highly sophisticated catalysts,[4, 6] the experimental procedure is extremely simple, because there is no need to quench the catalyst (see Experimental Section). Partial racemization that would result from using a catalyst is avoided. Furthermore, the use of toxic and expensive catalysts that are difficult to prepare is not necessary. This strategy, that is, pressure-mediated substrate-catalyzed reactions might also be amenable to other reactions (Michael, Mannich, Baylis–Hillman), which are accelerated by pressure.[12] Further work along these lines is in progress.

Experimental Section

3a: A solution **1a** (66 mg, 0.2 mmol) and **2a** (108 µL, 2.0 mmol) in acetonitrile (3 mL) was placed in a sealed Teflon vessel. The reaction mixture was stirred at room temperature under atmospheric pressure until most of **1a** had dissolved (5 min). The tube was placed in a high-pressure reactor, and pressurized to 8 kbar at 25 °C. After 12 h, the pressure was released, and the reaction mixture was transferred from the Teflon vessel into a flask. The solvent was removed under reduced pressure. The crude products were purified by means of column chromatography (SiO$_2$, hexane/Et$_2$O 10:1) to give the *anti* isomer **3a** (52 mg, 67 %) and the *syn* isomer (11 mg, 14 %) (total yield 81 %, *anti*/*syn* 83:17). The enantiomeric excess was determined by means of HPLC analysis on DAICEL CHIRALCEL OJ.

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[1] For the most recent reviews on the Henry condensation, see: a) G. Rosini in *Comprehensive Organic Synthesis*, *Vol. 2* (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon, Oxford, **1991**, pp. 321–340; b) F. A. Luzzio, *Tetrahedron* **2001**, *57*, 915, and references therein.

[2] For recent examples of non-asymmetric nitro-aldol reactions based on achiral catalysts and promoters, see: D. Simoni, R. Rondanin, M. Morini, R. Baruchello, F. P. Invidiata, *Tetrahedron Lett.* **2000**, *41*, 1607; S. W. Youn, Y. H. Kim, *Synlett* **2000**, 880; R. Ballini, G. Bosica, M. Parrini, *Chem. Lett.* **1999**, 1105; T. Saiki, Y. Aoyama, *Chem. Lett.* **1999**, 797; V. J. Bulbule, V. H. Deshpande, S. Velu, A. Sudalai, S. Sivasankar, V. T. Sathe, *Tetrahedron* **1999**, *55*, 9325; G. Jenner, *New J. Chem.* **1999**, *23*, 525; H. M. S. Kumar, B. V. Subba Reddy, J. S. Yadav, *Chem. Lett.* **1998**, 637; I. Morao, F. Cossio, *Tetrahedron Lett.* **1997**, *38*, 6461; R. S. Varma, R. Dahiya, S. Kumar, *Tetrahedron Lett.* **1997**, *38*, 5131; D. Simoni, F. P. Invidiata, S. Manfredini, R. Ferroni, I. Lampronti, G. P. Pollini, *Tetrahedron Lett.* **1997**, *38*, 2749; R. Ballini, G. Bosica, *J. Org. Chem.* **1997**, *62*, 425; R. Ballini, G. Bosica, P. Forconi, *Tetrahedron* **1996**, *52*, 1677; S. Kiyooka, T. Tsutsui, H. Maeda, Y. Kaneko, K. Isobe, *Tetrahedron Lett.* **1995**, *36*, 6531; F. A. Luzzio, R. W. Ficth, *Tetrahedron Lett.* **1994**, *35*, 6013; U. Costatino, M. Curini, F. Marmottini, O. Rosati, E. Pisani, *Chem. Lett.* **1994**, 2218; H. Sasai, S. Arai, M. Shibasaki, *J. Org. Chem.* **1994**, *59*, 2661; R. Ballini, G. Bosica, *J. Org. Chem.* **1994**, *59*, 5466.

