In contrast to the yttrium system, in which products with and without coordinated THF are accessible, treatment of $Cp_2LuRe_2H_7(PMe_2Ph)_4$ with 1 equiv of THF in C_6D_6 gives no spectral shifts; no evidence for THF binding is observed. The marginally smaller radius of lutetium (0.848 Å vs 0.88 Å for yttrium)[22] may cause this difference in chemical behavior.[23]

These results suggest that the $Cp_2LnRe_2H_7(PMe_2Ph)_4$ complexes may be particularly useful as a class of mixed-metal species: size-selective substrate binding may be possible by proper choice of Ln. For example, substrates more slender than THF may add to the lutetium complex. More importantly, these heterometallic polyhydrides appear to be able to accommodate addition and elimination of substrates without reverting back to their homometallic constituents. For example, when THF is lost from the yttrium complex, the vacant coordination position is filled by a hydride ligand, with concomitant conversion of the open L-shaped form to a closed metal triangle. Hence, selective and truly polymetallic chemistry may be achievable with complexes of this class.

Acknowledgment. This work was supported by grants from the National Science Foundation (to K.G.C.) and the Division of Chemical Sciences of the Office of Basic Energy Sciences of the Department of Energy (to W.J.E.). Funds for the purchase of the X-ray equipment were made available from NSF Grant CHE-85-14495. We thank Dr. S. Chang for assistance and Rhenium Alloys for material support.

Supplementary Material Available: ORTEP diagrams and tables of crystal data, positional parameters, bond distances and angles, and thermal parameters for $(C_5H_5)_2Y(THF)Re_2H_7(PMe_2Ph)_4$ and $(C_5H_5)_2LuRe_2H_7(PMe_2Ph)_4$ (24 pages). Ordering information is given on any current masthead page.

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[22] Cotton, F. A.; Wilkinson, G. *Adv. Inorg. Chem.*, 4th ed.; Wiley: New York, 1980.

[23] Similar effects have been observed before. See: Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 263-270.

Asymmetric Synthesis through the Topochemical Reaction in a Chiral Crystal of a Prochiral Diolefin Molecule Having a "Cisoid" Molecular Structure and Amplification of Asymmetry by a Seeding Procedure[1]

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Topochemically controlled reactions of organic crystals have become of interest in recent years as one means of asymmetric synthesis because these reactions proceed stereoselectively under the control of the crystal lattice. There have been a few successful examples regarding the production of optically active materials from achiral molecules by using the chiral environment of a crystal as the sole source of chirality in a photoreacting process.[2] Our earlier communication demonstrated that an alternating arrangement of both enantiomers was generated by a topochemical induction during the reaction of some prochiral molecules in achiral crystals.[3]

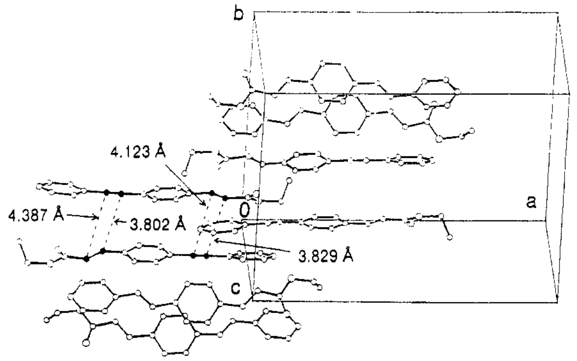
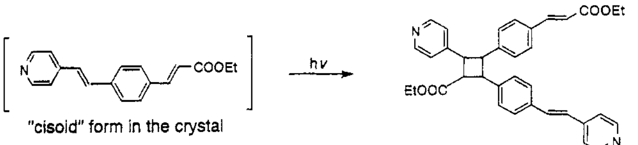


Figure 1. Crystal structure of **1**. The double bonds that may form cyclobutane are linked by the dotted lines.

