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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 $\leq$44% and $\leq$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.

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(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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(11) The number of times that material from individual, nonseeded crystallization batches of **1** has thus far been irradiated in the laboratories of Mülheim is in the order of 60. We are indebted to Professor J. Mattay and Mr. T. Kirschberg, University of Münster, for the independent preparation and crystallization of **1** affording one batch each of dextro- and levorotatory photoproducts with optical purities identical to ours.

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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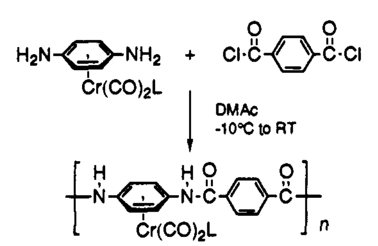
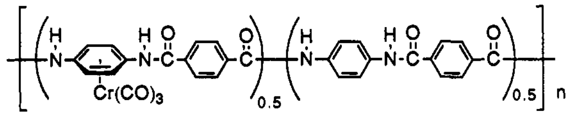
high molecular weight (PPTA)Cr(CO)$_3$ as opalescent, highly viscous DMAc solutions, with Cr(CO)$_3$ complexed to every diamine ring. Liquid crystalline solutions can be directly prepared in this way: polarizing optical microscopy shows a nematic liquid crystalline texture when the concentration is >4–6 wt % in DMAc at room temperature. This lyotropic behavior is similar to that of H_2SO_4 solutions of PPTA itself,[1] demonstrating that the Cr(CO)$_3$ organometallic substituent dramatically increases the solubility of PPTA while, surprisingly, maintaining its rigid-rod character.[7] (PPTA)Cr(CO)$_3$ is a rare example of a liquid crystalline organometallic polymer.[4,9]



L = CO, (PPTA)Cr(CO)$_3$
L = P(CH$_3$)$_3$, (PPTA)Cr(CO)$_2$P(CH$_3$)$_3$

(PPTA)Cr(CO)$_3$ can be isolated by precipitation or by casting the DMAc solution as a film and quenching with methanol, giving (PPTA)Cr(CO)$_3$ as a strong, air-stable yellow film. The metalloaramid does not redissolve in dipolar aprotic solvents after isolation, as is typical of polymers which are highly crystalline or form strong hydrogen-bonded networks in the solid state. Infrared spectra show characteristic strong absorptions at 1962 and 1884 cm^{-1} for the η^6-coordinated Cr(CO)$_3$ group[8] and at 1665 cm^{-1} for the amide carbonyl. The intrinsic viscosity in DMAc is 4.52 dL/g, and gel permeation chromatography using a viscosity detector (DMAc/LiBr/H_3PO_4/THF solution) gives an absolute molecular weight (M_w) of 78 000 (polydispersity = 1.7), confirming the high molecular weight. For comparison, PPTA has an inherent viscosity in H_2SO_4 in the range from 4 to 6 dL/g and a M_w in the range from 35 000–64 000.[1a] Thermal gravimetric analysis under nitrogen shows complete loss of CO from Cr(CO)$_3$ at ~250 °C and onset of PPTA decomposition above 450 °C. The CO loss was confirmed by the disappearance of the ligand C–O stretching frequencies in the IR spectrum. Differential scanning calorimetry shows broad endotherms in the temperature region for CO loss but no evidence for glass transition or melting temperatures.[10]

Interestingly, the metalloaramid is soluble even when only half of the diamines are Cr(CO)$_3$ complexed. This copolymer was prepared in a two-step polymerization by reaction of 1 equiv of (*p*-phenylenediamine)Cr(CO)$_3$ first with 2 equiv of terephthaloyl chloride, followed by reaction with 1 equiv of *p*-phenylenediamine, giving a composition that has, statistically, an organometallic substituent on alternating diamine rings. This sequential order of addition of the diamine monomers is necessary because of the decreased reactivity of (*p*-phenylenediamine)Cr(CO)$_3$ compared to *p*-phenylenediamine.[8] Analogous to (PPTA)Cr(CO)$_3$, the copolymer is soluble and lyotropic in DMAc.[11]



