Grignard (0.98 equiv), leading to isolation of complex **7** as a 2:1 mixture of *E* and *Z* isomers (Scheme II).[17] Consistent with previous spectroscopic observations, the allyl ligand in this complex is rapidly fluxional at ambient temperature, while the crotyl ligand is η^1-bonded exclusively at the primary carbon, but equilibrating slowly at room temperature between *E* and *Z* isomers.[18] The rearrangement of complex **7** proceeds even at room temperature and, as anticipated, occurs *exclusively by migration of the crotyl ligand*. Isomeric zirconacyclobutane complexes **8**[9] and **9**[9] are obtained in a ratio of 2:1; the major product **8** derives from crotyl migration with allylic transposition. Analytically pure zirconacycle **8** is obtained by fractional crystallization from cold pentane; solutions enriched in the minor isomer **9** have been characterized spectroscopically.[19]

Allylic transposition, however, is not a requirement for facile rearrangement. Allyl benzyl complex **10**[17] (Scheme II), prepared by the addition of benzyl Grignard to chloride complex **6**, rearranges under conditions similar to those for complex **7**, affording β-benzylzirconacyclobutane **11**[9] in high yield. Some "activation" of the migrating group is also necessary: $(C_5Me_5)_2Zr(allyl)Me$, **12**,[9] prepared from complex **6** and MeMgI, fails to rearrange, finally decomposing at 110 °C to yield a complex mixture of products including methane and "tuck-in" allyl complex (η^5-C_5Me_5)(η^5:η^1-$C_5Me_4CH_2$)Zr(allyl), **13**,[9] the latter confirmed by independent synthesis.[15] While this result suggests that radical-stabilizing substituents are required to observe facile migration, neither the precise nature of this stabilization nor the involvement of metal-carbon bond homolysis in the rearrangement mechanism has as yet been unambiguously determined.

The zirconacyclobutane complexes are versatile templates for conversion to organic ring systems. Oxidation of β-allylzirconacycle **3** with AgOTf induces reductive elimination,[20] giving allylcyclopropane **14** quantitatively (Scheme I), identified by comparison to an authentic sample.[21] Quantitative conversion to the carbocyclic enediolate **15**[9] is obtained on treatment with CO, a well-precedented transformation for metallocene dialkyl complexes.[22] The carbonylation procedure thus completes a zirconium-mediated net transformation of 2 equiv each of allyl Grignard and CO to a highly functionalized cyclopentanoid ring system, indicative of the potential utility of zirconacyclobutanes in synthetic transformations.

In summary, the thermal rearrangement of zirconocene bis(allyl) and related complexes to zirconacyclobutanes has been demonstrated, proceeding via an unprecedented reactivity pattern involving hydrocarbyl ligand migration to the β-carbon of an η^3-allyl moiety.[23] Although a concerted mechanism cannot be excluded, the product distribution obtained from the rearrangement of complex **7** is suggestive of a radical-mediated process. The concerted pathway, best visualized as the insertion of a tethered olefin into the zirconium-carbon bond of the migrating ligand, demands that the migration proceeds exclusively to the internal olefin carbon, leading to the observed Zr(IV) metallacycle, rather than the geometrically more accessible terminal carbon, leading to the formally Zr(II) olefin complex. It should be noted that thermal migratory insertion of olefins into *neutral* zirconocene alkyl complexes is unknown. Perhaps significantly, however, the photochemical, *free radical-mediated* insertion of ethylene into the metal-methyl bond of $(C_5H_5)_2ZrMe_2$ has been described.[24] Further definition of the scope and mechanistic details of this novel isomerization process are under investigation.

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Supplementary Material Available: Spectroscopic and analytical data for compounds **2-13** and **15** (7 pages). Ordering information is given on any current masthead page.

(17) Isomeric allyl crotyl complexes **7** and allyl benzyl complex **10** are too reactive in solution to be obtained in analytical purity; these complexes have been characterized spectroscopically.[9]

(18) This isomerization presumably occurs via intermediate η^3-crotyl and "internal" η^1-crotyl (3-butenyl) complexes, neither of which are detected spectroscopically.[10c]

(19) Trace quantities of a third product are observed by ^{13}C NMR spectroscopy of samples enriched in the minor isomer, consistent with a (*Z*)-butenyl-substituted zirconacyclobutane structure.

