was obtained, at which point the solution was chilled to −78 °C, using a dry ice/acetone bath, to give a white suspension. The addition funnel was then charged with *n*-BuLi (62.5 mL, 100 mmol), which was added dropwise with stirring. On completion of the addition, the cold bath was removed, and the light orange slurry was allowed to warm to 5 °C with stirring. The reaction was then once again chilled to −78 °C using the cold bath, and the addition funnel

was charged with trimethylsilyl chloride (12.7 mL, 100 mmol), which was then added dropwise at −78 °C. This caused the reaction mixture to change from orange to colorless. On completion of the addition, the cold bath was removed, and the reaction mixture was allowed to warm to room temperature. Stirring at room temperature was continued for 30 min. The reaction vessel was cooled to −78 °C again, and the addition funnel was again charged with *n*-BuLi (62.5 mL, 100 mmol), which was added dropwise with stirring, which caused the reaction mixture again to turn orange. The dry ice bath was removed after the addition was complete, and the reaction mixture was allowed to warm with stirring to 5 °C. The reaction mixture was then cooled to −78 °C again, and the addition funnel was charged with trimethylstannyl chloride (100 mL, 100 mmol, as supplied by Aldrich in THF solution), which was then added dropwise, which caused the orange suspension to bleach to a white suspension. The cold bath was then removed, and the reaction mixture was allowed to warm to room temperature and stirring was continued for 1 h. The clear, colorless reaction mixture, containing a copious amount of precipitated LiCl, was then washed with 200 mL of H$_2$O and dried over MgSO$_4$. It was then passed through a plug of 50 mL of silica, and solvents were removed under dynamic vacuum. The yield of colorless crystals was 29.78 g, 95%. ^{1}H NMR (500 MHz, benzene-d_6) δ 0.23 (s, 9H, Si(CH_3)$_3$), 0.25 (s, 9H, Sn(CH_3)$_3$), 7.52 (d, *J* = 7.5 Hz, 2H, phenylene), 7.49 (d, *J* = 7.5 Hz, 2H, phenylene); ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6) δ −9.52 (Sn(CH_3)$_3$), −0.75 (Si(CH_3)$_3$), 133.67, 136.03, 140.51, 143.28; GC-MS *m/z* 312 (M$^+$), 297 (M$^+$−CH$_3$), 239 (M$^+$−Si(CH$_3$)$_3$), 149 (M$^+$−Sn(CH$_3$)$_3$). Anal. Calcd for C$_{12}$H$_{22}$SiSn: C, 46.03; H, 7.08. Found: C, 46.43; H, 7.27.

5,5′-Bis(4-trimethylsilylphenyl)-2,2′-bipyridine. In the drybox, 1-trimethylsilyl-4-trimethylstannylbenzene (8.79 g, 28.1 mmol), 5,5′-dibromo-2,2′-bipyridine (4.19 g, 13.4 mmol), palladium dichloride (78.4 mg, 0.668 mmol), triphenylarsine (409 mg, 1.34 mmol), and lithium chloride (1.13 g, 26.7 mmol) were loaded into a 100-mL Schlenk flask with a Teflon stopper. Dry DMF (50 mL) was then added to the flask on the Schlenk line. The sealed flask was heated to 110 °C with vigorous stirring behind a shield. Over the next several hours, white product was observed to precipitate out of the green-brown homogeneous solution. The reaction was allowed to proceed for 96 h at 110 °C. The thick white slurry was treated with NaOH (1.12 g, 28 mmol) in H$_2$O (100 mL) to neutralize the toxic trimethylstannyl chloride byproduct and then collected on a medium frit. The product was then washed with H$_2$O (200 mL) and pentane (200 mL), and dried under dynamic vacuum. The yield of white powder was 5.60 g, 93%. ^{1}H NMR (500 MHz, benzene-d_6) δ 0.25 (s, 18H, Si(CH_3)$_3$), 7.42 (d, *J* = 8 Hz, 4H, phenylene), 7.48 (d, *J* = 8 Hz, 4H, phenylene), 7.68 (dd, *J* = 2.5, 8Hz, 2 H, pyridyl), 8.94 (dd, *J* = 1, 8 Hz, 2H, pyridyl), 9.12 (dd, *J* = 1, 2.5 Hz, 2H, pyridyl); ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6) δ -0.75 (Si(CH_3)$_3$), 121.73, 127.10, 134.71, 135.57, 137.11, 138.92, 140.44, 148.47, 155.92. EI-MS *m/z* 452 (M$^+$), 437 (M$^+$−CH$_3$). Anal. Calcd for C$_{28}$H$_{32}$N$_2$Si$_2$: C, 74.28; H, 7.12; N, 6.19. Found: C, 73.97; H, 7.27; N, 5.94.