[3] For recent examples of (diastereoselective) asymmetric nitro-aldol reactions, see: A. V. Davis, M. Driffield, D. K. Smith, *Org. Lett.* **2001**, *3*, 3075; K. R. Knudsen, T. Risgaard, N. Nishiwaki, K. V. Gothelf, A. K. Jorgensen, *J. Am. Chem. Soc.* **2001**, *123*, 5843; A. Menzel, R. Ohrlein, H. Griesser, V. Wehner, V. Jager, *Synthesis* **1999**, 1691; E. Takaoka, N. Yoshikawa, Y. M. A. Yamada, H. Sasai, M. Shibasaki, *Heterocycles* **1997**, *46*, 157; J. Oshida, M. Okamoto, S. Azuma, T. Tanaka, *Tetrahedron: Asymmetry* **1997**, *8*, 2579; S. Hanessian, P. V. Devasthale, *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2201; K. Iseki, S. Oishi, H. Sasai, M. Shibasaki, *Tetrahedron Lett.* **1996**, *37*, 9081; P. Magnus, P. Pye, *J. Chem. Soc. Chem. Commun.* **1995**, 1933; H. Sasai, S. Arai, Y. Tahara, M. Shibasaki, *J. Org. Chem.* **1995**, *60*, 6656; H. Sasai, T. Tokunaga, S. Watanabe, T. Suzuki, N. Itoh, M. Shibasaki, *J. Org. Chem.* **1995**, *60*, 7388; A. P. Davis, K. J. Dempsey, *Tetrahedron: Asymmetry* **1995**, *6*, 2829; T. Nataka, T. Komatsu, K. Nagasawa, H. Yamada, T. Takahashi, *Tetrahedron Lett.* **1994**, *35*, 8225; R. Chinchilla, C. Najera, P. Sanchez-Agullo, *Tetrahedron: Asymmetry* **1994**, *5*, 1393; H. Sasai, Y. M. A. Yamada, T. Suzuki, M. Shibasaki, *Tetrahedron* **1994**, *50*, 12313; H. Sasai, N. Itoh, T. Suzuki, M. Shibasaki, *Tetrahedron Lett.* **1993**, *34*, 855; H. Sasai, T. Suzuki, N. Itoh,; M. Shibasaki, *Tetrahedron Lett.* **1993**, *34*, 851; H. Sasai, T. Suzuki, S. Arai, M. Shibasaki, *J. Am. Chem. Soc.* **1992**, *114*, 4.

[4] H. Sasai, W.-S. Kim, T. Suzuki, M. Shibasaki, M. Mitsuda, J. Hasegawa, T. Ohashi, *Tetrahedron Lett.* **1994**, *35*, 6123, see also references in [3] from this group.

[5] S. Hanessian, P. V. Devasthale, *Tetrahedron Lett.* **1996**, *37*, 987.

[6] E. J. Corey, F.-Y. Zhang, *Angew. Chem.* **1999**, *111*, 2057; *Angew. Chem. Int. Ed.* **1999**, *38*, 1931.

[7] M. T. Reetz, *Angew. Chem.* **1991**, *103*, 1559; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 15.

[8] M. T. Reetz, M. W. Drews, A. Schmitz, *Angew. Chem.* **1987**, *99*, 1186; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1141.

[9] K. Matsumoto, *Angew. Chem.* **1984**, *96*, 599; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 617.

[10] For a review on stereoselective reactions under high pressure, see: G. Jenner, *Tetrahedron* **1997**, *53*, 2669.

[11] The effect of pressure and solvent on the diastereoselectivity of reactions under high pressure have been discussed extensively by Tietze and co-workers; see: M. Buback, K. Gerke, C. Ott, L. F. Tietze, *Chem. Ber.* **1994**, *127*, 2241; L. F. Tietze, M. Henrich, I. Rothert, G. Kuchta, M. Buback, *Pol. J. Chem.* **1997**, *71*, 1749; M. Buback, G. Kuchta, A. Niklaus, M. Henrich, I. Rothert, L. F. Tietze, *Liebigs Ann.* **1996**, 1151; L. F. Tietze, M. Henrich, A. Niklaus, M. Buback, *Chem. Eur. J.* **1999**, *5*, 297.

[12] For reviews of organic reactions under high pressure from our laboratory, see: *Organic Reactions at High Pressures* (Eds.: K. Matsumoto, R. M. Acheson), Wiley, New York, **1991**; M. Ciobanu, K. Matsumoto, *Liebigs Ann.* **1997**, 623; K. Matsumoto, M. Kaneko, H. Katsura, N. Hayashi, T. Uchida, R. M. Acheson, *Heterocycles* **1998**, *47*, 1135.

