Eight-Vertex Metallomesogens: Zirconium Tetrakis-β-diketonate Liquid Crystals

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Received August 3, 1998. Revised Manuscript Received October 8, 1998

Square antiprism zirconium tetrakis-β-diketonate complexes with 24 alkoxy chains organize in columnar liquid crystal phases. X-ray diffraction and polarized microscopy studies on complexes with *n*-alkoxy side chains revealed a columnar hexagonal phase. These sandwich-shaped compounds have much lower transition temperatures than their discotic analogues, which leads to the desirable attribute of room temperature liquid crystallinity. The addition of two branching methyl groups to the alkoxy chains was found to dramatically alter the properties of these materials. The branched side chain analogues exhibited a higher clearing point while the liquid crystallinity is maintained at room temperature. The branching methyl groups also induced a bulk reorganization of the material to a rare columnar oblique phase (Col_{ob}).

Introduction

Metallomesogens provide a number of new shapes and structures from which to test the limits of liquid crystal stability. Representative examples of these materials have been found for all major classes of rod- and disk-shaped liquid crystals.[1] Recently, several transition metal compounds with unusual shapes and high coordination numbers have been reported to exhibit liquid crystallinity.[2] These metal-containing materials demonstrate the versatility of the coordination geometries that will support liquid crystallinity and draw attention to new liquid crystal candidates that would have previously been considered unlikely.

One of the most studied ligands used in generating metallomesogens is the substituted β-diketonate.[1] There are several examples of square planar transition metal bis-β-diketonate compounds exhibiting disklike structures that align in columnar arrangements,[1] as well as β-diketonate-based metallomesogens with unusual shapes exhibiting novel alignments.[2b,3]

Our laboratory's studies of unusually shaped metallomesogens led us to investigate high coordinate zirconium tetrakis-β-diketonate compounds. These complexes are eight-vertex coordination compounds and have been reported to adopt square antiprismatic configurations.[4] This structure is best described as a sandwich of two pairs of β-diketonate ligands that are bent outward away from a planar environment around the zirconium atom. The antiprismatic structure requires the ligands to be rotated from an eclipsed to a staggered conformation. This structure can most simply be envisioned as a dimer of two disk-shaped mesogens bound together as shown in Figure 1, and thus are possible liquid crystal candidates. While this is the first report of an eight-vertex liquid crystalline β-diketonate, lutetium bisphthalocyanine "sandwich" complexes, which are also eight-coordinate about the metal center, have been previously reported to be liquid crystalline.[5]

An additional aspect that sparked our interest is the highly fluxional nature of zirconium tetrakisacetylacetonates. Fay et al. reported that zirconium tetrakisacetylacetonate rapidly interconverts between enantiomers and displays a coalescence temperature of −145 °C in a variable temperature 90 MHz NMR experiment.[6] It is hoped that similar dynamics in these zirconium tetrakis-β-diketonate liquid crystals will lead to new properties and switching processes.

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10.1021/cm980550k CCC: $18.00
Published on Web 12/05/1998

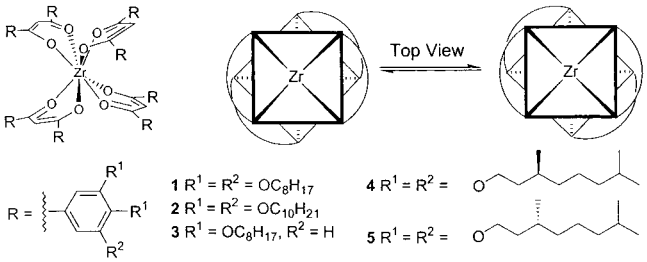

Figure 1. Illustration depicting the disklike top and bottom faces of zirconium tetrakis-β-diketonate complexes.

