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Synthesis and Properties of Optically Active Helical Metallocene Oligomers

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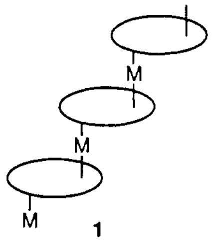
Abstract: Syntheses are described for optically active oligomers **9** and **27**. The steps required have three essential features. (1) A bromine directs a photocyclization, blocking both the position it occupies and the one adjacent. (2) An acid scavenger (propylene oxide) prevents benzylic ethers from being eliminated during photocyclization. (3) The stereogenicity of one carbon controls the direction in which the helix winds. The oligomers are the first to be prepared in which metallocenes are joined by conjugated systems of double bonds. Their optical activity is very high. The cyclic voltammogram of **9** shows two cathodic waves whose closeness implies that the interaction between adjacent units is weak. When **9** is reduced electrochemically on Pt, a film of neutral oligomers is produced. This film is conductive, and it catalyzes charge transfer. Its weight, measured using a quartz crystal microbalance after the amount of reduction was analyzed coulometrically, measured the molecular weight of **9**.

Introduction

No conductive materials are known that cause electron currents passing through to spiral in only one direction. There are, in other words, no chiral conductors of electricity. However, these should be possible to construct, for conductivity is observed in many polymers that have conjugated mobile electrons and component monomeric units in nonintegral oxidation states.[1] Thus the goal might be achieved if such polymers were also helical and optically active.

Toward this end, we examine here a way to prepare a helical metallocene with unbroken conjugation in the carbon skeleton. It extends an effort made over a number of years to synthesize a polymer like **1**, in which rings of conjugated hydrocarbons and metal atoms alternate. In the early work, a number of polyanions that had pairs (or in one case a triplet)[2] of conjugated cyclopentadienyl rings, like **2**,[3] **3**,[4] and **4**,[5] were synthesized and combined with transition-metal salts. But in each case, the only characterizable products were dimers like **5**.[6]



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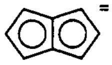

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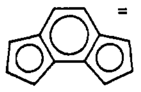

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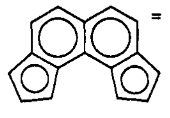

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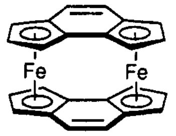

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To circumvent the formation of such dimers, structures **6**[7] and **7**[8] were synthesized, in which the number of benzene rings is increased. This increase forces the molecules into helical shapes that cannot give dimers but should still be electronically conjugated from end to end.[9] Indeed, as we reported in communications, neither hydrocarbon **6** nor hydrocarbon **7** when treated with strong bases and then transition-metal halides gives a dimer.[7,8] With cobaltous bromide followed by oxidation, the former gives a monomer (**8**) because the two five-membered rings are almost superimposed, while the latter gives oligomer **9**, an example of the sought-after polymer. Below we record experiments showing how **9** can be synthesized optically active, and we report some of the properties of this helical oligomer. We also report experiments to make mixed-valence derivatives of **9** and to measure their properties.

Results

[9]Helicene Synthesis. Scheme I shows how the synthesis was achieved. The (*R*,*R*)-bis-stilbene **11**, a mixture of cis and trans isomers synthesized in a Wittig reaction from siloxyaldehyde **10**, when photocyclized gives the helicene **12** as a single diastereomer—almost surely the exo,exo isomer shown—which when the

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(1) (a) Ferraro, J. R.; Williams, J. M. *Introduction to Synthetic Electrical Conductors*; Academic: Orlando, 1987. (b) *Handbook of Conducting Polymers*; T. A. Skotheim, Ed.; Dekker: New York, 1986; Vols. 1 and 2. (c) Heinze, J. *Top. Curr. Chem.* **1990**, *152*, 1. (d) Billingham, N. C.; Calvert, P. D. *Adv. Polym. Sci.* **1989**, *90*, 1. (e) Marks, T. J. *Science (Washington, DC)* **1985**, *227*, 881. (f) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1981**, *41*, 149. (g) Baughman, R. H.; Brédas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209. (h) Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355. (i) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79.