Sigmatropic Shiftamers: Fluxionality in Broken Ladderane Polymers[**]

Dean J. Tantillo and Roald Hoffmann[*]

Construction principles: Consider the hypothetical ladder polymer **1**-“[∞]-ladderane.”[1, 2] A formal [2+2] cycloreversion would lead to **2** in which a local “defect,” consisting of two parallel π bonds, is formed. Cope rearrangement via a boatlike transition structure would give **2′**, which is, of course, equivalent to **2** (Scheme 1). Continued indefinitely, this process would lead to a pair of double bonds running down the polymer chain.

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[*] Prof. R. Hoffmann, Dr. D. J. Tantillo
Department of Chemistry
Baker Laboratory
Cornell University, Ithaca NY 14853-1301 (USA)
Fax: (+1) 607-255-5707
E-mail: rh34@cornell.edu

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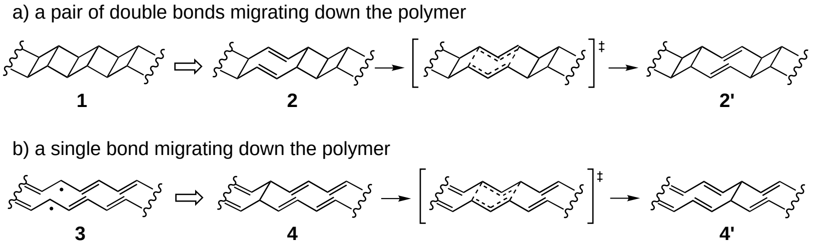
Supporting information for this article (Coordinates and energies for computed structures from Scheme 2, as well as structures involved in the Cope rearrangements of **6** and **7**.) is available on the WWW under http://www.angewandte.com or from the authors.



Scheme 1.

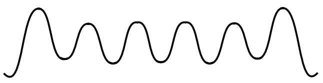
Next, consider another hypothetical system, **4**, which can be derived formally by dimerization of two neutral solitons,[3] each on a different polyacetylene chain (**3**). Sequential Cope rearrangements in **4** would send a single bond traveling down the infinite chain (Scheme 1). One can also envisage systems in which 2, 3, or more sigma bonds are moving. Of course, the dangling chains in **4** would not stay in the requisite geometry for propagation unless they were constrained by some feat of molecular engineering. A variety of linking architectures can be envisioned, and we are currently investigating ones based on the barbaralane framework.[4]

If the barriers to Cope rearrangement were low enough in these systems, **2** and **4** would be fluxional polymers. We suggest that such polymers be called "sigmatropic shiftamers"[5] to indicate the source of their fluxionality. We describe computations on oligomeric models of **2** and related systems, which suggest that fluxionality in these shiftamers should indeed occur at room temperature.[6]

Computational methods: All calculations were performed with the Gaussian 98 program.[7] Geometries were optimized at the B3LYP/6-31G(d) level,[8] which has been shown to perform well in describing structures and energetics for pericyclic reactions, including Cope rearrangements.[9, 10] All structures were characterized by frequency calculations at the B3LYP/6-31G(d) level, and zero-point energy corrections (scaled by 0.9806)[11] from these calculations are included in the reported energies.

Oligomeric models: Relative energies for diene isomers derived from [2]-[10] to [7]-ladderanes and the transition structures for their interconversion are shown in Scheme 2, and the geometries of a selected "internal" diene and transition structure in Figure 1.[12, 13] In the internal dienes, bridging cyclobutane bonds on the perimeter of cyclooctadiene substructures are consistently elongated (1.63 – 1.64 Å) relative to the other C–C single bonds, which range from 1.55 to 1.57 Å. The alkene carbon atoms are also significantly pyramidalized (arrow, Figure 1). These distortions lead to structures which are preorganized for Cope rearrangement.

Barriers for internal rearrangements—those that interconvert isomers containing cyclooctadiene substructures—converge to approximately 15 kcal mol^{-1} as more cyclobutanes are fused to the ends (Scheme 2).[14, 15] This provides an estimate of the barrier for Cope rearrangement in the infinitely extended system—the shiftamer **2**. A barrier of 15 kcal mol^{-1} is low enough that fluxionality should be observable without the need for elevated temperatures. For a typical oligomer, the potential surface will resemble that shown in **5**: a series of low internal barriers of comparable height which mimic the surface for the infinite system, flanked by higher barriers for rearrangement to the most stable isomers with terminal acyclic hexadiene substructures.