Results and Discussion

The zirconium tetrakis-β-diketonate compounds were synthesized by directly substituting the acetylacetonate ligands of commercially available zirconium tetrakisacetylacetonate with β-diketonates which were prepared following published procedures.[7] In a typical reaction, 1 equiv of zirconium tetrakisacetylacetonate was combined in a Schlenk tube with 4 equiv of the desired β-diketone. The tube was heated to 130 °C under dynamic vacuum for 1 h resulting, in a clear, yellow-orange oil.

Straight Chain Complexes. Examination of these viscous oily compounds by variable temperature polarized microscopy revealed that the 24 side chain materials (**1** and **2**) were liquid crystalline. Reducing the number of side chains to 16 (**3**) resulted in a loss of all mesomorphic properties. With slow cooling from the isotropic phase, **1** and **2** exhibited birefringent textures, as shown in Figure 2, with small linear birefringent defects characterizing the liquid crystals as columnar hexagonal (Col_{hd}) phases. As discussed previously, **1** and **2** were expected to align in a columnar arrangement due to the structure being similar to two disk-shaped moieties bound together.

Differential scanning calorimetry (DSC) investigations revealed that **1** and **2**, while displaying a limited range of liquid crystallinity, have the desirable attribute of being room-temperature liquid crystals. As shown in Table 1, the clearing points for **1** and **2** were 48.8 and 45.4 °C, respectively. The low clearing enthalpies are indicative of liquid crystal-to-isotropic phase transitions. DSC also revealed that both compounds undergo some degree of supercooling (12.1−13.9 °C) at a scan rate of 10 °C/min. This kinetic behavior can be attributed to the high molecular weights of **1** and **2** (4061 and 4735 Da, respectively) and the low transition temperatures, both of which lead to a high viscosity.

X-ray diffraction experiments confirmed the presence of Col_{hd} phases for **1** and **2**. As shown in Figure 3, the materials exhibit a sharp high-intensity peak and two lower intensity peaks at wider angles, which index to the (100), (110), and (200)[8] reflections of a two-dimensional hexagonal lattice. Two halos at wider angles were observed at $d = 6.35$ and 4.50 Å. The wide angle halo at 4.50 Å is very typical for all thermotropic liquid crystals due to the liquidlike correlations between the alkoxy side chains of the molecules. The origin of the halo at 6.35 Å cannot be assigned conclusively at this time, but most likely indicates short-range correlations of a higher length scale than seen for typical discotic materials. This halo may be a direct result of the dimerized disk structure, which produces a higher periodicity along the column than typical discotic mesogens.