(2) Katz, T. J.; Slusarek, W. *J. Am. Chem. Soc.* **1980**, *102*, 1058.

(3) Katz, T. J.; Rosenberger, M.; O'Hara, R. K. *J. Am. Chem. Soc.* **1964**, *86*, 249.

(4) Katz, T. J.; Schulman, J. *J. Am. Chem. Soc.* **1964**, *86*, 3169.

(5) Katz, T. J.; Slusarek, W. *J. Am. Chem. Soc.* **1979**, *101*, 4259.

(6) **2**: (a) Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1972**, *94*, 3281. (b) Katz, T. J.; Acton, N.; McGinnis, J. *J. Am. Chem. Soc.* **1972**, *94*, 6205. **3**: (c) Reference 4. (d) Katz, T. J.; Balogh, V.; Schulman, J. *J. Am. Chem. Soc.* **1968**, *90*, 734. (e) Gitany, R.; Paul, I. C.; Acton, N.; Katz, T. J. *Tetrahedron Lett.* **1970**, 2723. **4**: (f) See reference 5.

(7) (a) Katz, T. J.; Pesti, J. *J. Am. Chem. Soc.* **1982**, *104*, 346. (b) Pesti, J. Ph.D. Dissertation, Columbia University, New York, 1981. (c) Sudhakar, A.; Katz, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 179.

(8) Sudhakar, A.; Katz, T. J.; Yang, B.-W. *J. Am. Chem. Soc.* **1986**, *108*, 2790.

(9) Katz, T. J.; Sudhakar, A.; Yang, B.; Nowick, J. S. *J. Macromol. Sci. Chem.* **1989**, *A26*, 309.

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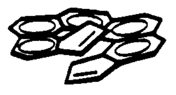

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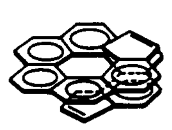

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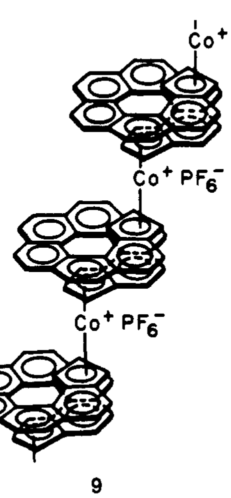
8 (M = $Co^+ PF_6^-$)



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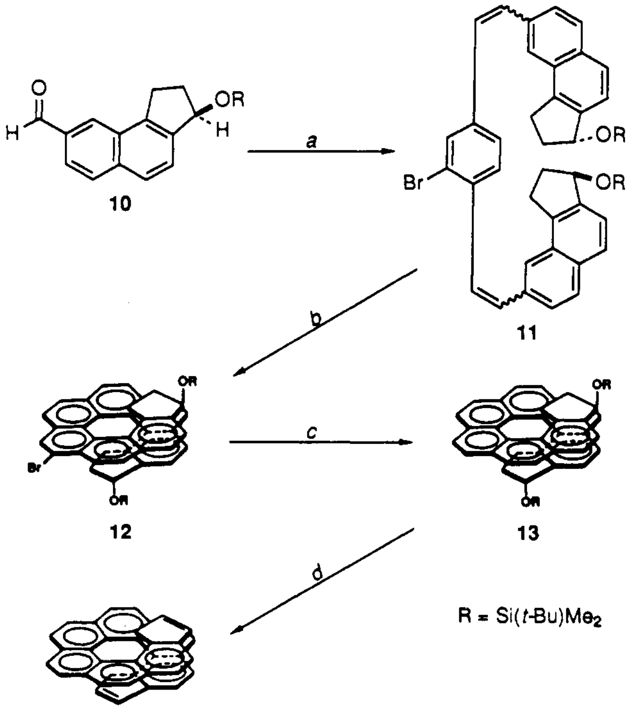
bromine is removed and the siloxy groups eliminated gives helicene **14**, the precursor to helical oligomer **9**.