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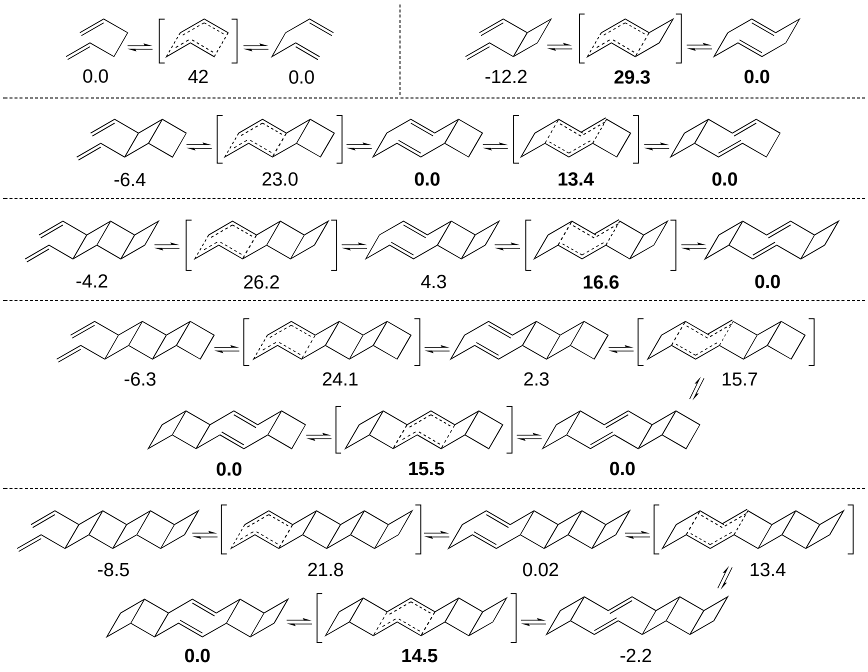


Scheme 2. Relative energies [kcal mol^{-1}] for rearrangements in oligomer models of **2**. For each system, energies are shown relative to that of the diene isomer with the innermost alkenes. Estimated barriers for the innermost Cope rearrangement in each system are highlighted in bold.

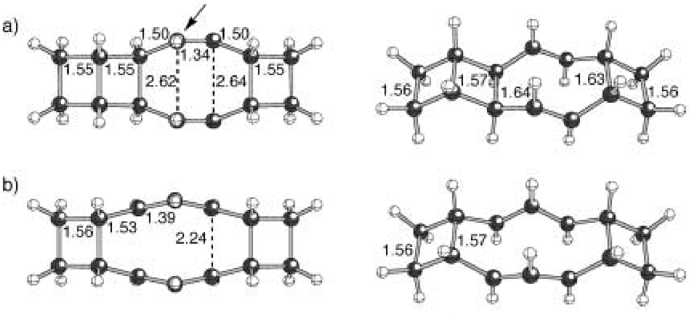
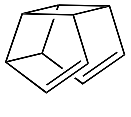


Figure 1. Selected carbon – carbon distances [Å] for a representative oligomer (a) and Cope rearrangement transition structure (b). Two views of each are shown. The arrow points to one of the highly pyramidalized alkene carbon atoms.

Running rings around: The oligomers shown in Scheme 2 extrapolate to the infinite linear polymer **2** by *trans* fusion of additional cyclobutanes. *cis* fusions produce systems that curl up on themselves and eventually "close" to discrete cyclic molecules, thereby achieving infinity through circularity.

Hypostrophene **6** (a "broken" pentaprismane) is one such molecule. Experiments indicate that **6** rearranges rapidly at 35 °C,[16a] and our calculations predict a rearrangement barrier of 21.9 kcal mol^{-1},[16b] considerably larger than the barrier we predict for rearrangement in the broken ladderane polymer **2** ($\sim$15 kcal mol^{-1}).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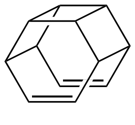
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Insertion of an additional cyclobutane ring into **6** leads to the broken hexaprismane **7**. We predict a rearrangement barrier of 25.0 kcal mol^{-1} for **7**, again much higher than that in **2**. Although this molecule has been synthesized,[17] it seems that its degenerate Cope rearrangement has not been observed experimentally, perhaps due to its propensity for decomposition to two molecules of benzene.