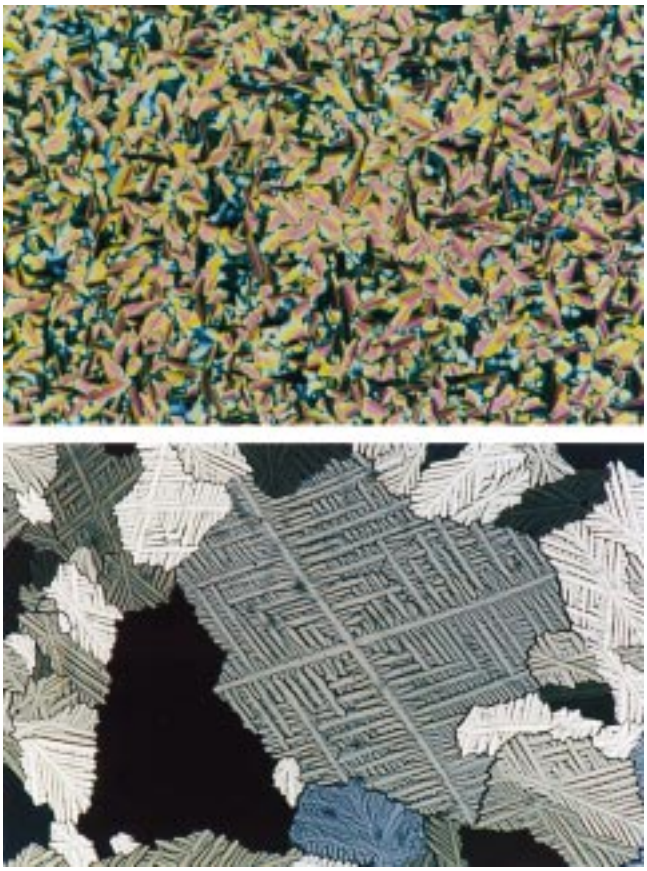

Figure 2. (a, top) Micrograph illustrating the textures observed for **2** through cross polarizers at 30.5 °C. (b, bottom) Micrograph illustrating the textures observed for **4** through cross polarizers at 36.4 °C.

Table 1. Phase Behavior of 1−5[a]

compd	phase behavior
1	$Col_{hd} \underset{36.7\ (-1.2)}{\overset{48.8\ (1.6)}{\rightleftharpoons}} I$
2	$Col_{hd} \underset{31.5\ (-1.7)}{\overset{45.4\ (2.2)}{\rightleftharpoons}} I$
3	$K \underset{50.0\ (10.9)}{\overset{97.0\ (15.6)}{\rightleftharpoons}} I$
4	$Col_{ob} \underset{56.9\ (-3.1)}{\overset{68.5\ (3.5)}{\rightleftharpoons}} I$
5	$Col_{ob} \underset{58.5\ (-3.4)}{\overset{71.5\ (3.4)}{\rightleftharpoons}} I$

[a] The transition temperatures (°C) and enthalpies, in parentheses (kcal/mol), were determined by DSC (scan rate 10 °C/min) and are given above and below the arrows. The designations I, Col_{hd}, K, and Col_{ob} represent isotropic, columnar hexagonal disordered, crystal, and columnar oblique phases, respectively.

Comparisons of the DSC data of **1** and **2**, listed in Table 1, with the analogous square planar copper and palladium complexes of the identical β-diketonate ligands yielded interesting contrasts in behavior. For example, the clearing point for **1** is 54.5 and 96.7 °C lower than

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(8) The (200) reflection was not observed for **1**.

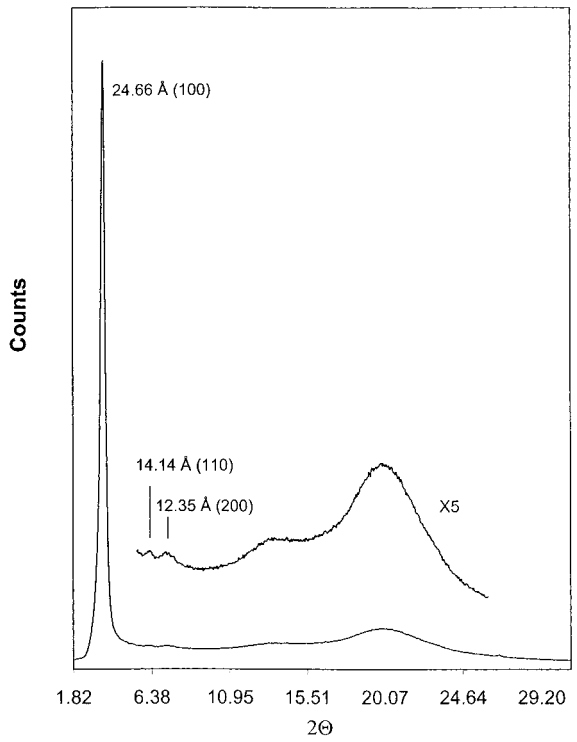

Figure 3. X-ray diffraction pattern of **2** at 25 °C.