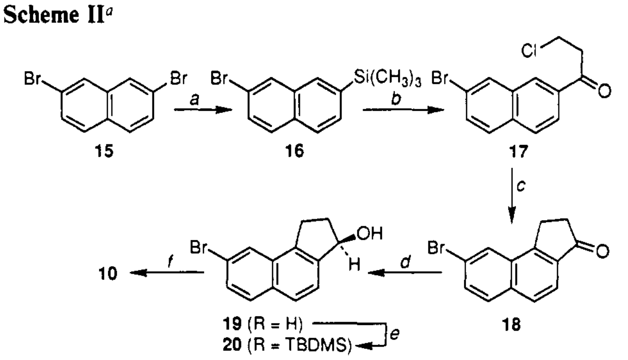
The required siloxyaldehyde **10** was synthesized as summarized in Scheme II, while the bis-phosphonium salt with which it was combined was prepared by brominating 2-bromo-*p*-xylene with *N*-bromosuccinimide and displacing the two benzylic bromines with triphenylphosphines. In Scheme II we used Mayer and Müller's procedure to fuse the five-membered ring to the naphthalene,[10] and we used the directing effect of silyl substituents[11] to force the acylation to naphthalene's 7-position. In the absence of the trimethylsilyl group, the acylation takes place mainly at the 8-position (and to a small extent also at the 6-),[12] so the bromobenzindanone produced is mainly the isomer of **18** with the ketone at C-1.[7c] The required 2-bromo-7-(trimethylsilyl)naphthalene (**16**) was prepared by combining 2,7-dibromonaphthalene with 1 mol of *n*-butyllithium in tetrahydrofuran[13] and then with chlorotrimethylsilane.[14]

Scheme I[a]



[a] (a) 1,4-Bis[$(C_6H_5)_3P^+CH_2$]-2-Br-C_6H_3 2Br (0.5 equiv), LiOEt (1.05 equiv), EtOH, 25 °C, 12 h, 78% yield. (b) $h\nu$, PhH, I_2 (2.2 equiv), propylene oxide, rt, 14 h, 50% yield. (c) *n*-BuLi, tetrahydrofuran, -78 °C, 30 min; H_2O–NH_4Cl, 92% yield. (d) *p*-Toluenesulfonic acid, PhH, reflux, 30 min, 97% yield.

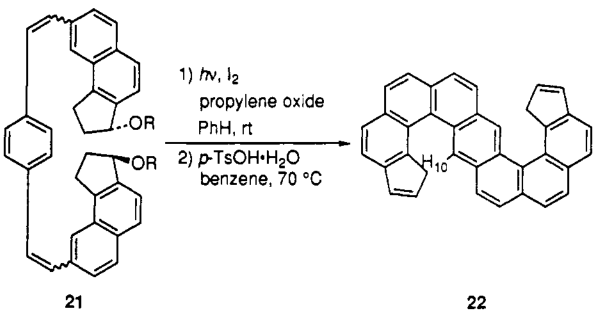
Scheme II[a]



[a] (a) *n*-BuLi, THF, -78 °C, 50 min, $(CH_3)_3SiCl$, 100% yield. (b) $ClCH_2CH_2COCl$, $AlCl_3$, CH_2Cl_2, -78 °C to rt, 90 min, 76% yield. (c) Concd H_2SO_4, 90 °C, 2 h, 97% yield. (d) *i*-PrCH(NH_2)CPh_2OH, BH_3·THF, THF, 0 °C to rt, 12 h, 99% yield, 98% ee. (e) *t*-$BuMe_2SiCl$, imidazole, DMF, rt, 10 h, 85–99% yield (R = *t*-$BuMe_2Si$). (f) **20** + *n*-BuLi, THF/Et_2O, -78 °C, 40 min; DMF, 86% yield.