5,5′-Bis(4-iodophenyl)-2,2′-bipyridine. A 500-mL, thick-walled Schlenk flask with a Teflon stopper was loaded with 5,5′-bis(4-trimethylsilylphenyl)-2,2′-bipyridine (1.80 g, 3.98 mmol) and purged with N$_2$. On the Schlenk line, dry CH$_2$Cl$_2$ (200 mL) was added, and the mixture was stirred until a clear, colorless solution was obtained.

(30) Romero, F. M.; Ziessel, R. *Tetrahedron Lett.* **1995**, *36*, 6471.

(31) Romero, F. M.; Ziessel, R. *Tetrahedron Lett.* **1994**, *35*, 9203.

(32) Derome, A. E. *Modern NMR Techniques for Chemistry Research*, 1st ed.; Pergamon: Oxford, 1987.

Iodine monochloride was melted by immersing the reagent bottle in a warm water bath (40 °C), and ICl (0.811 mL, 15.9 mmol) was added as a liquid under N_2 counterflow using a warm pipet. Reaction ensued immediately, with copious formation of a yellow precipitate from the burgundy solution. The stopper of the flask was closed, and the reaction was heated behind a shield to 45 °C (Caution! CH_2Cl_2 boils at 40 °C at 1 atm pressure) for 48 h. Once the reaction mixture had cooled to room temperature, a solution of NaOH (0.80 g, 19.8 mmol) and $Na_2S_2O_3$ (2.14 g, 15.9 mmol) in H_2O (50 mL) was added, and the flask was resealed. The reaction mixture was vigorously stirred for 12 h until the yellow precipitate had completely converted to a light tan precipitate. The organic phase, containing much precipitate, was then separated, washed with 2 N NH_4OH (50 mL), and reduced in volume to 100 mL under dynamic vacuum. The precipitate was then collected on a fine frit; was washed with H_2O (50 mL), CH_2Cl_2 (30 mL), and pentane (100 mL); and dried under dynamic vacuum. The yield was 1.82 g, 82%. ^{1}H NMR (500 MHz, dichloromethane-d_2) δ 7.45 (d, $J = 8.5$ Hz, 4H, phenylene), 7.86 (d, $J = 8.5$ Hz, 4H, phenylene), 8.03 (dd, $J = 3$, 8 Hz, 2H, pyridyl), 8.54 (dd, $J = 1$, 8 Hz, 2H, pyridyl), 8.91 (dd, $J = 1$, 3 Hz, 2H, pyridyl); EI-MS m/z 560 (M^+), 433 (M^+-I). Anal. Calcd for $C_{22}H_{14}I_2N_2$: C, 47.17; H, 2.52; N, 5.00. Found: C, 47.95; 2.48; N, 4.74.

5,5′-Bis(4-(trimethylsilylethynyl)phenyl)-2,2′-bipyridine (3). In the drybox, a 500-mL thick-walled Schlenk flask with a Teflon stopper was loaded with 5,5′-bis(4-iodophenyl)-2,2′-bipyridine (7.19 g, 12.8 mmol), Pd(PPh$_3$)$_4$ (297 mg, 0.257 mmol), and CuI (98 mg, 0.51 mmol). On the Schlenk line, dry toluene (250 mL) and diisopropylamine (50 mL) were added, and the mixture was stirred for 15 min, yielding a pink suspension. Trimethylsilylacetylene (5.44 mL, 38.5 mmol) was then added via syringe, and the flask was closed. The reaction mixture, which turned yellow over several hours, was stirred vigorously for 24 h. The solvents were then removed under dynamic vacuum, and the product (solubility in CH_2Cl_2 = 1.5 g/L) was taken up in 4 L of CH_2Cl_2. This suspension (diisopropylammonium iodide has very low solubility) was filtered through a plug of silica (500 mL), and the CH_2Cl_2 was removed under dynamic vacuum. The orange product was added to 500 mL of toluene in a 1-L flask, which was then stirred and brought to a boil and then allowed to cool to room temperature. The product was isolated on a medium frit, as white flakes, and dried under dynamic vacuum. The yield of pure product was 5.06 g, 79%. ^{1}H NMR (500 MHz, benzene-d_6) δ 0.28 (s, 18H, Si(CH_3)$_3$), 7.06 (d, $J = 8.5$ Hz, 4H, phenylene), 7.42 (dd, $J = 1$, 8 Hz, 2H, pyridyl), 7.49 (d, $J = 8.5$ Hz, 4H, phenylene), 8.83 (d, $J = 8$ Hz, 2H, pyridyl), 8.88 (d, $J = 1$ Hz, 2H, pyridyl); ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6) δ 0.41 (Si-(CH_3)$_3$), 96.11 (alkynyl), 106.06 (alkynyl), 121.59, 123.72, 127.03, 127.85, 133.23, 135.43, 136.03, 138.33, 148.27. EI-MS m/z 500 (M^+), 485 (M^+-CH_3). Anal. Calcd for $C_{32}H_{32}N_2Si_2$: C, 76.75; H, 6.44; N, 5.59. Found: C, 76.78; H, 6.44; N, 5.59.