Table 2. XRD for 1 and 2

compd	mesophase	lattice constant (Å)	spacing obsd	Miller indices	Å (calcd)	halos obsd
1	Col_{hd}	25.66	22.22	100		6.18
	at 25 °C		12.51	110	(12.83)	4.47
2	Col_{hd}	28.47	24.66	100		6.35
	at 25 °C		14.14	110	(14.24)	4.50
			12.35	200	(12.33)	
4	Col_{ob}	$a = 21.88$	21.88	100	(21.88)	4.85
	at 25 °C	$b = 21.88$	14.35	110	(14.35)	
		$\gamma = 98.0°$	8.23	$2\bar{1}0$	(8.26)	
			7.54	300	(7.29)	
			7.23	220	(7.18)	
5	Col_{ob}	$a = 22.22$	22.22	100	(22.22)	4.88
	at 25 °C	$b = 22.22$	14.42	$1\bar{1}0$	(14.42)	
		$\gamma = 99.1°$	8.26	$2\bar{1}0$	(8.45)	
			7.56	300	(7.41)	
			7.28	220	(7.21)	

for the analogous copper and palladium compounds, respectively.[7b] Likewise, the clearing point for **2** is 62.6 °C lower than that of the analogous copper compound and 95.8 °C lower than that of the analogous palladium compound.[7b] This dramatic reduction in clearing points may be attributed to both the deviation from planarity of the β-diketonate ligands in **1** and **2** and the reported fluxional nature of zirconium tetrakis-β-diketonates.[6] As mentioned earlier, the crystal structure of zirconium tetrakisacetylacetonate has shown the ligands to be tilted outward in a convex shape away from the metal center.[4c] This deviation from planarity of the ligands limits the cofacial contacts between neighboring molecules in a columnar environment, which lowers the clearing points of **1** and **2**. Other supporting evidence for this structure is found in the measured lattice constants for **1** and **2** listed in Table 2. We find that the lattice constant (a) is 2.5−3.5 Å shorter for **1** and **2** than those reported for the planar copper and palladium bis-β-diketonates.[7b] The convex distortion from planarity decreases the diameters of the two pseudo-disk-shaped moieties bound to the central zirconium atom, contributing to the smaller lattice constant.

Branched Chain Complexes. The addition of two branching methyl groups on the side chains of the zirconium tertakis-β-diketonates was found to increase the clearing point over that of the straight chain analogues. Commercially available (*R*)- and (*S*)-citronellyl bromides were separately hydrogenated over Adam's catalyst by a method similar to the one reported by Drenth et al.[9] to generate the branched (*R*)- and (*S*)-alkyl bromides. The procedures used are reported to produce enantiomerically pure alkyl bromides.[10] The enantiomeric purity of these alkyl bromides was indeed verified by gas chromatography using a β-cyclodextrin-capped column. These branched alkyl bromides were integrated into β-diketonate ligands by straightforward extension of reported procedures.[7] The subsequent Williamson ether reactions are unlikely to isomerize the β-position; hence, the ligands are considered to be enantiomerically pure. Compounds **4** and **5** were then synthesized by the same method used to make **1** and **2**, yielding a material with 24 chiral centers around the fluxional zirconium core.

DSC measurements revealed that the addition of the branching methyl groups stabilized the liquid crystal phases of **4** and **5** to higher temperatures while preserving the liquid crystallinity at room temperature. As shown in Table 1, the clearing points of **4** and **5** are approximately 20 °C higher than those of **1** and **2**, indicating that subtle structural changes can translate to dramatic changes in the bulk properties of these materials.

Compounds **4** and **5** exhibited unusual textures when investigated with polarized microscopy. Large domains formed with slow cooling from the isotropic phase, as shown in Figure 2. These domains contained dendritic patterns, suggesting a columnar arrangement. Clearly a columnar phase was expected on the basis of the structural similarities between **4** and **5** and **1** and **2**. However, the textures observed were not characteristic of a hexagonal packing of the columns and were also not typical of a rectangular liquid crystal phase. The defect lines did show a predominance of intersecting features at almost 90° angles, possibly indicating the presence of an unusual columnar rectangular, tetragonal, or oblique phase.