More elaborate systems can also be imagined.[18] For example, consider the very highly strained—yet to our eyes beautiful—**8** (Figure 2), a product of multiple pentaprismane fusions, which bears the burden of multiple [2.2.2]propellane subunits. Formal [2+2] cycloreversions of various cyclobutane rings in **8** would produce a series of molecules with pairs of parallel π bonds (**9**–**11**). All of these isomers could, in theory, interconvert by combinations of different flavors of Cope rearrangement (**A**–**D**).[19]

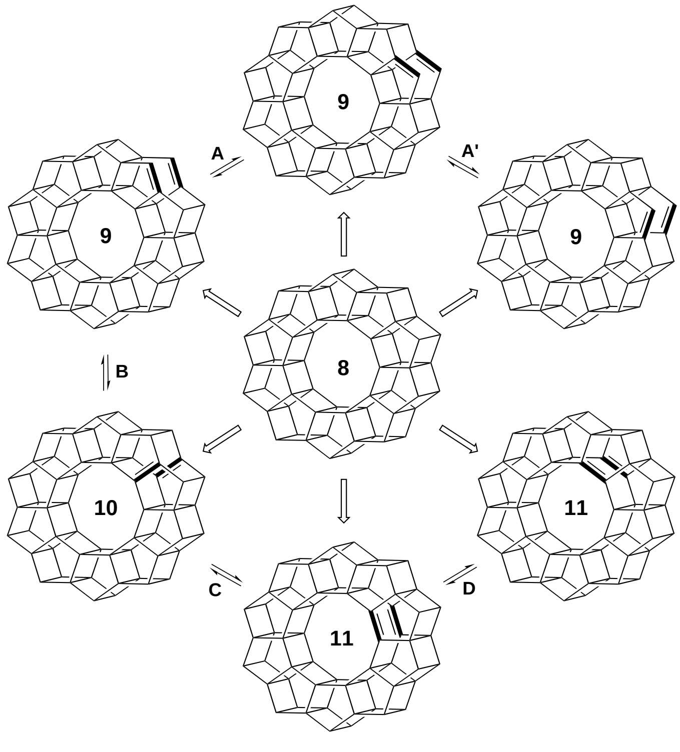

Figure 2. Hypothetical system (**8**) constructed from fused pentaprismanes. Various formal [2+2] cycloreversions in **8** lead to molecules (**9**–**11**) with pairs of parallel π bonds that can interconvert by various combinations of Cope rearrangements (**A**–**D**).

Conclusions: We predict that the shiftamer **2** should be fluxional at room temperature, its pair of parallel alkenes running back and forth along the polycyclobutane framework. Other sigmatropic shiftamers are currently under investigation.

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[1] Studies on [*n*]-ladderanes include: a) M. A. Miller, J. M. Schulman, *J. Mol. Struct. (THEOCHEM)* **1988**, *163*, 133–141; b) G. Mehta, M. B. Viswanath, G. N. Sastry, E. D. Jemmis, D. S. K. Reddy, A. C. Kunwar, *Angew. Chem.* **1992**, *104*, 1557; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1488–1490; c) R. N. Warrener, I. G. Pitt, E. E. Nunn, C. H. L. Kennard, *Tetrahedron Lett.* **1994**, *35*, 621–624; d) R. N. Warrener, G. Abbenante, C. H. L. Kennard, *J. Am. Chem. Soc.* **1994**, *116*, 3645–3646; e) G. Mehta, M. B. Viswanath, A. C. Kunwar, K. R. Kumar, D. S. K. Reddy, *J. Chem. Soc. Chem. Commun.* **1994**, 739–740; f) G. Mehta, M. B. Viswanath, A. C. Kunwar, *J. Org. Chem.* **1994**, *59*, 6131–6132; g) G. Mehta, M. B. Viswanath, A. C. Kunwar, *Synlett* **1995**, 317–318; h) G. Mehta, M. B. Viswanath, *J. Braz. Chem. Soc.* **1996**, *7*, 219–224; i) J. Delaunay, A. Orliac, J. Simonet, *C. R. Acad. Sci. Ser. II B* **1997**, *324* 269–273; j) H. Hopf, H. Greiving, P. G. Jones, P. Bubenitschek, *Angew. Chem.* **1995**, *107*, 742; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 685–687.