The film properties of the two metalloaramids are remarkably different, even though both films were prepared by drawing liquid crystalline solutions and rapidly quenching with methanol to maximize anisotropy.[12,13] The tensile properties of (PPTA)Cr(CO)$_3$ films are isotropic in the plane of the film, while those of the partially complexed analog are highly anisotropic, suggesting that orientation in liquid crystalline domains of (PPTA)Cr(CO)$_3$ relaxes more rapidly than orientation of the partially complexed analog.

Ligand exchange on the organometallic moiety offers control of the metalloaramid polymer properties. To demonstrate this concept, the trimethylphosphine derivative of (PPTA)Cr(CO)$_3$ was prepared by polycondensation of (*p*-phenylenediamine)Cr(CO)$_2$P(CH$_3$)$_3$[8] with terephthaloyl chloride in DMAc to give highly viscous, red solutions of high molecular weight (PPTA)Cr(CO)$_2$P(CH$_3$)$_3$.[14] A biphasic texture at concentrations >11 wt % in DMAc solution shows that the critical concentration for liquid crystal formation is much higher for the phosphine derivative than for (PPTA)Cr(CO)$_3$. The critical concentration for liquid crystal formation of rigid rods decreases with the ratio of the persistence length to the diameter (L/d ratio). Consistent with theory, the phosphine derivative has a larger diameter than (PPTA)Cr(CO)$_3$, decreasing the L/d ratio and thus raising the critical concentration.[15] Preliminary experiments show that the more sterically demanding butyl- or phenylphosphine derivatives of (PPTA)Cr(CO)$_2$(PR$_3$) have critical concentrations, if they exist at all, greater than 11 wt % in DMAc. The breadth of ligand-exchange reactions available makes this a powerful tool for polymer modification.

The reversibility of the organometallic modification approach is illustrated by oxidative decomplexation (I_2 in THF)[8] of the Cr(CO)$_3$ group from (PPTA)Cr(CO)$_3$. Infrared spectra of iodine-treated films show complete loss of the ligand C–O absorptions (1962, 1884 cm^{-1}); elemental analysis indicates that only ca. 2% Cr remains in the film. Interestingly, the tensile properties of the decomplexed film are virtually unchanged from (PPTA)Cr(CO)$_3$.[16] These studies demonstrate the potential utility of the organometallic substituent for polymer processing: the metalloaramid can be processed from organic media and then decomplexed to yield the processed parent polymer.

The organometallic modification approach offers broad control of polymer properties for the PPTA system. We anticipate that this approach should provide tunability of polymer properties for a broad range of high-performance aromatic polymers. Studies of these and related metallopolymers, including a range of polymer substrates and organometallic substituents, model studies, and surface chemistry, are in progress.

Acknowledgment. We thank M. Han for the molecular weight measurements, H. Williams for the tensile measurements, Dr. W. Memeger and Dr. Y. Kim for insightful discussions, and J. M. Barker for technical assistance.

Supplementary Material Available: Experimental details including preparations and analytical data for the synthesis of (*p*-phenylenediamine)Cr(CO)$_2$L, where L = CO and P(CH$_3$)$_3$,

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(10) For (PPTA)Cr(CO)$_3$: Anal. Calcd: C, 54.56; H, 2.69; N, 7.48; Cr. 13.89. Found: C, 54.13; H, 3.61; N, 6.70; Cr. 12.30.

(11) For 50% complexed (PPTA)Cr(CO)$_3$: IR (film) 1959, 1890 (ν_{CO} ligand), 1649 (ν_{CO} amide) cm^{-1}. Inherent viscosity: 4.18 dL/g (DMAc, 0.1%, 25 °C). Anal. Calcd: C, 60.79; H, 3.29; N, 9.15; Cr, 8.49. Found: C, 60.91; H, 4.25; N, 8.46; Cr, 6.96.