1,4-Bis(4-(trimethylsilyl)ethynyl-phenyl)-2,3-diphenyl-1,4-diazabuta-1,3-diene (4). Titanium tetrachloride (1.31 mL, 2.27 g; 12.0 mmol) was dissolved in diethyl ether (125 mL) and the resulting solution was added to a solution of 4-(trimethylsilyl)ethynyl-aniline (5.18 g, 27.3 mmol), benzil (2.05 g, 9.70 mmol), and triethylamine (20 mL) in diethyl ether (300 mL). The mixture was stirred at 25 °C for 12 h and then filtered through diatomaceous earth and evaporated to dryness under dynamic vacuum. The crude product was recrystallized from diethyl ether. The yield was 4.55 g (74%) of yellow crystals. ^{1}H NMR (400 MHz, chloroform-d) δ 0.22 (s, 18H, Si(CH_3)$_3$), 1.20 (t, $J = 7.0$, 6H, CH_3 of Et$_2$O), 3.47 (q, $J = 7$, 4H, CH_2 of Et$_2$O), 6.41 (d, $J = 8.6$ Hz, 4H, phenylene), 7.19 (d, $J = 8.6$ Hz, 4H, phenylene), 7.3−7.5 (m, 6H, phenyl), 7.84 (d, $J = 7.1$ Hz, 4H, phenyl); ^{13}C NMR (100 MHz, chloroform-d) δ 0.24 (Si(CH_3)$_3$), 15.4 (CH_3 of Et$_2$O), 66.01 (CH_2 of Et$_2$O), 93.76 (alkynyl), 105.13 (alkynyl), 119.35, 119.96, 128.31, 128.82, 131.51, 132.23, 137.18, 149.32, 164.15 (C=N). EI-MS: M/z 552 (M^+), 372 ($M^+-C_{11}H_{13}NSi$), 276 ($M^+/2$).

Macrocycle 5. Diyne **3** (1.50 g, 3.00 mmol) and Cp$_2$Zr(pyr)(Me$_3$-SiC≡CSiMe$_3$) (1.41 g, 3.00 mmol) were loaded into a 100-mL Schlenk flask equipped with a Teflon stopper, which was then charged with dry benzene (90 mL). The flask was sealed, and the reaction mixture was sonicated at room temperature for 30 min, until it had become a deep brown homogeneous solution. The reaction mixture was then

heated to 40 °C for 24 h. Brown crystals of the product, some of which were of X-ray quality, precipitated from solution over this time. The solvent was removed by cannula filtration, and the product was dried under dynamic vacuum. The isolated yield was 1.97 g, 91%. ^{1}H NMR (500 MHz, benzene-d_6) δ −0.12 (s, 18 H, Si(CH_3)$_3$), 6.21 (s, 10H, cyclopentadienyl), 6.79 (d, $J = 8$ Hz, 4H, phenylene), 7.16 (d, obscured by solvent, phenylene), 7.36 (dd, $J = 2$, 8 Hz, 2H, pyridyl), 8.61 (d, $J = 8$ Hz, 2H, pyridyl), 8.85 (d, $J = 2$ Hz, 2H, pyridyl). Anal. Calcd for $C_{126}H_{126}N_6Si_6Zr_3$: C, 69.85; H, 5.86; N, 3.88. Found: C, 69.62; H, 5.85; N, 3.62.

