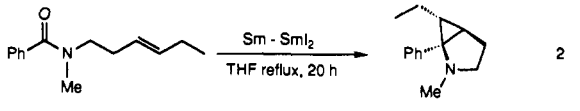
tramolecular coupling (run 5). Likewise, aliphatic amide **1g** underwent deoxygenative coupling with Sm/SmI_2 in the presence of HMPA[10] upon heating at 110 °C (run 6).

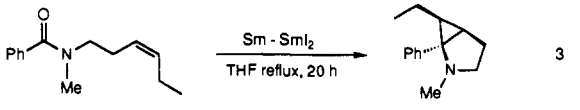
Two mechanistic pathways can be proposed for this coupling reaction, each beginning with a one-electron reduction of the amide to afford anion radical **4a**.[11] The first postulates dimerization of **4a** followed by deoxygenation to provide *vic*-diaminoalkene. The second hypothesis suggests that the initially formed anion radical **4a** undergoes further reduction to give α-aminocarbene intermediate **5a**. To explore the mechanism of this reaction, amide

4a **5a**

1h having an olefinic unit at an appropriate position was prepared and, upon subjection to the coupling conditions, yielded bicyclic product **3h** (41%) together with the coupling product **2h** (12%) (run 7). The formation of a three-membered ring is intriguing,[12] deserving additional inquiry into the stereochemistry of cyclopropanation.[13] As represented in eqs 2 and 3, the reaction of *trans*- and *cis*-3-hexenyl-substituted amides (*trans*- and *cis*-**1i**) gave rise to exo and endo products **3i**, respectively, with high stereoselectivity.[14] The stereospecificity observed in the cyclopropanation suggests the intermediacy of an α-aminocarbene.[15,17]



trans-1i *exo*-3i 2



cis-1i *endo*-3i 3

In summary, this work describes the first example of efficient deoxygenative coupling of amides, which has been achieved by the novel combination of Sm with SmI_2, and thus provides a straightforward access to *vic*-diaminoalkenes. Further studies on the scope and the precise mechanism of this coupling reaction are underway.

Acknowledgment. This research was supported by a Grant in Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining mass spectra with a JEOL JMS-DX303 instrument.

Supplementary Material Available: Listings of analytical data for the compounds prepared (IR, ^1H NMR, ^{13}C NMR, and mass spectra; elemental analyses) (5 pages). Ordering information is given on any current masthead page.

(10) Inanaga, J.; Ishikawa, M.; Yamaguchi, M. *Chem. Lett.* **1987**, 1485.
(11) When the reaction of **1a** with Sm/SmI_2 was carried out at room temperature, benzil (7%) was formed in addition to **2a** (59%), probably via the dimerization of anion radical **4a** followed by hydrolysis.
(12) For the samarium-promoted cyclopropanation of allylic alcohols and ethers, see: (a) Sasaki, M.; Collin, J.; Kagan, H. B. *Tetrahedron Lett.* **1988**, *29*, 6105. (b) Molander, G. A.; Etter, J. B. *J. Org. Chem.* **1987**, *52*, 3942. (c) Molander, G. A.; Harring, L. S. *J. Org. Chem.* **1989**, *54*, 3525. (d) Imamoto, T.; Kamiya, Y.; Hatajima, T.; Takahashi, H. *Tetrahedron Lett.* **1989**, *30*, 5149.
(13) Shono, T.; Masuda, H.; Murase, H.; Shimomura, M.; Kashimura, S. *J. Org. Chem.* **1992**, *57*, 1061.
(14) The exo/endo selectivity of this cyclopropanation is as follows: exo/endo = 9/1 (starting from *trans*-**1i**), 1/8 (from *cis*-**1i**).
(15) The reaction of *N*-benzylbenzamide with Sm/SmI_2 provided dibenzylamine (43%),[16] probably via an imine intermediate ($PhCH{=}NCH_2Ph$).[2] The formation of the imine may be explained by N-H insertion of the α-aminocarbene. For the N-H insertion of carbenes, see: (a) Husinec, S.; Juranic, I.; Llobera, A.; Porter, A. E. A. *Synthesis* **1988**, 721. (b) Singh, S. B.; Mehrotra, K. N. *Can. J. Chem.* **1981**, *59*, 2475. (c) Mehrotra, K. N.; Prasad, G. *Tetrahedron Lett.* **1978**, *43*, 4179.
(16) Kamochi, Y.; Kudo, T. *Tetrahedron Lett.* **1991**, *32*, 3511.
(17) For reports concerning α-aminocarbenes, see: (a) Schöllkopf, U.; Hauptreif, M.; Dippel, J.; Nieger, M.; Egert, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 192. (b) Gambaryan, N. P.; Kaitmazova, G. S.; Kagramanova, E. M.; Simonyan, L. A.; Safronova, Z. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 1102. (c) Moreno, M.; Lluch, J. M.; Oliva, A.; Bertran, J. *J. Chem. Soc., Perkin Trans. 2* **1986**, 183.