Finally, Itsuno's method, using (*S*)-(−)-2-amino-3-methyl-1,1-diphenylbutan-1-ol (diphenylvalinol) and borane in THF gave the optically active alcohol in 99% yield and 98% enantiomeric excess.[15] Corey's variant, using the amino alcohol in only catalytic amounts, worked as well (99% yield, 99% enantiomeric excess).[16] The enantiomeric purities were determined by analyzing the ^1H NMR spectra of the mixed diastereomeric esters produced when the alcohol was combined with the acid chloride of (*S*)-(+)-*O*-methylmandelic acid.[17]

Role of the Bromine Substituent. The bromine atom in structure **11** (Scheme I) plays a critical role in the synthesis. If experiments like those that transform **11** to **14** are attempted with the analogue of **11** that lacks the bromine (structure **21**), no helicene is produced. Given instead is the isomeric structure **22** (eq 1). Thus, in the ^1H NMR spectrum of the reaction product there is a very prominent resonance at particularly low fields (δ 8.95), attributable to H_{10} in **22**.[18] This resonance is not seen in the spectrum of the helical hydrocarbon. Moreover, the spectrum shows almost no absorption at δ 5.82, where **14** exhibits a characteristic



(1)

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[10] (a) Mayer, F.; Müller, P. *Chem. Ber.* **1927**, *60*, 2278. (b) Dannenberg, H.; Rahman, A.-U. *Chem. Ber.* **1955**, *88*, 1405. (c) Hart, R. T.; Tebbe, R. F. *J. Am. Chem. Soc.* **1950**, *72*, 3286. (d) Arnold, R. T.; Rondestvedt, E. *J. Am. Chem. Soc.* **1945**, *67*, 1265.

[11] (a) Dey, K.; Eaborn, C.; Walton, D. R. M. *Organomet. Chem. Synth.* **1970/71**, *1*, 151. (b) Eaborn, C. *J. Organomet. Chem.* **1975**, *100*, 43.

[12] Analogous products form in the acetylation of 2-bromonaphthalene acetyl chloride: Girdler, R. B.; Gore, P. H.; Hoskins, J. A. *J. Chem. Soc. (C)* **1966**, 518.

[13] Porzi, G.; Concilio, C. *J. Organomet. Chem.* **1977**, *128*, 95. These authors reported that the naphthalene is appreciably butylated when the solvent is tetrahydrofuran, but we do not find this.

[14] Häbich, D.; Effenberger, F. *Synthesis* **1979**, 841.

[15] Itsuno, S.; Nakano, M.; Miyazaki, K.; Masuda, H.; Ito, K.; Hirao, A.; Nakahama, S. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2039.

[16] Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551.

[17] (a) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1968**, *90*, 3732. (b) Raban, M.; Mislow, K. *Tetrahedron Lett.* **1966**, 3961. (c) Yamaguchi, S. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1983; Vol. 1, Chapter 7. (d) Parker, D. *Chem. Rev.* **1991**, *91*, 1441.

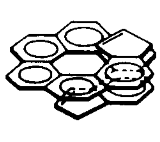
[18] Brison, J.; de Bakker, C.; Defay, N.; Geerts-Evrard, F.; Marchant, M.-J.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1983**, *92*, 901.

resonance. The intensity around this position implies that at most 5% as much **14** as **22** is present. The spectrum also excludes the possibility that instead of **14** some of its double-bond isomers had formed. Helical indenes in general,[7b] like **14**, **6**,[7a,b] and the isomer of **6** in which both double bonds are shifted to their allylic positions,[7b] exhibit olefinic resonances at much higher fields than nonhelical analogues.[5] In the isomer of **14** in which both double bonds have shifted to their allylic positions, structure **23** (whose preparation is described below), the resonances appear at δ 5.77 and 5.65. In the product of eq 1, however, no appreciable peaks are observed between δ 5 and 6. Thus very little helicene is produced.