Macrocycle 6. Diyne **4** (1.13 g, 1.80 mmol) and Cp$_2$Zr(pyr)(Me$_3$-SiC≡CSiMe$_3$) (0.89 g, 1.80 mmol) were dissolved in benzene (50 mL) and stirred at 55 °C for 24 h. The resulting orange solution was filtered and evaporated to dryness. The residue was washed twice with hexane (20 mL). Yield: 0.88 g (63%) of yellow microcrystals. Single crystals suitable for an X-ray analysis of the macrocycle could be grown by slow diffusion of pentane into a diethyl ether solution at −10 °C. ^{1}H NMR (400 MHz, benzene-d_6): δ −0.30 (br s, 36H, Si(CH_3)$_3$), 5.7−6.0 (br), 6.05 (br s, 20H, cyclopentadienyl), 6.5−6.7 (br), 6.8−7.1 (br), 7.8−8.2 (br); ^{1}H NMR (500 MHz, dichloromethane-d_2): δ −0.42 (s, 36H, Si(CH_3)$_3$), 5.62 (m, 4H, phenylene), 6.02 (m, 4H, phenylene), 6.29 (s, 20H, cyclopentadienyl), 6.61 (m, 8H, phenyl), 7.37 (m, 12H, phenyl), 7.84 (m, 8H, phenyl). FAB-MS (NPOE): m/z 1547 (M^+), 1327 (M^+-Cp_2Zr), 1107 ($M^+-2\ Cp_2Zr$). Anal. Calcd for $C_{100}H_{112}N_4Si_4O_2$-Zr$_2$: C, 70.79; H, 6.65; N, 3.30. Found: C, 71.04; H, 6.23; N, 3.28.

Macrocycle 7. Macrocycle **5** (1.97 g, 0.907 mmol) and benzoic acid (1.00 g, 8.19 mmol) were loaded into a 100-mL flask in the drybox. On the Schlenk line, dry benzene (50 mL) was added, and the reaction was stirred at room temperature for 12 h until the yellow color of the zirconacycle had faded. The solvent was then removed under dynamic vacuum, and the product mixture was suspended in CH_2Cl_2 (300 mL). The translucent suspension was washed with concentrated NH_4OH (100 mL) and H_2O (2 × 100 mL washes), dried over Na_2CO_3, and filtered through a plug of silica (100 mL). The CH_2Cl_2 was then removed under dynamic vacuum, and the product was recrystallized from boiling hexane/toluene. The isolated yield was 1.20 g, 88%. ^{1}H NMR (500 MHz, dichloromethane-d_2) δ −0.02 (s, 18H, Si(CH_3)$_3$), 6.31 (s, 2H, C=CH), 7.19 (d, $J = 8$ Hz, 4H, phenylene), 7.49 (d, $J = 8$ Hz, 4H, phenylene), 7.96 (dd, $J = 2$, 8 Hz, 2H, pyridyl), 8.41 (d, $J = 8$ Hz, 2H, pyridyl), 8.83 (d, $J = 2$ Hz, 2H, pyridyl); DEPT ^{13}C{^{1}H} NMR (125 MHz, dichloromethane-d_2) δ 0.43 (Si(CH_3)$_3$), 121.07 (C=CH), 126.23 (CH), 130.62 (CH), 131.78 (CH), 135.04 (C), 135.91 (CH), 136.22 (C), 142.02 (C), 147.75 (CH), 154.97 (C), 162.13 (C). FAB-MS m/z 1508 (M^+), 1473 (M^+-SiMe_3). Anal. Calcd for $C_{96}H_{102}N_6Si_6$: C, 76.44; H, 6.82; N, 5.57. Found: C, 76.52; H, 6.74; N, 5.62.

Reaction of Cp$_2$Zr(pyr)(Me$_3$SiC≡CSiMe$_3$) with 4,4′-Bis(trimethylsilylalkynyl)-biphenyl. Cp$_2$Zr(pyr)(Me$_3$SiC≡CSiMe$_3$) (8.29 g, 17.6 mmol) and 4,4′-bis(trimethylsilylalkynyl)biphenyl (6.16 g, 17.8 mmol) were loaded in the drybox into a 100-mL Schlenk flask with a Teflon stopper, and benzene (90 mL) was added. The dark purple color of the zirconocene reagent was seen to fade within minutes, passing through a deep amber color, which faded to a light yellow-orange within 2 h at 25 °C. The reaction was stirred for 48 h at 60 °C, and the orange supernatant was cannula-filtered off at room temperature. The isolated yield of orange crystals was 9.91 g, 99%. By ^{1}H and ^{13}C NMR, the product consisted solely of pure **8**. ^{1}H NMR (500 MHz, benzene-d_6) δ −0.26 (s, 18H, Si(CH_3)$_3$), 6.13 (s, 10H, cyclopentadienyl), 6.71 (d, $J = 8.4$ Hz, 2H, phenylene), 7.16 (d, obscured by solvent, phenylene).