Variable temperature powder X-ray diffraction experiments were conducted to determine the packing arrangement of the columns in the liquid crystal phases of **4** and **5**. As shown in Figure 4, the diffraction patterns of **4** and **5** showed one sharp low-angle high-intensity peak, another pronounced sharp, lower intensity peak at higher angles, two other sharp peaks of low intensity in the midangle region, and a wide angle diffuse halo centered at 4.88 Å. As previously discussed, the textures observed with polarized microscopy for **4** and **5** are not characteristic of a hexagonal packing arrangement such as the one observed for **1** and **2**. The X-ray diffraction data confirms this conclusion due to

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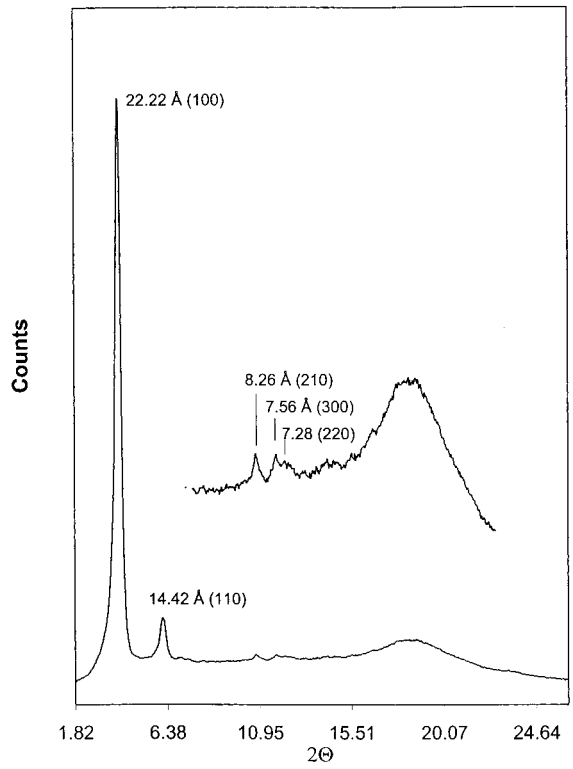

Figure 4. X-ray diffraction pattern of **5** at 25 °C.

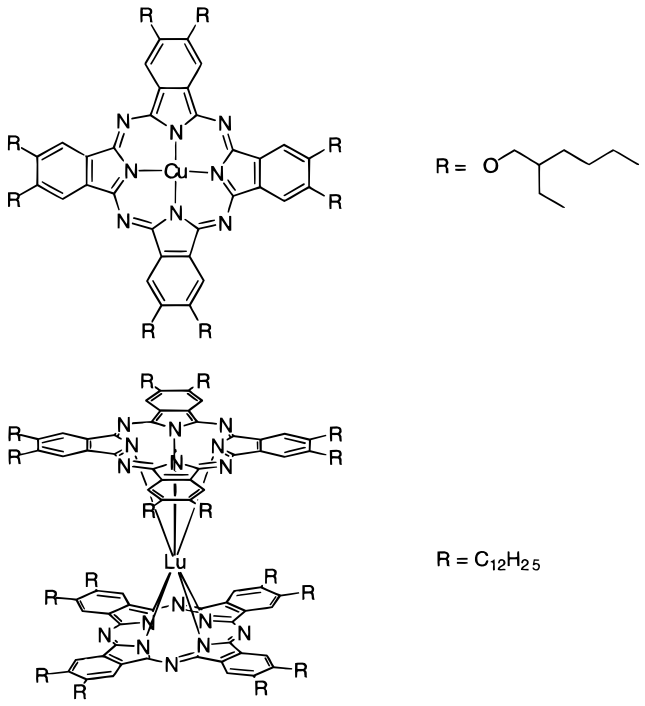

Figure 5. Mesogens possessing structural similarities to **4** and **5** that align in columnar oblique phases.[11,5f]