Compound **22** was not isolated and purified. However, its structure was assigned because in the ^{1}H NMR spectrum (displayed in the supplementary material) the aromatic region shows the required six AB quartets and the characteristic singlet mentioned above. The spectrum also shows two doublets of triplets, characteristic of indene olefins, at δ 7.0 and 6.45, and two broad doublets, assigned to the methylenes, at δ 4.5 and 2.9. Moreover, irradiating the resonance at δ 4.5 transforms the olefin resonances into doublets, as expected for an indene, and it causes the resonance at δ 2.9 to disappear, presumably because the molecule undergoes a conformational change that interconverts the methylene hydrogens.

In contrast to **21**, when **11** is photoirradiated, no analogue of **22** is produced. The structure would be recognized because, like **22**, it should show a singlet resonance at ca. δ 9.0, at much lower fields than in helicene **12**. We estimated the minimum intensity we would have detected around this position and compared it in three experiments with the intensity of the resonance at δ 8.31, which is characteristic of **12** (and of its *O*-silyl epimer). These measurements show that less than 6 ± 2% of the structure with **22**'s ring-system contaminated the **12** that was produced. Thus the bromine in structure **11** prevents the dinaphthanthracene ring system from forming, whereas in the absence of bromine, that ring-system forms to the exclusion of the helix.

Mechanism of Asymmetric Helix Winding. In the Discussion section we show that the conversion of **11** to **12** takes place in such a way that essentially all the OR groups end up outside the helix, causing the helices to wind in only one direction. Placing both OR groups on the inside is avoided. We consider here the following question: if the cyclization of such a bis-stilbene could place only *one* OR group on the outside—that is, if it *had* to place one on the inside—would the helix form as easily? This question can be answered by analyzing the products of the transformation of a bis-stilbene that differs from **11** by being prepared from **10** that is *not* optically pure. The experiment was performed using a sample derived from the (*S*)-(−)-stereoisomer of **19** that formed when ketone **18** was reduced in ether at room temperature with the combination of lithium aluminum hydride, (+)-(1*S*,2*R*)-*N*-methylephedrine, and 2 mol of 3,5-dimethylphenol.[19] The specific rotation of the resulting bromoalcohol, $[\alpha]_D$ −37.3°, corresponds to an optical purity of 63%. The bis-stilbene prepared from this alcohol—notice that it was predominantly the enantiomer of **11**—was photocyclized, and when the product was chromatographed, *two* helicenes related to **12** were isolated. The predominant one, obtained in 27% yield, was the expected enantiomer of **12**, the exo,exo bis-siloxy-(*M*)-helicene. However, a diastereomer was also obtained in 12% yield. This material was easily recognized to be the exo,endo bis-siloxyhelicene **24** because its ^{1}H and ^{13}C NMR spectra are similar to those of **12**, while the resonances associated with the t-BuMe$_2$SiOCH groups are clearly doubled. Its optical activity was only ca. 3% that of the enantiomer of **12** from which it was separated. It is remarkable that this isomer forms to an appreciable extent despite one siloxy group being forced into the helix. A quantitative analysis implies that the yields of the exo,exo helicene (the enantiomer of **12**) and the exo,endo helicene **24** are both ca. 40%.[20] But the yield of the endo,endo helicene isomeric with **12** and **24** must be small, for its direction would be opposite that of the dominant helix.[21] If this isomer formed as easily as the exo,exo, the siloxy groups would—contrary to observation—induce no apparent asymmetry in the winding of the helix.



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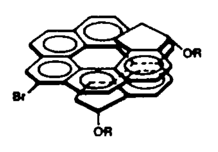