Synthesis of Three-Dimensional Nanoscaffolding†

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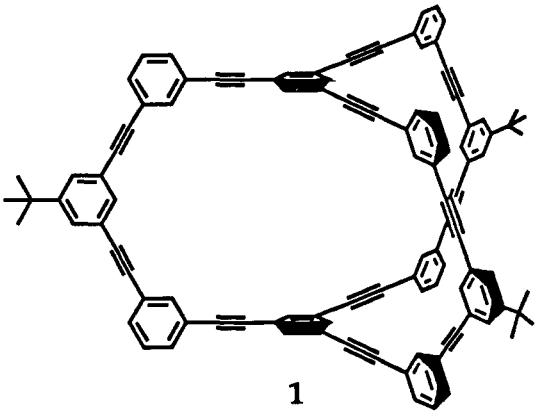
Recently there has been growing interest in the development of efficient synthetic methods that can function as "nanosize construction tools" for the assembly of geometrically well-defined objects on the molecular level.[1] Interest in these nanoarchitectures is driven by a diverse array of emerging ideas: the fabrication of multienzyme arrangements that provide unique catalytic possibilities,[2] the modular construction of large, discrete, and ordered molecular assemblies from prefabricated molecular components,[3] the achievement of mechanical control on the nanometer scale,[3] the assembly of devices that store and process information on the molecular level,[4] the fabrication of molecular monolayers of defined structure on the nanometer scale,[5] and the formation of perforated monolayers based on rationally designed molecular pores.[6] We have previously described an efficient method for synthesizing linear, phenylacetylene sequences[7] and showed how these could be cyclized into large planar macrocycles.[8]



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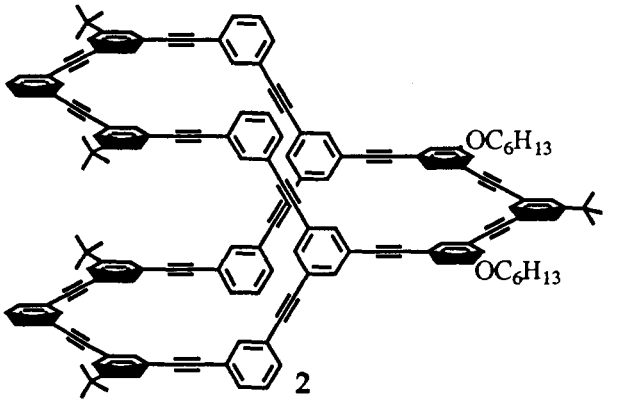

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† Nanoarchitectures. 4. For part 3, see: Zhang, J.; Moore, J. S. Aggregation of Hexa(phenylacetylene) Macrocycles in Solution: A Model System for Studying π–π Interactions. Submitted for publication.
‡ National Science Foundation Young Investigator, 1992–1997.