Scheme I



Ethyl 4-[2-(4-pyridyl)ethenyl]cinnamate[4a] (**1**) is highly photoreactive in the crystalline state and was converted by [2 + 2] photocyclodimerization into dimer **2** in high yield (Scheme I). The cyclobutane structure of **2** was confirmed by ^{1}H NMR and MS spectroscopy[4b] and by topochemical considerations based on X-ray crystal structure analysis. It was proved that optically active **2** was obtained by the photoirradiation of a single crystal of 1 and, furthermore, that the amplification of asymmetry was successfully performed by seeding during the recrystallization of **1**.

Light-yellow prisms (mp 115-116 °C, 10-17 mg) were obtained from an ethanolic solution of **1** by slow evaporation. The single crystal was cut into two pieces, and one piece was then finely powdered and photoirradiated by a 500-W super-high-pressure mercury lamp for 5 h at room temperature. A cut-off filter ($\geq$365 nm) was employed for exciting only the monomer molecule in order to maximize the chemical yield of dimer **2**. After photoirradiation, **2** was purified by TLC and the sign of optical rotation confirmed. The single crystal that gave (+)-**2** or (−)-**2** was called (+)-**1** or (−)-**1**, respectively. Crystals of (+)-**1** or (−)-**1** (ca. 200 mg) were obtained from an ethanolic solution of **1** respectively by seeding with finely powdered crystals of another piece of (+)-**1** or (−)-**1** (3-6 mg). Finely powdered crystals of **1**, obtained by seeding, were dispersed in 30% aqueous $CaCl_2$ containing a few drops of surfactant (NIKKOL TL-10FF) to avoid the flotation of crystals and were irradiated, with vigorous stirring, by a mercury lamp located outside of the flask, through the same cut-off filter under a nitrogen atmosphere at −40 °C for 10 h. The enantiomeric excess of the resulting **2**, after purification by TLC, was determined by HPLC on an optically active solid phase.[5] The enantiomeric excess for (+)-**2** was 92%, $[\alpha]_D$ +72° (*c* 1.0 in CH_2Cl_2), and for (−)-**2**, 95%, $[\alpha]_D$ −75°. Although the crystals gradually became amorphous as the photoreaction proceeded, the chemical yield of **2** was more than 60%.

The photochemical behavior and asymmetric induction could be readily interpreted by an X-ray structure analysis of a crystal of **1**.[6] The crystal structure of **1** is shown in Figure 1.

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[1] The term "amplification of asymmetry by seeding" means that a large quantity of crystals that gave a dimer of the same optical rotation as that of the dimer obtained from seed crystals was attainable in a very high optical yield by seeding with a slight amount of seed crystals.

[2] (a) Addadi, L.; van Mil, J.; Lahav, M. *J. Am. Chem. Soc.* **1982**, *104*, 3422-3429. (b) Evans, S. V.; Garcia-Garibay, M.; Omkaram, N.; Scheffer, J. R.; Trotter, J.; Wireko, F. *J. Am. Chem. Soc.* **1986**, *108*, 5648. (c) Sekine, A.; Hori, K.; Ohashi, Y.; Yagi, M.; Toda, F. *J. Am. Chem. Soc.* **1989**, *111*, 697-699.

[3] Hasegawa, M.; Kunita, A.; Chung, C. M.; Hayashi, K.; Sato, S. *Chem. Lett.* **1989**, 641-644.

[4] (a) The methyl derivative gave a linear polymer on photoirradiation: Hasegawa, M.; Harashina, H.; Kato, S.; Saigo, K. *Macromolecules* **1986**, *19*(4), 1276-1278. (b) ^{1}H NMR: δ 0.95 (t, 3 H), 1.29 (t, 3 H), 3.91 (m, 3 H), 4.21 (q, 2 H), 4.40 (q, 1 H), 4.46 (t, 1 H), 4.73 (t, 1 H), 6.30 (d, 1 H), 6.93 (d, 1 H), 6.96 (d, 2 H), 7.09 (d, 2 H), 7.18 (d, 1 H), 7.23-7.36 (m, 8 H), 7.53 (d, 1 H), 8.54-8.56 (m, 4 H); mass spectrum, *m/e* 513 (M − C_2H_5O), 381 (asymmetric cleavage of cyclobutane ring), 279 (M/2), 250 (M/2 − C_2H_5), 234 (M/2 − C_2H_5O), 206 (M/2 − $COOC_2H_5$), 177 (asymmetric cleavage of cyclobutane ring).