the failure of the observed reflections to fit the characteristic *d* spacing ratio of 1:1/√3. The peaks listed in Table 2 also could not be indexed to any rectangular lattice, which would generally result in two more closely spaced low-angle peaks indexing to the (200) and (110) planes. However, the observed peaks indexed closely to the reflections of a columnar oblique lattice. A copper phthalocyanine with branched side chains[11] and a sandwichlike lutetium compound[5f] illustrated in Figure 5 are some of the literature examples of materials reported to organize in columnar oblique phases (Col_{ob}). The structural similarities between **4** and **5** and these literature examples as well as the fit of the observed X-ray reflections, listed in Table 2, suggest that **4** and **5** are aligning in columnar oblique phases.

The diffuse halo centered at 4.88 Å is again due to the liquidlike correlations between the alkoxy side chains of the molecules. These halos for **4** and **5** are centered around a larger *d* spacing than that observed for the halos of **1** and **2**. This can be attributed to the branched structure of the side chains of **4** and **5** preventing correlations as close as those observed for **1** and **2**, causing an increase in the distance over which the branched side chains associate.

Summary

Mesomorphic zirconium tertakis-β-diketonates represent another example of how transition metal complexes provide a fertile route to the discovery of novel liquid crystalline systems. These eight-vertex complexes with square antiprismatic coordination environments are room temperature columnar liquid crystals and are stable over good to moderate temperature ranges. Analogous square planar complexes displayed much higher transition temperatures, demonstrating the utility of these novel-shaped mesogens. Slight structural modifications have been shown to dramatically alter the properties of this system. The addition of two branching methyl groups on the side chains of these materials stabilized liquid crystalline ranges by increasing the clearing point over those seen for straight side chain systems. Additionally, the two branching methyl groups greatly affected the organization of the columns in the liquid crystal phase and produced a columnar oblique phase. This sensitivity to side chains illustrates the ability to induce macroscopic reorganizations by tailoring the molecular architecture of materials.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Bruker AC-250. ^{13}C NMR spectra were recorded on a Varian Unity VXR 500. Chemical shifts are reported in ppm relative to residual $CHCl_3$ (δ = 7.24, ^{1}H; 77.0, ^{13}C). Multiplicities are given as s (singlet), t (triplet), and m (multiplet). Elemental analyses were obtained from Desert Analytics. Optical characterization was performed using covered microscope slides on a Leica DMRXP polarizing microscope equipped with a Wild Leitz MPS46 Photoautomat along with a Mettler FP 82 HT hot stage and a Mettler FP 80 HT central processor. Transition temperatures and heats of fusion were determined at scan rates of 10 °C/min by differential scanning calorimetry using a Perkin-Elmer DSC 7 with a Perkin-Elmer 7700 thermal analysis data station. Variable temperature X-ray diffraction was measured using Cu Kα radiation on an Inel CPS 120 position-sensitive detector with a XRG 2000 generator, a fine-focus X-ray tube, and a home-built heating stage. The temperature was regulated with a Minco CT 137 controller with ±1 °C stability. Approximately 2 mg of sample was suspended in 1.5 mm Lindermann glass capillaries. The detector was calibrated using mica and silicon standards obtained from the National Bureau of Standards (NBS).

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Unless otherwise indicated, all chemicals and solvents were purchased commercially and used as obtained without further purification. All 1,3-bis(3′,4′,5′-trialkoxyphenyl)-1,3-propandione ligands were synthesized following literature procedures.[7] Air and moisture sensitive reactions were carried out in oven-dried glassware under an atmosphere of dry argon employing standard Schlenk techniques.