Reaction of Cp$_2$Zr(pyr)(Me$_3$SiC≡CSiMe$_3$) with 5,5′-bis(trimethylsilylalkynyl)-2,2′-bipyridine in benzene-d_6. Cp$_2$Zr(pyr)(Me$_3$SiC≡CSiMe$_3$) (13.5 mg, 28.8 μmol) and 5,5′-bis(trimethylsilylalkynyl)-2,2′-bipyridine (10.0 mg, 28.8 μmol) were loaded in the drybox into a J-Young NMR tube, and benzene-d_6 (0.5 mL) was added. After 24 h at 25 °C, by ^{1}H NMR, only resonances corresponding to the two reported[5] rotamers of macrocycle **1**, pyridine, bis(trimethylsilyl)-acetylene, and those assigned to chelate **10** were present. ^{1}H NMR (500 MHz, benzene-d_6) bis(trimethylsilyl)acetylene δ 0.15 (s, 18H); pyridine δ 8.52 (m, 2H), 6.97 (m, 1H), 6.66 (m, 2H); macrocycle **1** δ −0.36, −0.37 (overlapping s, 31.5H, Si(CH_3)$_3$), 5.98, 5.99, 6.00 (overlapping s, 17.5H, cyclopentadienyl), 6.59 (dd, $J = 2$, 8 Hz, 1H, pyridyl), 6.78 (dd, $J = 2$, 6.5 Hz, 1H, pyridyl), 6.79 (dd, $J = 2.5$, 7 Hz, 1H, pyridyl),

6.92 (dd, $J = 2.5$, 8 Hz, 0.5H, pyridyl), 7.95 (d, $J = 8$ Hz, 1H, pyridyl), 8.18 (d, $J = 2.5$ Hz, 0.5H, pyridyl), 8.25 (d, $J = 7.5$ Hz, 1H, pyridyl), 8.25 (s, 1H, pyridyl), 8.35 (s, 0.5H, pyridyl), 8.37 (d, $J = 1$ Hz, 1H, pyridyl), 8.43 (d, $J = 1.5$ Hz, 1H, pyridyl), 8.55 (d, $J = 8.5$ Hz, 1H, pyridyl); putative chelate **8** δ 0.32 (s, 18H, Si(CH_3)$_3$), 5.16 (s, 10H, cyclopentadienyl), 6.43 (dd, $J = 1$, 8 Hz, 2H, pyridyl), 6.45 (dd, $J = 2$, 8 Hz, 2H, pyridyl), 7.75 (dd, $J = 1$, 2 Hz, 2H, pyridyl).

An Improved Synthesis of Bipyridine-Containing Macrocycle 1. Cp$_2$Zr(pyr)(Me$_3$SiC≡CSiMe$_3$) (3.14 g, 6.66 mmol) and 5,5′-bis-(trimethylsilylalkynyl)-2,2′-bipyridine (2.32 g, 6.66 mmol) were loaded in the drybox into a 400-mL Schlenk flask. On the Schlenk line, dry pentane (200 mL) was added via cannula. The reaction mixture changed color from opaque purple to opaque green over several minutes as the reagents dissolved. The reaction mixture was stirred for 48 h, during which time solid **1** precipitated from solution. The opaque green supernatant was removed by cannula filtration, and the dark green solid was washed with pentane (100 mL). The yellow, microcrystalline product was dried under dynamic vacuum for 2 h at 25 °C. The isolated yield was 3.49 g, 92%. NMR data match those previously reported.[4]

Reaction of Cp$_2$Zr(pyr)(Me$_3$SiC≡CSiMe$_3$) with 2,2′-Bipyridine. Cp$_2$Zr(pyr)(Me$_3$SiC≡CSiMe$_3$) (15.1 mg, 32.0 μmol) and 2,2′-bipyridine (5.0 mg, 32.0 μmol) were loaded into a J-Young NMR tube, and benzene-d_6 (0.5 mL) was added. By ^{1}H and ^{13}C NMR, only resonances corresponding to Cp$_2$Zr(2,2′-bipyridine), bis(trimethylsilyl)acetylene, and pyridine were observed after 24 h at 25 °C. The resonances assigned to Cp$_2$Zr(2,2′-bipyridine) match those reported in the literature.[25] ^{1}H NMR (500 MHz, benzene-d_6) bis(trimethylsilyl)acetylene δ 0.15 (s, 18H); pyridine δ 8.52 (m, 2H), 6.97 (m, 1H), 6.66 (m, 2H); Cp$_2$Zr-(bipyridine) δ 5.37 (m, 2H, pyridyl), 5.39 (s, 10H, cyclopentadienyl), 6.30 (m, 2H, pyridyl), 6.92 (m, 2H, pyridyl), 7.41 (m, 2H, pyridyl).

Supporting Information Available: Tables of crystal, data collection, and refinement parameters; bond distances and angles; and anisotropic displacement parameters for **5** and **6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0020310