(12) For (PPTA)Cr(CO)$_3$, physical properties in machine direction (MD): tensile strength (TS), 208 MPa; modulus, 8811 MPa; elongation, 2.8%. In transverse direction (TD): TS, 165 MPa; modulus, 6971 MPa; elongation 3.3%. For 50% complexed (PPTA)Cr(CO)$_3$, MD: TS, 325 MPa; modulus, 12.9 GPa; elongation 1.7%. TD: TS, 9.9 MPa; modulus, 4344 MPa; elongation, 2.0%. For comparison, isotropic PPTA films: TS, 165 MPa; modulus, 5516 MPa; elongation, 5% (see ref 13).

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(14) For (PPTA)Cr(CO)$_2$P(CH$_3$)$_3$; IR (film) 1874, 1819 (ν_{CO} ligand), 1655 (ν_{CO} amide) cm^{-1}. Inherent viscosity: 4.12 dL/g (DMAc, 0.1%, 25 °C). Anal. Calcd: C, 54.03; H, 4.53; N, 6.63; Cr, 12.31. Found: C, 53.61; H, 5.25; N, 6.21; Cr, 12.27.

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(16) Iodination (50 equiv of I_2 in THF, 2 h, room temperature) of a (PPTA)Cr(CO)$_3$ film (η_{inh} = 1.88 dL/g, H_2SO_4, 0.5%, 25 °C) gave a PPTA film (η_{inh} = 2.33 dL/g, H_2SO_4, 0.5%, 25 °C) whose tensile properties were virtually unchanged: TS, 188 MPa; modulus, 8777 MPa, elongation 2.5%.

preparations of (PPTA)Cr$(CO)_3$ (fully and partially complexed) and (PPTA)Cr$(CO)_2P(CH_3)_3$, and polarized light optical micrograph of (PPTA)Cr$(CO)_3$ (5 pages). Ordering information is given on any current masthead page.

Molecular Reception Catalysis of the Decarboxylation of *N*-Carboxyimidazolidinone. A Model for Activation by Distortion of *N*-Carboxybiotin

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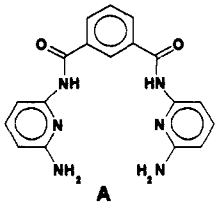
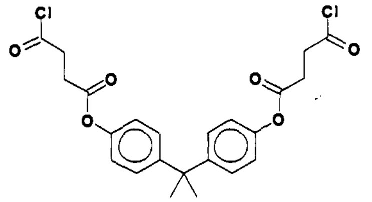
It has been proposed that the observed substrate-induced decarboxylation of enzyme-bound *N*-carboxybiotin[1] can result from movement of the exocyclic carboxyl group out of the plane of the imidazolidinone ring upon binding to an enzymic receptor[2,3] (Scheme I). On the basis of this proposal, we designed a synthetic host (**H**) to induce distortion of a functional model of *N*-carboxybiotin. Hamilton's methodology provides a convenient route to appropriate hosts.[4-9] While host-guest chemistry has been used to promote decarboxylation reactions by electrostatic and nucleophilic catalysis,[10,11] binding that distorts a substrate toward a transition-state structure has not previously been tested.

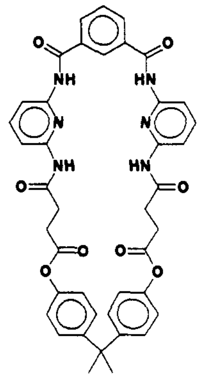
High-dilution coupling of diamine **A** with diacid dichloride **B** (THF, 2 equiv of triethylamine) produces **H** (chromatography, neutral alumina (2% MeOH/CH_2Cl_2); HPLC, C8 reverse phase, eluted with acetonitrile; recrystallization, THF/heptane). Relative concentrations of complexed and uncomplexed **H** with imidazolidinone derivatives in THF solutions were determined by changes in UV spectra. Spectral titration gave data which were used to derive association constants (Table I).