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Efficient Chiral Crystallization and Asymmetric Synthesis via Solid-State Di-π-methane-Type Photorearrangements

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The hitherto reported examples of so-called absolute asymmetric crystallization and synthesis[1,2] have established a simple, inexpensive, and nonclassical approach to the preparation of optically enriched compounds. In these cases, a molecularly achiral substrate adopts a chiral orientation—in the absence of "external" chiral inducing agents—during crystallization. The chirality of the molecule in the crystal can then be trapped through a solid-state (photo)reaction into product stereocenters.[2a] In a project aimed at a novel synthetic concept for access to mixed linearly and angularly fused polycyclic natural products, we came across photochemical solid-state di-π-methane-type rearrangements[3a,4]

(1) For an early reference to spontaneous asymmetric crystallization, see Havinga, E. *Chem. Weekbl.* **1941**, *38*, 642-649; *Biochim. Biophys. Acta* **1954**, *13*, 171-174.

(2) For some leading references on absolute asymmetric synthesis, see (a) Green, B. S.; Lahav, M.; Rabinovich, D. *Acc. Chem. Res.* **1979**, *12*, 191-197. (b) Scheffer, J. R.; Garcia-Garibay, M. In *Photochemistry on Solid Surfaces*; Anpo, M., Matsuura, T., Eds.; Elsevier: Amsterdam, 1989; pp 501-525. (c) Sekine, A.; Hori, K.; Ohashi, Y.; Yagi, M.; Toda, F. *J. Am. Chem. Soc.* **1989**, *111*, 697-699. (d) Vaida, M.; Popovitz-Biro, R.; Leiserowitz, L.; Lahav, M. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; Verlag Chemie: Weinheim, 1990; pp 247-302. (e) Chung, C.-M.; Hasegawa, M. *J. Am. Chem. Soc.* **1991**, *113*, 7311-7316. (f) Chen, J.; Scheffer, J. R.; Trotter, J. *Tetrahedron* **1992**, *48*, 3251-3274.

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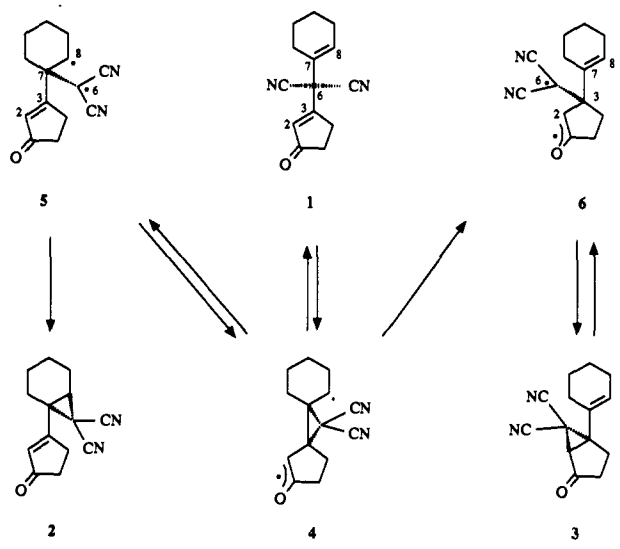
Table I. Product Ratios and Enantiomeric Purities from the Di-π-methane-type Photorearrangements of **1** → **2** + **3** in Homogeneous Solution and the Solid State

entry	aliquot of **1**	medium[a]	*hν*[b]	temp (°C)	time (h)	conv[c] (%)	ratio[c] **2**:**3**	ee(%)[d] (+)-**2**	ee(%)[d] (+)-**3**
1	50 mg	CH_3CN	ray	18	22	100	3.2:1	0	0
2	sc[e]	neat	ray	18	3	9	1:1.9	34	96
3	sc[e]	neat	HPK	−21	2	16	1:1.3	44	87
4	sc[e]	neat	HPK	−21	4	28	1:1.1	36	78
5	sc[e]	neat	HPK	−21	6	36	1:1	34	71
6	sc[e]	neat	HPK	−21	8	51	1.2:1	22	55
7	7 g[f]	H_2O	ray	18	128	52	1:1.2	26[g]	86[h]
8	6 g[i]	H_2O	ray	18	90	49	1:1.3	26	84
9	10 g[j]	H_2O	ray	18	63	32	1:1.5	25	88