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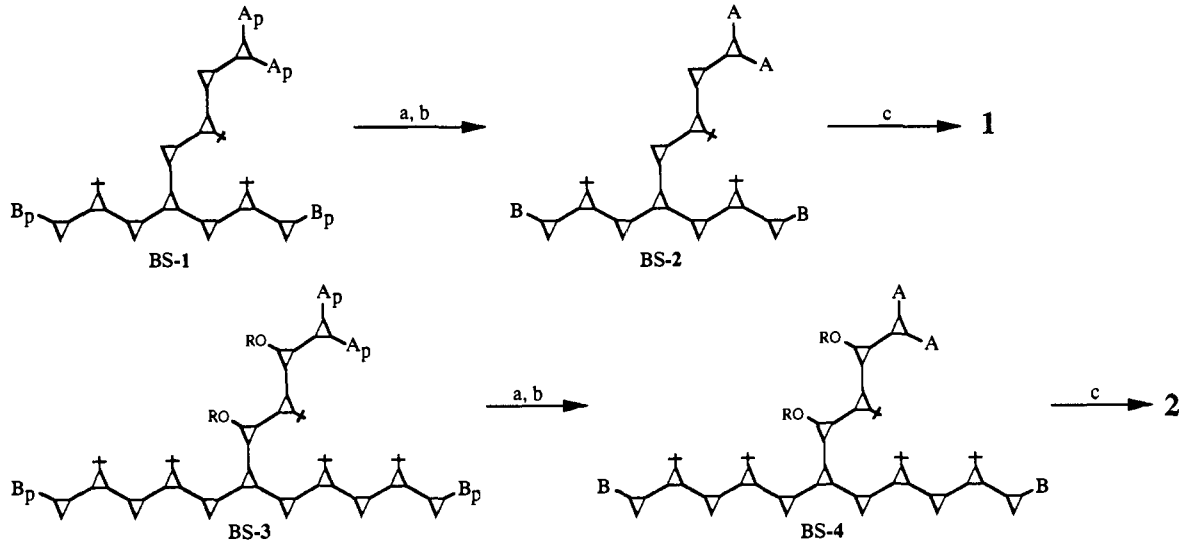
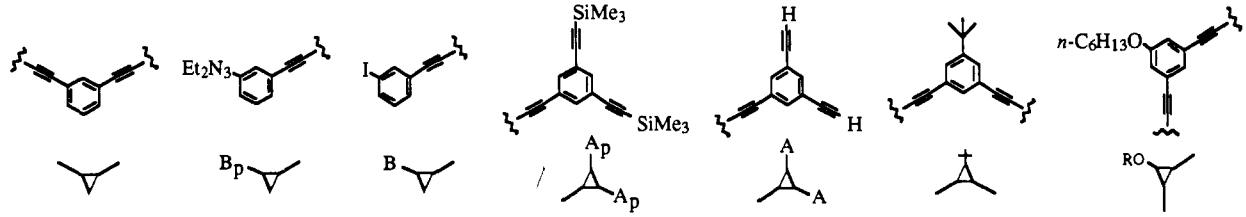
Scheme I[a,b]



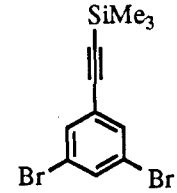
[a] Conditions: (a) CH_3I/100 °C; (b) KOH (catalyst)/CH_3OH/CH_2Cl_2/room temperature; (c) $[Pd(dba)_2]$/Ph_3P/CuI/Et_3N/toluene/70 °C. [b] Structure key:



Here we demonstrate that these methods can be extended to include branched sequences which, upon double cyclization, yield three-dimensional (3D) nanoscaffolding.

Macrobicyclic compounds[9] **1** and **2** were identified as interesting targets to test the double-cyclization concept. These structures represent fragments of trigonal networks whereby the aromatic rings can be pictured as network vertices and the acetylene bonds as network edges. The 120° bonding connectivity results from the all *m*-phenylacetylene repeat units. Out-of-plane angles are realized by 90° torsions about sp–sp^2 carbon–carbon single bonds. Compound **1** possesses 11 phenylacetylene repeat units and has D_{3h} symmetry while compound **2** contains 15 repeat units and has C_{2v} symmetry (in the conformations shown). Molecular models show that **1** is conformationally stiff and unable to undergo large torsional changes, while **2** can exist in a number of different conformations. One of the conformations of **2** includes a "collapsed form" in which the 15 aromatic rings are nearly all coplanar. This conformation can be realized by concerted torsional rotation about the set of six colinear bonds of macrobicyclic **2**. As an indication of the size of these molecules, the face-to-face separation between the triconnected aromatic rings of **1** is approximately 11.4 Å.

The synthesis of target macrobicyclics **1** and **2** was accomplished by double-cyclization of branched sequences **BS-2** and **BS-4** as shown in Scheme I. The symmetrical branch juncture of the corresponding protected sequences **BS-1** and **BS-3** was obtained by coupling 2 equiv of an α-diethyltriazene-ω-ethynyloligo(phenylacetylene) with dibromoarene **3**. Further elaborations at the



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branch junctures were then carried out following our previously reported repetitive phenylacetylene sequence synthesis.[7,10] The overall yields for the synthesis of **BS-1** and **BS-3** starting from monomeric compounds were 54% and 30%, respectively. Following deprotection at both ends, double-cyclization of **BS-2** and **BS-4**

(1) (a) Geometrical Objects from DNA. Zhang, Y.; Seeman, N. C. *J. Am. Chem. Soc.* **1992**, *114*, 2656–2663. (b) Molecular-Size Tinkertoy Construction Set. Kaszynski, P.; Friedli, A. C.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601–620. (c) Tectons. Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696–4698. (d) Molecular Lego. Kohnke, F. H.; Mathias, J. P.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl. Adv. Mater.* **1989**, *28*, 1103–1110. (e) Molecular Lines. Dietz, T. M.; Stallman, B. J.; Kwan, W. S. V.; Penneau, J. F.; Miller, L. L. *J. Chem. Soc., Chem. Commun.* **1990**, 367–369. (f) Polycubyls. Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230–7232.