[2] Infinite ladderane substructures are present in hundreds of Zintl phases crystallizing in the BaIn$_2$ (CeCu$_2$) and TiNiSi structures: a) G. Nuspl, K. Polborn, J. Evers, G. A. Landrum, R. Hoffmann, *Inorg. Chem.* **1996**, *35*, 6922–6932; b) G. A. Landrum, R. Hoffmann, J. Evers, H. Boysen, *Inorg. Chem.* **1998**, *37*, 5754–5763. The orbitals of ladderane polymers are discussed in a).

[3] The language of solitons (or polarons) is not an accident here; sigmatropic shiftamers can be also viewed in the context of this language, developed for polyacetylene and other conjugated polymers: J. C. W. Chien, *Polyacetylene*, Academic Press, Orlando, **1984**.

[4] For leading references, see: a) H. Quast, M. Seefelder, C. Becker, M. Heubes, E.-M. Peters, K. Peters, *Eur. J. Org. Chem.* **1999**, 2763–2779; b) W. v. E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, M. Saunders, *Tetrahedron* **1967**, *23*, 3943; c) R. V. Williams, *Chem. Rev.* **2001**, *101*, 1185–1204.

[5] Both **2** and **4** would be [3,3]-shiftamers.

[6] Results on derivatives of **4** will be reported in due course.

[7] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

[8] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372–1377; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.

[9] Reviews: a) O. Wiest, D. C. Montiel, K. N. Houk, *J. Phys. Chem. A* **1997**, *101*, 8378–8388; b) K. N. Houk, B. R. Beno, M. Nendel, K. Black, H. Y. Yoo, S. Wilsey, J. K. Lee, *J. Mol. Struct. (THEOCHEM)* **1997**, *398–399*, 169–179; c) D. A. Hrovat, B. R. Beno, H. Lange, H.-Y. Yoo, K. N. Houk, W. T. Borden, *J. Am. Chem. Soc.* **2000**, *122*, 7456–7460.

[10] Representative recent calculations on Cope rearrangements: a) D. J. Tantillo, R. Hoffmann, *J. Org. Chem.* **2002**, in press; b) O. Wiest, K. A. Black, K. N. Houk, *J. Am. Chem. Soc.* **1994**, *116*, 10336–10337; c) H. Jiao, P. von R. Schleyer, *Angew. Chem.* **1995**, *107*, 329; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 334–337.

[11] A. P. Scott, L. Radom, *J. Phys. Chem.* **1996**, *100*, 16502–16513.

[12] Only "chairlike" (as opposed to "twist") isomers[13] of 1,5-cyclooctadiene substructures were considered due to the geometric constraints of the polymers.

[13] Experiments and force-field calculations on 1,5-cyclooctadiene: a) G. M. Whitesides, G. L. Goe, A. C. Cope, *J. Am. Chem. Soc.* **1967**, *89*, 7136–7137; b) D. Boeckh, R. Huisgen, H. Noeth, *J. Am. Chem. Soc.* **1987**, *109*, 1248–1249; c) N. L. Allinger, J. T. Sprague, *J. Am. Chem. Soc.* **1972**, *94*, 5734–5747.

[14] Barriers for Cope rearrangement of species with terminal acyclic hexadiene units were found to converge rapidly upon cyclobutane fusion to approximately 30 kcal mol^{-1} (from 42 kcal mol^{-1} in the parent boatlike cyclohexadiene,[10] Scheme 2). Also, [*n*]-ladderane oligomers were generally found to be <4 kcal mol^{-1} more stable than the broken [*n*]-ladderane isomers with central cyclooctadiene substructures derived from them (i.e. those species whose relative energies are set to 0.0 in Scheme 2).

[15] We have not yet investigated substituent effects on this rearrangement; appropriately designed, they may lower the barrier even further.

[16] a) R. Pettit, J. S. McKennis, L. Brener, J. S. Ward, *J. Am. Chem. Soc.* **1971**, *93*, 4857–4958; b) previous calculations predict similar rearrangement barriers: B. Das, K. L. Sebastian, *Chem. Phys. Lett.* **2000**, *330*, 433–439, and references therein.

[17] a) N. C. C. Yang, B. J. Hrnjez, M. G. Horner, *J. Am. Chem. Soc.* **1987**, *109*, 3158–3159; b) N. C. C. Yang, M. G. Horner, *Tetrahedron Lett.* **1986**, *27*, 543–546; c) HF/6-31G* calculations on the structure and energy of **7** relative to other $C_{12}H_{12}$ isomers have also been reported: G. W. Schriver, D. J. Gerson, *J. Am. Chem. Soc.* **1990**, *112*, 4723–4728.