[a] CH_3CN: 0.1 M solution under Ar. Neat: solid in an NMR tube under argon. H_2O: vigorously stirred suspension. [b] Ray: Rayonet reactor equipped with RPR-3500-Å lamps. HPK: Philips 150-W medium-pressure Hg lamp. [c] Conversion and ratio values determined by GC. [d] Enantiomeric excesses determined by chiral-phase GC of crude irradiation material (37 m PSO86 per-*O*-methyl-β-cyclodextrin; 100–200 °C with 1 deg/min increments; 1.1 bar; R_f (−)-**3** 69.33 min, (+)-**3** 69.75 min, **1** 73.55 min, (+)-**2** 93.38 min, (−)-**2** 93.88 min); value for **3** in entry 7 was corroborated (±5%) by Eu(hfc)$_3$ NMR experiments with the isolated product. [e] Single crystal, approximate dimensions 2.5 × 0.5 × 0.5 mm^3. [f] Derived from a chromatographic fraction of **1** during rotoevaporatory solvent removal (fast crystallization, see text). [g] $[\alpha]^{20}_D$ +16.5° (*c* 0.99, $CHCl_3$). [h] $[\alpha]^{20}_D$ +137.5° (*c* 0.24, $CHCl_3$). [i] Derived from slow crystallization of a single unagitated and unseeded batch of **1**. [j] Derived from six independent unagitated and unseeded crystallization batches of **1**.

Scheme I. Proposed Pathways for the Rearrangement of **1** via a Common Intermediate (**4**)



of seemingly homochirally crystallized **1** to give preparative quantities of **2** and **3** (Scheme I). The rearrangements proceed so that the products are obtained in respective enantiomeric excesses of ≤44% and ≤96%.

A considerable change in product selectivity was observed for the rearrangement **1** → **2** + **3** for runs in homogeneous solution vs the solid state.[5] Whereas irradiation of **1** in CH_3CN gave a 3.2:1 ratio of **2**:**3** (Table 1, entry 1), a neat single crystal afforded a ratio of 1:1.9 (entry 2). Over a series of timed irradiations on morphologically similar crystals (entries 3–6, all runs under the same reaction conditions), the reaction selectivity gradually favored

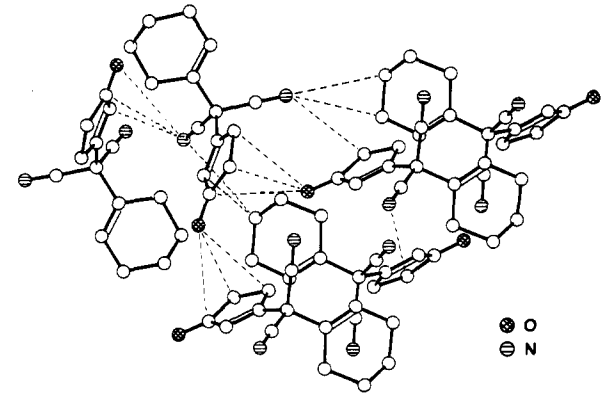


Figure 1. Short (3.26–3.90 Å) intermolecular distances in the crystal of **1**[7] (one of two cyclohexene conformational minima is shown).

2 over **3** with increasing conversion. While the major product determining driving force in solution is likely the thermodynamically favorable re-formation of the enone moiety (**4** → **5** and **2**, Scheme I), the solid-state rearrangement possibly becomes dominated by packing constraints to movement in the crystal.[6] This is substantiated by the X-ray analysis[7] of **1** (Figure 1) which reveals relatively short intermolecular distances, and hence more rigid packing, of the cyclopentenone and malononitrile moieties and relative mobility of the cyclohexene unit. Assuming similar interactions for all biradical intermediates, **5** should revert more easily to **4** in the solid state (disfavoring formation of **2**) than in solution because of the "frozen" geometry and spacial proximity of the enone and C-6. As a consequence of the more mobile cyclohexene moiety, an analogous argument does not apply to **6**. Finally, the decrease in reaction selectivity in the crystal as a function of conversion is likely due to increasing disorder in the