[5] The column used was Chiralcel OC of Daicel Chemical Industries, Ltd., Himeji, Japan.

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The structure of the molecule is a "cisoid form" as is shown in Scheme I, which is very rare among diolefinic molecules having photoreactivity in the crystalline state; a "transoid form" has been confirmed in many cases by X-ray crystal structure analysis. Every pair of reactive molecules having a quasi-C_2 symmetry is arranged according to β-type packing.[7] No stack for the formation of a high molecular weight polymer exists; the dimer is thus formed as a major product when only the monomer is excited. The intermolecular distances of two facing double bonds are approximately within the normal photoreactive distance (3.802 and 4.387 Å for one pair of facing double bonds, and 3.829 and 4.123 Å for another). Due to the different distances and nonparallelisms, the two pairs of reacting double bonds are expected to differ from one another in reactivity. It is apparent, however, that a dimer having the same chirality is formed by a reaction of either of the two pairs of double bonds. On the other hand, in the β-type packing crystal of "transoid" molecules, two reacting molecules are related by centrosymmetry, and therefore the four carbons on a cyclobutane ring derived from reacting pairs of double bonds should have opposite chiralities resulting in the racemic dimer.[8]

In contrast to asymmetric synthesis using α-type packing chiral crystals as reported by Addadi et al.,[2a] this result is the first demonstration of asymmetric synthesis in a β-type packing crystal. The formation of a chiral space group in a β-type packing crystal is caused by the "cisoid form" of the molecular structure of **2**. The present results contribute to the further development of photoreactive chiral crystals for asymmetric synthesis.

Acknowledgment. We thank Dr. S. Sato (Sankyo Co., Tokyo, Japan) for making available to us the X-ray diffraction data of **1**.

Supplementary Material Available: Atomic coordinates and thermal parameters for **1** (2 pages). Ordering information is given on any current masthead page.

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(6) Crystal data: MW = 279, orthorhombic, $P2_12_12_1$, a = 19.442 (5) Å, b = 15.112 (4) Å, c = 10.192 (3) Å, V = 2994.6 Å^3, Z = 8, R = 0.068 (R_w = 0.076).

(7) The arrangement of diolefinic molecules in photoreactive organic crystals may be conveniently divided into two groups: α-type packing, in which molecules are stacked with displacement along the molecular axis by half a molecule, and β-type packing, in which molecules are stacked with overlap.

(8) Kato, S.; Nakatani, M.; Harashina, H.; Saigo, K.; Hasegawa, M.; Sato, S. *Chem. Lett.* **1986**, 847-850.

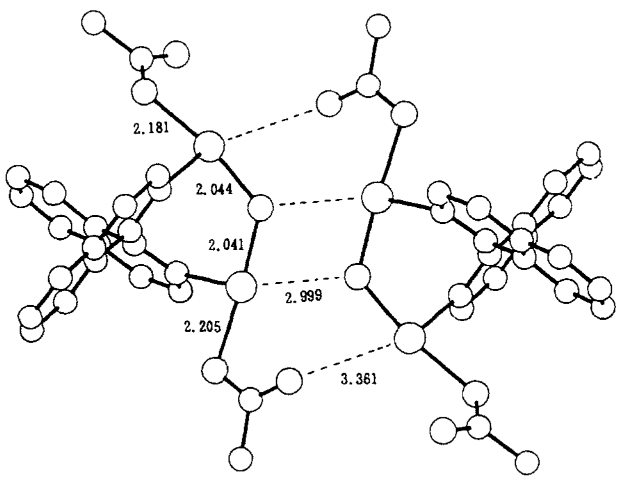

Figure 1. Molecular arrangement around an inversion center, showing a bimolecular unit formed in the crystal of the inclusion compound of racemic **5** and benzene, and critical bond length (Å).[11]