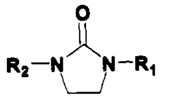
A



B



H



1, $R_1 = R_2 = H$
2, $R_1 = H$, $R_2 = CH_3$
3, $R_1 = R_2 = CH_3$
4, $R_1 = H$, $R_2 = C(O)OCH_3$
5, $R_1 = H$, $R_2 = COO^- NBu_4^+$

Scheme I

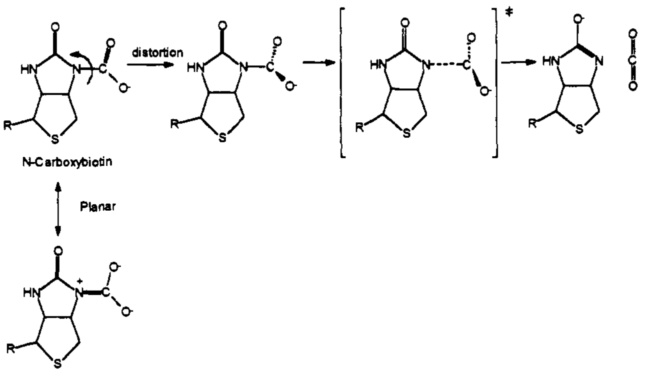


Table I. Association Constants (K_1) for Host H with Cyclic Ureas[a]

guest	K, M^{-1} (25 °C, THF)
imidazolidinone (**1**)	5.7×10^4
N-methylimidazolidinone (**2**)	9.0×10^2
N,N-dimethylimidazolidinone (**3**)	0
N-carbomethoxyimidazolidinone (**4**)	8.5×10^2

[a] Concentration of H is 10^{-5}–10^{-6} M. Titration curves show a 1:1 stoichiometry and were fit to ligand-association expressions by nonlinear regression.

The affinity of **H** for **1**, **2**, and **3** parallels the number of possible hydrogen bonds between the host and the guest according to the mode proposed by Hamilton.[6-8] *N*-Carbomethoxyimidazolidinone (**4**) is stable in the presence of **H** and was used to estimate the binding affinity of **5** for **H**. The affinity of **H** for **5** is lower than that of **H** for **1**, presumably due to a combination of steric effects and one fewer hydrogen bonding sites in **5**. Since the transition state for decarboxylation of **5** will have lower bond order to the carboxyl group and partial formation of a hydrogen bond, the host should bind it with a greater affinity than it does the reactant. Stabilization of the transition state upon binding is the requirement for catalysis of decarboxylation by the host, paralleling the proposal for distortion of *N*-carboxybiotin in Scheme I. Molecular modeling of **5** (with the program Insight II using a Silicon Graphics system) shows that the stable conformation is the expected coplanar arrangement of all heavy atoms. Docking of **5** onto **H** gives a minimized structure in which the carboxyl group of **5** moves out of the plane of the imidazolidinone ring while the ring associates with the hydrogen bond donors of the host (which is in a twisted conformation accommodating the carboxylate group). Thus, it is expected that the association of host and guest will direct the guest toward the conformation predicted for the transition state for decarboxylation.

The rate of decarboxylation of **5** in anhydrous THF at 25 °C was followed at 228 nm (over 3 half-lives). The product is the conjugate base of imidazolidinone, which was converted to imidazolidinone by a trace of methanol and analyzed (GC-MS: 50 °C, 2 min, 20 °C/min to 250 °C; retention time = 8:33 min, MH^+ 87; HPLC (C_{18} Novapak, CH_3CN) 9.05 min). The host was unchanged during the course of the reaction. In the absence of **H**, reaction of **5** was too slow to observe over 3 days. Controls which cause no reaction of **5** included addition of benzamide, 2,6-diaminopyridine, and *N*-methylbenzamide (which have the functionality of **H** but are not expected to be receptors). *N,N'*-

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