(4) The present case comprises a di-π-methane chromophore extended by a carbonyl moiety. For the earliest such example, see Nann, B.; Gravel, D.; Schorta, R.; Wehrli, H.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1963**, *46*, 2473–2482. For recent reviews on the general di-π-methane rearrangement, see (a) Zimmerman, H. E. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1991; Vol. 11, pp 1–36. (b) De Lucchi, O.; Adam, W. In *Comprehensive Organic Synthesis: Selectivity, Strategy & Efficiency in Modern Organic Chemistry*; Paquette, L. A., Vol. Ed.; Pergamon: Oxford, 1991; Vol. 5, pp 193–214.

(5) Such phase-dependent selectivity changes in unimolecular photoreactions are known (a) Consult refs 2b, 2f. (b) Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 7974–7989. (c) Scheffer, J. R.; Pokkuluri, P. R. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; Verlag Chemie: Weinheim, 1990; pp 185–246. (d) Teng, M.; Lauher, J. W.; Fowler, F. W. *J. Org. Chem.* **1991**, *56*, 6840–6845. (e) Garcia-Garibay, M. A.; Scheffer, J. R.; Watson, D. G. *J. Org. Chem.* **1992**, *57*, 241–247. (f) Pokkuluri, P. R.; Scheffer, J. R.; Trotter, J.; Yap, M. *J. Org. Chem.* **1992**, *57*, 1486–1494.

(6) See reaction cavity model: Cohen, M. D. *Angew. Chem.* **1975**, *87*, 439–447; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 386–394. For a new perspective on topochemical processes, see Kaupp, G. *Angew. Chem.* **1992**, *104*, 606–609, 609–612; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 592–595, 595–598.

(7) X-ray crystal structure of **1**. A suitable crystal (0.09 × 0.39 × 0.49 mm^3) was mounted under argon in a glass capillary. Data (±*h*+*k*+*l*) were collected at room temperature on an Enraf–Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.710 69 Å). Cell constants and systematic absences correspond to the orthorhombic space group $P2_12_12_1$ with cell dimensions *a* = 6.818(1) Å, *b* = 11.747(1) Å, *c* = 15.482(2) Å, *V* = 1240(1) Å^3; *Z* = 4, calculated density = 1.21 g cm^{-3}, *F*(000) = 480 e, and μ = 0.73 cm^{-1} (no absorption correction applied). A total of 3076 reflections [ω − 2θ scan technique, $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}] were collected, of which 1645 were unique (R_{av} = 0.02). 1128 observed reflections [$I \geq 2\sigma(I)$] were used for the structure solution (direct methods, SHELXS-86) and subsequent full-matrix least-squares refinement. *R* = 0.054, R_w = 0.058 [$w = 1/\sigma^2(F_o)$], atoms C(10) and C(11) disordered 60:40; GOF = 1.97; final residual electron density = 0.20 e Å^{-3}.

packing caused by (a) the presence of product and (b) local melting of the crystal by excess radiation energy.

Interestingly, **1** adopts chiral packing (space group $P2_12_12_1$)[8] and a helical molecular conformation.[9] GC analyses of the crude product mixtures from the irradiation of single crystals of **1** (entries 2–6) showed that **2** and **3** were obtainable in respective enantiomeric excesses (ees) of ≤44% and ≤96% and that the ees decreased proportionately with conversion. This constitutes a second general case of asymmetric synthesis through a solid-state di-π-methane rearrangement, preceded only by the substituted dibenzobarrelene examples of Scheffer and co-workers, it is also a variation on the dual pathway induction difference reported by the same group.[2f] Degeneration of the ground-state conformation of **1** through selective rotation of either the five- or the six-membered ring prior to the rearrangement could account for the ee disparity between **2** and **3**.[3] A measure of regio- and enantioselectivities as a function of conversion, as shown in Table I and in additional measurements,[3a] is unique to this work. Attempts to unequivocally determine the absolute configurations of **1**, **2**, and **3** by anomalous scattering have thus far been unsuccessful.