[18] Such systems include, for example, the asteranes[1a]—isomers of large prismanes with combinations of *cis* and *trans* fused cyclobutanes.

[19] The size of these molecules has, so far, precluded computations on their putative fluxionality.

Ultrastable and Highly Acidic, Zeolite-Coated Mesoporous Aluminosilicates**

Do Trong On and Serge Kaliaguine*

The acidity and hydrothermal stability of mesoporous aluminosilicates (MesoAS) are relatively low compared to those of zeolites, which limits their potential applications as catalysts in petroleum refining and fine chemicals synthesis.[1–7] Much effort has therefore been undertaken to synthesize a new type of materials, which combines the advantages of both zeolites and mesoporous molecular sieves. One might expect to improve both the stability and acidity of these materials if zeolite-like order could be introduced into the mesopore walls. Recent advances showed that amorphous walls of the mesostructure could indeed be converted to a partially zeolitic product.[8–13] For example, MCM-41/MFI composites containing interconnected mesopores and micropores were prepared by using dual templates and exhibited enhanced acidity and steam stability compared to the corresponding MCM-41.[8, 9] Furthermore, the use of zeolite seeds as precursors for the assembly of mesoporous aluminosilicates with high hydrothermal stability and acidity was reported by Pinnavaia et al.[10] A similar zeolite beta type of materials was also prepared in the presence of co-templates of tetraethylammonium hydroxide and cetyltrimethylammonium bromide.[11] Recent results from our group showed the preparation of a new type of materials with semicrystalline zeolitic mesopore walls based on a templated solid-state secondary crystallization of zeolites starting from the amorphous walls of SBA-15. Bright- and dark-field transmission electron microscope (TEM) images recorded on the same area of the sample indicated that nanocrystals were embedded in the continuous amorphous inorganic matrix to form semicrystalline wall structures while preserving the mesoporous structure. The resulting mesoporous materials had much stronger acidity than those of the corresponding amorphous alumosilicates and a much improved hydrothermal stability.[12]

Herein, we describe a new approach for the production of unusual zeolite-coated mesoporous aluminosilicates (ZCMeso-AS) using diluted clear solutions containing primary zeolite units. Hydrothermally ultrastable and highly acidic ZCMeso-AS result owing to the nanocrystalline zeolitic nature of their pore wall surface. These features open new possibilities for using this type of materials as acid catalysts.

It is of special concern that due to the size of primary ZSM-5 units templated by tetrapropylammonium ions (2.8 nm in diameter),[13–14] the pore diameter of the mesoporous precursor molecular sieves should be higher than 30 Å. The methods in references [2] and [3] are therefore useful in this context for the preparation of mesoporous precursors, such as SBA-15 and siliceous mesostructured cellular foams (MCFs).

The N_2 adsorption/desorption isotherms obtained from the calcined sample before and after coating are shown in Figure 1A. The parent and ZSM-5-coated samples display the typical behavior of a mesoporous molecular sieve with a mesopore volume saturation capacity of about 1.56 and 0.78 cm^3 g^{-1}, respectively (Table 1). The P/P_0 position of the inflection point is related to a diameter in the mesopore range, and the sharpness of these steps indicates the uniformity of the pore size. A narrower distribution of the pore diameter of the coated sample compared to that of the parent sample was observed (Figure 1B). Furthermore, a significant decrease in pore diameter (from 70 to 54 Å) and in surface area (from 800 to 465 m^2 g^{-1}) could conceivably be ascribed to the ZSM-5 nanocrystals coated inside the mesopore channels of the host. Figure 2 shows a TEM image of the ZSM-5-coated MesoAS. A uniform pore size with a highly ordered structure is still observed for this sample after the coating procedure.

The ZSM-5-coated MesoAS sample shows a FTIR absorption band at 550 cm^{-1}, which is not present in the parent MesoAS sample (Figure 3). The band around 550 cm^{-1} has been assigned to the asymmetric stretching mode in double-

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[*] Prof. S. Kaliaguine, Dr. D. Trong On
Department of Chemical Engineering
Laval University
Quebec G1K7P4 (Canada)
Fax: (+1) 418-656-3810
E-mail: kaliagui@gch.ulaval.ca

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