Tetrakis[1,3-bis(3′,4′,5′-tridecyloxyphenyl)-1,3-propanedionato]zirconium(IV) (General Procedure for Zirconium Tetrakis-*β*-diketonates). Zirconium(IV) acetylacetonate (0.066 g, 0.14 mmol) and 1,3-bis(3′,4′,5′-tridecyloxyphenyl)-1,3-propanedione (0.595 g, 0.512 mmol) were combined in an oven-dried 25 mL Schlenk tube under an argon purge. The sealed tube was evacuated and then heated to 130 °C under dynamic vacuum. After 1 h, the reaction mixture was cooled to room temperature and the tube was refilled with argon. Approximately 3 mL of hexane was added to the bottom to the Schlenk tube, taking care to avoid washing any material off of the sidewalls of the tube. The yellow solution was removed from the bottom of the tube and the process was repeated two more times. The hexane was removed from the combined fractions, yielding a viscous yellow oil. This oil was dissolved in warm acetone and then stored at −15 °C for 24 h. A yellow oil collected at the bottom of the flask during that time. The acetone solution above the oil was removed with a pipet, yielding the product as a yellow oil (0.606 g, 81%). ^{1}H NMR ($CDCl_3$): 0.85 (t, 72H, C*H*$_3$), 1.23−1.68 (m, 384H, OCH$_2$-(C*H*$_2$)$_8$CH$_3$), 3.59 (t, 32H, *m*-OC*H*$_2$), 3.87 (t, 16H, *p*-OC*H*$_2$), 6.74 (s, 4H, COC*H*CO), 7.13 (s, 16H, ArH). ^{13}C NMR ($CDCl_3$): 14.11, 22.70, 22.72, 26.15, 26.40, 29.42, 29.49, 29.55, 29.70, 29.74, 29.79, 29.80, 29.82, 30.46, 31.95, 31.99, 68.90, 73.33, 91.82, 106.28, 133.49, 141.30, 152.61, 180.67. Calculated for $C_{300}H_{524}O_{32}Zr_1$: C, 76.10; H, 11.16. Found: C, 75.96; H, 11.26.

(*S*)-3,7-Dimethyloctyl Bromide (General Procedure for Chiral Alkyl Bromides). This compound was synthesized by modifying a procedure reported by Drenth et al.[9] (*S*)−(+)-Citronellyl bromide (21.978 g, 100.28 mmol) was added to a 250 mL Schlenk flask containing approximately 60 mL of ethyl acetate under an argon atmosphere. Platinum(IV) oxide (0.550 g, 2.42 mmol) was then added to the solution. Hydrogen was bubbled through the reaction mixture for 1 h. A balloon filled with hydrogen was placed over the neck of the round-bottom flask and tied in place with copper wire. The reaction was stirred for 3 days while the balloon was periodically refilled with hydrogen. The solvent was removed under vacuum and the remaining residue was dried under vacuum for 1 h. Approximately 60 mL of hexane was added to the residue, which was then filtered to remove the catalyst. The catalyst was then washed with several aliquots of hexane. The combined hexane fractions were passed through a plug of silica gel. The hexane was removed under vacuum, yielding the clear and colorless liquid product (20.21 g, 91%). ^{1}H NMR ($CDCl_3$): 0.75−0.94 (m, 9H, C*H*$_3$), 1.08−1.71 (m, 8H, (CH$_3$)$_2$-C*H*C*H*$_2$C*H*$_2$C*H*$_2$C*H*(CH$_3$)CH$_2$CH$_2$Br), 1.81−1.91 (m, 2H, C*H*$_2$-CH$_2$Br), 3.33−3.47 (m, 2H, C*H*$_2$Br). ^{13}C NMR ($CDCl_3$): 18.91, 22.53, 22.63, 24.50, 27.89, 31.62, 31.90, 36.68, 39.13, 40.06. Calculated for $C_{10}H_{21}Br_1$: C, 54.30; H, 9.57; Br, 36.13. Found: C, 54.14; H, 9.68; Br, 36.22.

Acknowledgment. We are grateful for financial support provided by the National Science Foundation (DMR-9811377) and the Office of Naval Research.

Supporting Information Available: Table listing all of the elemental analysis data for the tetrakis-*β*-diketonates presented in this manuscript (1 page). Ordering information is given on any current masthead page.

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