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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Received July 9, 1992

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]

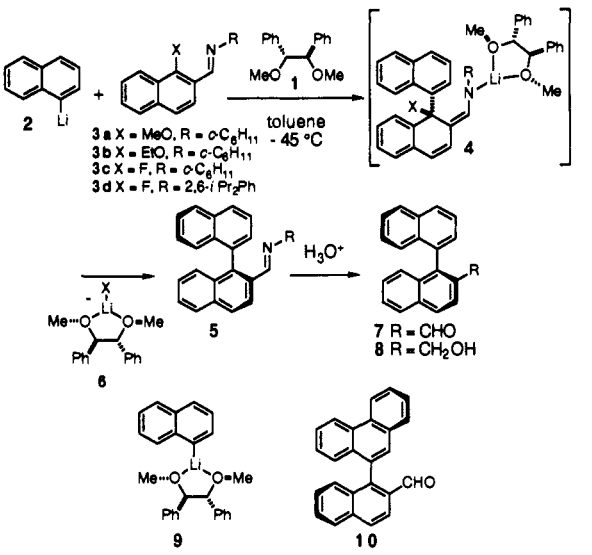

Figure 1.

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.

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0002-7863/92/1514-8732$03.00/0

Table I. Asymmetric Nucleophilic Aromatic Substitution Providing Binaphthyls[a]

entry	X	R	2[b]	1/2[c]	time, h	5, 7	ee, %[d]	yield, %[e]
1	MeO	c-hex	A	1.1	1.5	7	85 (98)[f]	90 (64)[f]
2	EtO	c-hex	A	1.1	3	7	62	86
3	F	c-hex	A	1.1	1.5	7	57	94
4	MeO	c-hex	A	0.16	6.5	7	78	29
5	MeO	c-hex	A	0.16	2.5 (0 °C)	7	34	81
6	F	c-hex	A	0.16	6	7	49	98
7	F	2,6-iPr_2Ph	A	0.16	0.5	5	64	>99
8	F	2,6-iPr_2Ph	B	0.16	2	5	83	>99
9	F	2,6-iPr_2Ph	B	1.1	1	5	90	>99
10	F	2,6-iPr_2Ph	B	0.045	3.5	5	82	>99
11	F	2,6-iPr_2Ph	B	0.025	3.5	5	82	97
12	F	2,6-iPr_2Ph	B	0	3.5	5	0	17

[a] The reaction procedure is described in the text. [b] 1.5-2.0 equiv of naphthyllithium **2** was used. Method A: prepared from naphthyl bromide and *tert*-BuLi; method B: prepared from naphthylpropyltellurium and BuLi.[6] [c] Equivalent of the chiral diether **1**/naphthyllithium **2**. [d] Absolute configuration was determined by optical rotation;[8] ee was determined by HPLC analysis using chiral column (Daicel ChiralPak AD hexane/isopropyl alcohol (9/1), 0.5 mL/min). [e] Yield refers to purified product by column chromatography. [f] Number in parentheses represents ee and yield after a single recrystallization from ether and hexane.

to the amount of **1** employed (entry 4). At temperatures above 0 °C, the reaction proceeded smoothly to afford **7** in 81% yield; however, the ee was only 34% (entry 5). At 0 °C, naphthyllithium **2** was able to react with **3** without the aid of the ligand **1**. It was observed that fluoro imine **3c** was a good substrate in both stoichiometric and catalytic reactions at −45 °C to provide high yields of **7** in 57 and 49% ee, respectively (entries 3 and 6). This strongly indicates that regeneration of the active species, naphthyllithium complex **9**, is possible from lithium fluoride–**1** complex **6** (X = F) through ligand exchange and is impossible or quite sluggish from lithium methoxide–**1** complex **6** (X = MeO).[9]

An improvement in the stereoselectivity was realized by using (2,6-diisopropylphenyl)imino group (**3d**),[10] with the increasing bulk probably sterically promoting effective chirality preservation in passing from central chirality to axial chirality.[11] A dramatic improvement in ee (83%) was achieved by using lithium bromide free naphthyllithium **2**, prepared from naphthylpropyltellurium and butyllithium (method B)[6] (entry 8).[12] It is highly probable that lithium bromide, produced in a lithium–halogen exchange between naphthyl bromide and *tert*-butyllithium (method A), activates **2**, allowing it to react without the aid of **1**.

Nearly constant ee (90–82%) was obtained in the range between stoichiometric amounts to 2.5 mol % of **1** (entries 8–11). The process is applicable to the reaction of 9-phenanthrenyllithium with **3d** by the addition of 4.5 mol % of **1**, providing **10**[13] in 83% ee and 83% yield.

Although further studies are required to determine the precise nature of the catalytic cycle, we believe that the results demonstrated here provide the basis for further new catalytic asymmetric reactions.[14]

Supplementary Material Available: A description of the procedure for the preparation of lithium bromide free **2** and listings of experimental details and data for **3** and **5–8** (7 pages). Ordering information is given on any current masthead page.

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(7) The new compounds described herein gave satisfactory analytical and spectroscopic data.

(8) Meyers, A. I.; Lutomski, K. *J. Am. Chem. Soc.* **1982**, *104*, 879.

(9) Since no precipitation was observed, it is apparent that lithium fluoride is soluble in the reaction solution.

(10) Other groups, 2,6-dimethylphenyl and 2,4,6-tri-*tert*-butylphenyl, did not gave satisfactory stereochemical results.

(11) Since conjugate addition of an organolithium to a naphthylimine is highly stereoselective,[4] the initial addition step is assumed to be selective. Subsequent elimination of lithium fluoride, corresponding to the transformation of central to axial chirality, determines the efficacy of the process. There are very few examples of this; see: Meyers, A. I.; Wettlaufer, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 1135.

(12) Tin compounds were found to be unsatisfactory in toluene; for example. Bu_3NaphSn–BuLi gave 1-butylnaphthaldehyde imine.

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(14) We are grateful to the Japan Research Foundation for Optically Active Compounds, Hoansha Foundation, and a Grant-in-Aid for Scientific Research from the Ministry of Education, Japan, for partial financial support.

Carborane Ligands in Organometallic Chemistry: A New Class of Fischer Carbene Complexes[1]

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Received February 10, 1992

nido-Carborane anions, especially the icosahedral fragment $R_2C_2B_9H_9^{2-}$ ("dicarbollide") and pentagonal-pyramidal $R_2C_2B_4H_4^{2-}$ species, are demonstrably versatile ligands in transition metal organometallic chemistry.[2] When η^5-coordinated to metal centers, such ligands have been shown to stabilize a remarkable variety of organometallic structures, many of which exhibit unusual geometries and/or electronic properties.[3] The metal–C_2B_4 complexes can be converted to metal–C_2B_3 building-block units

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