(2) Chen, J. H.; Kallenbach, N. R.; Seeman, N. C. *J. Am. Chem. Soc.* **1989**, *111*, 6402–6407.

(3) Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Ganolfi, M. T.; Goodnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 193–218.

(4) (a) *Molecular Electronic Devices II.* Carter, F., Ed.; Marcel Dekker: New York, 1987. (b) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, England, 1991.

(5) Kwan, W. S. V.; Atanasoska, L.; Miller, L. L. *Langmuir* **1991**, 1419–1425.

(6) Markowitz, M. A.; Janout, V.; Castner, D. G.; Regen, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8192–8200.

(7) Zhang, J.; Moore, J. S.; Xu, Z.; Aguirre, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 2273–2274.

(8) Moore, J. S.; Zhang, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 922–924.

(9) For recent reviews of other large and complex synthetic cyclic compounds, see: (a) Knops, P.; Sendhoff, N.; Mekelburger, H.-B.; Vögtle, F. *Top. Curr. Chem.* **1992**, *161*, 1–36. (b) Seel, C.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 528–549. (c) Cram, D. J. *Nature* **1992**, *356*, 29–36.

proceeded smoothly to give macrobicyclics **1** and **2** in yields of 60% and 65%, respectively, after purification by silica gel chromatography.[11]

The cyclization products were white solids that were soluble in a wide range of organic solvents (e.g., $CHCl_3$, benzene, THF). The D_{3h} symmetry of **1** is evident from its ^1H NMR spectrum. This $C_{102}H_{66}$ hydrocarbon has only seven chemical shift nonequivalent aromatic protons in addition to a sharp singlet at δ 1.07 ppm corresponding to the *tert*-butyl groups. The ^1H NMR spectrum of **2** is somewhat more complex since 17 chemical shift nonequivalent aromatic protons are expected. Using H,H-COSY NMR (300 MHz, benzene-d_6), we have unambiguously identified the six isolated aromatic spin systems expected for **2**. The aromatic spin systems consisted of the following types: A_2X, ABX, A_2X, ABMX, ABX, and A_2MX present in relative ratios 1:2:2:4:4:2, respectively. The identification of these spin systems in their expected relative ratios leaves little doubt about the constitution of macrobicyclic **2**. Further confirmation of chemical structure has been obtained by FAB mass spectrometry.

Thin, hexagonal-shaped platelets of **1** have been grown from 1,4-dioxane. Interestingly, these crystals have proven to be fragile and extremely sensitive to solvent loss.[12] Crystals of **2** suitable for single-crystal structure determination have not yet been obtained. In summary, the combination of efficient double-cyclization and the ability to prepare branched phenylacetylene sequences of controlled structure offers chemists a powerful nanoscale construction set. The design of functionalized scaffolding that may order into nonclose packed hydrogen-bonded networks is in progress. Given our observations on crystals of **1**, such materials have intriguing possibilities as microporous organic solids.

Acknowledgment. This work was funded by the NSF under Grant CHE-9202095 (J.S.M.). J.S.M. thanks the 3M company for support through their nontenured faculty awards program.

Supplementary Material Available: Experimental procedures, characterization data of compounds **1**, **2**, and all oligophenylacetylene sequences, ^1H NMR spectrum of **1**, 2D H,H-COSY spectrum of **2**, and micrographs of crystals of **1** (22 pages). Ordering information is given on any current masthead page.

(10) Sequences were characterized by ^1H and ^{13}C NMR, elemental analyses, and size-exclusion chromatography. All compounds gave satisfactory characterization data. Complete experimental procedures and characterization data are given in the supplementary material.

(11) Except for elemental analyses, **1** and **2** gave satisfactory characterization data. Elemental analyses were hampered by incomplete combustion that left a significant char residue. Complete experimental procedures and characterization data for **1** and **2** are given in the supplementary material.

(12) Within seconds after removing the crystals from their mother liquor, they are observed to fracture and turn opaque. Representative micrographs are shown in the supplementary material. Unfortunately, X-ray diffraction even from pristine crystals left in the vapor of this mother liquor has been extremely weak.