Synthesis of Chiral Hypervalent Organoiodinanes, Iodo(III)binaphthyls, and Evidence for Pseudorotation on Iodine

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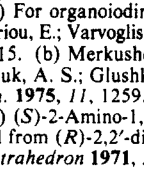
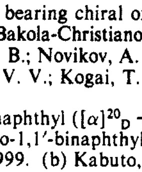
Received March 12, 1990

Hypervalent organoiodinanes are versatile reagents in organic synthesis and continue to find many applications for the preparation of a variety of functional groups.[1] Asymmetric oxidation of sulfides to sulfoxides by utilizing organoiodinanes generated in situ from iodosylbenzene and L-tartaric anhydrides has been reported.[2,3] We report herein the first example of synthesis of hypervalent organoiodinanes bearing chiral carbon ligands, acetoxyiodo(III)binaphthyls, and their degenerate isomerization of acetoxy ligands about iodine.

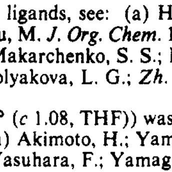
Diazotization of optically active (S)-2-amino-1,1′-binaphthyl[4] with $NaNO_2$ in H_2SO_4 and then $KI-ZnI_2$, followed by decomposition of the resulting diazonium salt, afforded (S)-2-iodo-1,1′-binaphthyl (**1**). Treatment of the corresponding (dichloroiodo)binaphthyl, prepared from **1** by chlorination in dry hexane,[6] with mercuric acetate in carbon tetrachloride gave the desired (S)-2-(diacetoxyiodo)-1,1′-binaphthyl (**2**) ($[\alpha]^{18}_{\mathrm{D}}$ +51.9° (c 0.97, $CHCl_3$)) in 83% yield.[7] More conveniently, (S)-**2** could be prepared quantitatively by sodium perborate oxidation of **1** in acetic acid.[8] Oxidation of the known (R)-diiodide **3**, previously prepared by Murdoch and his co-workers,[5] with sodium perborate gave an 85% yield of the C_2 chiral tetraacetate (R)-**4** ($[\alpha]^{21}_{\mathrm{D}}$ −35.7° (c 0.90, AcOH)), which gradually decomposed to the cyclic μ-oxo-diiodinane (R)-**5** ($[\alpha]^{19}_{\mathrm{D}}$ +254.4° (c 0.75, $CHCl_3$)) in chloroform solution at room temperature. The reaction is reversible, and exposure of **5** to warm acetic acid gave **4**. Chlorination of (R)-**3** and then ligand exchange using mercuric bis(trifluoroacetate) afforded the μ-oxo-bis(trifluoroacetate) (R)-**6** ($[\alpha]^{17}_{\mathrm{D}}$ +185.0° (c 0.98, $CHCl_3$)) (75% yield).



1 : X = I
2 : X = I(OAc)$_2$



3 : X = I
4 : X = I(OAc)$_2$



5 : X = OAc
6 : X = OCOCF$_3$

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(2) Imamoto, T.; Koto, H. *Chem. Lett.* **1986**, 967.

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(4) (S)-2-Amino-1,1′-binaphthyl ($[\alpha]^{20}_{\mathrm{D}}$ +87.7° (c 1.08, THF)) was prepared from (R)-2,2′-diamino-1,1′-binaphthyl:[5b] (a) Akimoto, H.; Yamada, S. *Tetrahedron* **1971**, *27*, 5999. (b) Kabuto, K.; Yasuhara, F.; Yamaguchi, S. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1263. (c) Tomoda, S.; Iwaoka, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1283.

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(6) (a) Willgerodt, C. *J. Prakt. Chem.* **1886**, *33*, 155. (b) Lucas, H. J.; Kennedy, E. R. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 482.

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