The ees obtained from the irradiation of a large batch of **1** as a suspension in H_2O (Table I, entry 7) bore witness to the high optical purity within individual crystallization batches of the dienone. While this material stemmed from rapid crystallization of the solute in a chromatographic fraction during rotoevaporatory solvent removal, the batch of entry 8 was collected from an unagitated[10] and unseeded solution of **1**. That largely one enantiomorph of **1** has been forming in our laboratories is most poignantly underscored by the example of entry 9, in which **1** was collected from six independent crystallization batches. However, the manifestation of essentially exclusive enantioselectivity of crystallization affording dextrorotatory photoproducts only (see Table) is seemingly due to the localized presence of a chiral nucleating agent.[11] This bias calls for caution in interpreting examples of so-called absolute asymmetric crystallization and synthesis.

In conclusion, it should also be noted that the synthetic potential of **1** vis-à-vis polycyclic compounds, via vinylcyclopropane → cyclopentene rearrangement followed by additional ring constructions, has already been demonstrated, as have facile optical resolutions with 97–99% optical purity of the antipodes of **2** and **3** by selective crystallizations.[3a]

Acknowledgment. We wish to thank Mr. H. Behlau for the chiral-phase GC analyses and Dr. U. Vitinius (our institute) and Dr. W. Dahlhoff/K. Radkowski (Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr) for reinvestigating the crystallization/photorearrangement sequence. Dr. R. Goddard we thank for invaluable discussions. Financial support from the Max-Planck-Gesellschaft (postgraduate scholarship to A.L.R.) and from the Alexander-von-Humboldt-Stiftung (postdoctoral fellowship to M.M.) is gratefully acknowledged.

Supplementary Material Available: Listings of crystal data, atomic coordinates, bond distances and angles, and thermal parameters for **1**, experimental details and characterization data for compounds **1–3** (9 pages); listings of observed and calculated structure factors for **1** (6 pages). Ordering information is given on any current masthead page.

(8) Three of eight commonly adopted space groups for organic molecular crystals are chiral, see ref 2a. Consult also Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic: New York, 1973.

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Organometallic Modification Approach to Control of Polymer Properties: A Soluble, Liquid Crystalline, π-Complexed Aromatic Polyamide

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High-performance aromatic polymers, such as aromatic polyamides (aramids), polyimides, or liquid crystalline polyesters, have high strength, stiffness, stability at high temperatures, and chemical resistance for technologically demanding applications.[1] Their limited solubility necessitates extreme synthesis and processing conditions. For example, the polyamide poly(*p*-phenyleneterephthalamide) (PPTA) forms high-strength and high-modulus fibers (Kevlar[2]), but must be processed from concentrated sulfuric acid at elevated temperatures.[3]

Previous reports suggest complexation of rigid-rod polymers as a method to increase solubility and mediate processing. Jenekhe studied the solubilization, processing, and liquid crystalline character of heterocyclic rigid-rod polymers by reversible complexation of the heteroatoms by Lewis acids such as $AlCl_3$.[4] The aromatic rings of high-performance polymers should provide a platform for transition metal π-complexation since they bond tenaciously to a wide variety of transition metal complexes.[5,6] Synthesis of organosoluble chromium tricarbonyl π-complexes of low molecular weight PPTA has been described.[6d] We now show that organometallic η^6-coordination offers broad control of the properties of high-performance aromatic polymers, as exemplified by PPTA. π-Complexation solubilizes even high molecular weight PPTA in organic solvents and, remarkably, still allows formation of ordered liquid crystalline solutions.[7] These solutions can be used to prepare high-quality films of the metallopolymers. The extent of chromium tricarbonyl substitution on the aromatic ligands dictates the orientation of PPTA films on a molecular level, and the steric bulk of the η^6-organometallic substituent, defined by ligand substitution reactions, controls the liquid crystallinity of the organoaramid solutions.

Polycondensation of (*p*-phenylenediamine)$Cr(CO)_3$[8] with terephthaloyl chloride in *N,N*-dimethylacetamide (DMAc) gives

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