A Catalytic Method for Asymmetric Nucleophilic Aromatic Substitution Giving Binaphthyls†

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A catalytic method for asymmetric reactions has long been a considerable challenge in synthetic organic chemistry.[1] Indeed, there have been many reports on chiral modifications of well-established catalysts such as phosphine–transition metals and Lewis acids and bases.[2] However, there have been very few reports on catalytic asymmetric carbon–carbon bond forming reactions in which organolithiums are controlled by a catalytic amount of asymmetric mediator.[3] We now describe a process wherein the reaction of naphthyllithium **2** with naphthyl imine **3**, containing a leaving group at C-1, is catalyzed by the dimethyl ether of (*R*,*R*)-1,2-diphenylethane-1,2-diol (**1**),[4] leading to the corresponding binaphthyl **7** in high enantiomeric excess (ee).[5]

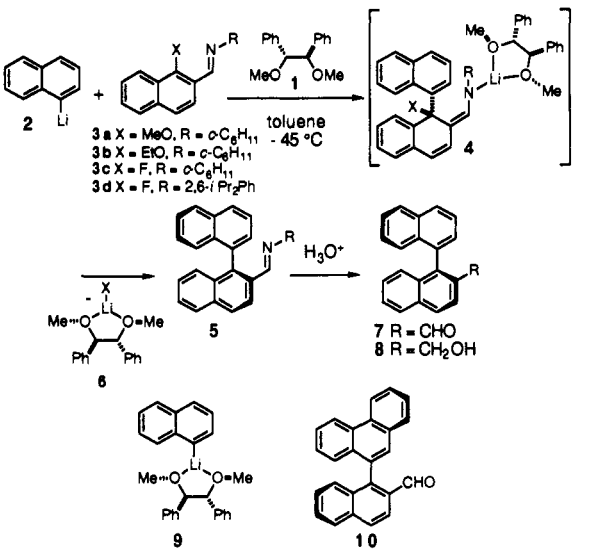

Figure 1.

The catalytic process (2.5 mol % of **1**/**2**) is exemplified by the following (Table I, entry 11): A solution of **1** (6.1 mg, 0.025 mmol) in toluene (1 mL) was added to a suspension of **2** (1.1 mmol, prepared from naphthylpropyltellurium and butyllithium)[6] in toluene (5 mL), and the mixture was stirred for 10 min at −23 °C. A solution of 1-fluoro-2-naphthaldehyde (2,6-diisopropylphenyl)imine (**3d**) (167 mg, 0.50 mmol) in toluene (1.5 mL) was added to the mixture at −78 °C, and the whole was stirred at −45 °C for 3.5 h. Usual workup and purification by silica gel column chromatography (hexane/Et_2O, 40/1) afforded (*R*)-*N*-(1,1′-binaphthalen-2-ylmethylidene)-2,6-diisopropylaniline (**5d**) ($[\alpha]^{25}_D$ −232° (*c* = 1.13, benzene)) in 82% ee and 97% yield.[7] The catalyst **1** was recovered quantitatively without any loss of optical purity. Hydrolysis ($H_2O/CF_3CO_2H/Na_2SO_4$ in THF) of **5d** and then reduction ($NaBH_4$ in methanol) of the corresponding aldehyde **7** furnished (*R*)-**8** ($[\alpha]^{25}_D$ +62.1° (*c* = 0.058, $CHCl_3$))[8] in 80% yield. Optically pure aldehyde **7** was obtained by a single recrystallization from ether/hexane in high yield. It is important to note that the reaction did not proceed smoothly in the absence of **1** in toluene, affording racemic **5d** in only 17% yield (80% recovery of **3d**) (entry 12).

The nucleophilic aromatic substitution giving **5** consists of two successive stereoselective processes; the first is enantioselective conjugate addition of the naphthyllithium–diether complex **9** to **3** giving **4**, and the second involves elimination of the LiX–diether complex **6** from **4** in which transfer of central chirality to axial chirality occurs. Regeneration of the complex **9** from **6** through ligand exchange is essential for the propagation of the catalytic asymmetric process.

We began our studies with the stoichiometric asymmetric reaction of cyclohexylimines **3a–c** bearing methoxy, ethoxy, and fluoro leaving groups. Methoxy imine **3a** was found to give, after hydrolysis, **7** with the best ee of 85% (entry 1). The catalytic version of this process, using 16 mol % of **1**, gave **7** in 78% ee. However, the chemical yield was only 29%, which corresponded

† We dedicate this paper to Professor S. Yamada on the occasion of his 77th birthday and to Professor A. I. Meyers on the occasion of his 60th birthday.
‡ University of Tokyo.
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