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R = OSi(t-Bu)Me$_2$

The same conclusions are drawn from experiments in which Yang determined the optical purity of a sample of **14** made from a sample of bromo alcohol **19** that was not optically pure.[8,22] The (*S*)-(−)-alcohol **19** used for this experiment was prepared as in the experiment above. It had $[\alpha]_D$ −41°, corresponding to an optical purity of 67%. According to the steps in Schemes I and II, this alcohol was converted into a stereoisomer of **14**, $[\alpha]_D$ −4200°. The optical purity of the hydrocarbon was determined by combining it in CDCl$_3$ with 2 equiv of Ag(fod)[23] and 2 eq of Eu(hfc)$_3$.[24] This splits into two the methylene doublet that in the unperturbed ^{1}H NMR spectrum appears at δ 1.91.[17d,25] The ratio of the intensities of these two doublets (at δ 2.32 and 2.45), measured as 4.03 ± 0.05, implied that the enantiomeric excess was 60%.[22] If only (*R*,*R*)-**11** and its enantiomer (*S*,*S*)-**11** photocyclized to the helix and the (*R*,*S*)-diastereomer did not, then the enantiomeric excess would have been higher in the helicene (up to 92%) than in the bromo alcohol from which it was derived.[20] Since this was not observed, it follows that (*R*,*S*)-**11** must yield *exo,endo*-**24** at a rate comparable to the rate at which (*S*,*S*)-**11** gives (*M*)-*exo,exo*-**12** and (*R*,*R*)-**11** gives (*P*)-*exo,exo*-**12**.[26] But (*S*,*S*)-**11** must give the endo,endo (*P*) helicene much more slowly, for otherwise the product would not consist mainly of the exo,exo (*M*) isomer.

The experiment described in Scheme I demonstrates the last point in another way as well. If, as we saw, helicene **14** with specific optical activity $[\alpha]_D$ 4200° is 60% optically pure, then a sample that is 100% optically pure should have $[\alpha]_D$ 7000°. Since the helicene produced in Scheme I had a specific rotation $[\alpha]_D$ 7800° and was produced from bromo alcohol **19** whose enantiomeric excess was 98–99%, the asymmetry of the alcohol translates into asymmetry of the helix with seemingly perfect fidelity.

Role of Propylene Oxide. For this fidelity to be achieved, however, the siloxy groups in structure **11** must not move from their points of attachment, and the propylene oxide and stoichiometric amounts of iodine in Scheme I, step b, forestall this detrimental occurrence. Thus when the photocyclization is carried out as related reactions have been in the past, using catalytic amounts of iodine, air, and no propylene oxide,[27] the siloxy groups are eliminated. The reason, presumably, is that HI generated in

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(19) Vigneron, J. P.; Jacquet, I. *Tetrahedron* **1976**, *32*, 939.

(20) If the ee of **19** is 63%, 82% has the *S*-configuration and 18% the *R*. Assuming the bis-stilbene incorporates these stereoisomers randomly, it should be 67% *S,S*, 3% *R,R*, and 30% *R,S*. The yield of the *exo,endo*-helicene **24** is then 12/0.3 = 40% and of the *exo,exo*-helicene 27/0.7 = 39%.

(21) To be *endo,endo* and form from *S,S-bis*-stilbene, it would have to be the *P* helix.

(22) Yang, B. V. Ph.D. Dissertation, Columbia University, New York, 1987.

(23) 6,6,7,7,8,8,8-Heptafluoro-2,2-dimethyl-3,5-octanedionato)silver, Resolve-Al AgFOD from Aldrich Chemical Co.

(24) Tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium.

(25) (a) Offermann, W.; Mannschreck, A. *Tetrahedron Lett.* **1981**, *22*, 3227. (b) Wenzel, T. J.; Sievers, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 382.

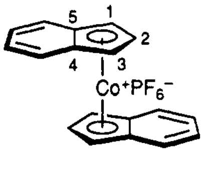
(26) *P* ≡ right-handed and *M* ≡ left-handed helix. See: Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

(27) Mallory, F. B.; Mallory, C. W. *Organic Reactions*; Wiley and Sons: New York, 1984; Vol. 30, p 1.

this procedure facilitates the formation of the benzylic cations. Moreover, even though the optical activity of the bis-stilbene **11** is high, that of the product is essentially negligible. The specific rotation of the bromo alcohol **19** used to make this bis-stilbene was $[\alpha]_D$ 46.7°,[28] while that of the crude product of the photocyclization was $[\alpha]_D$ 82°, not the 7800° of **14**. This means that the optical purity of the bromo alcohol was 79%, while that of the product was $\leq$1%. Thus the siloxy groups must eliminate to a large extent before the photocyclization takes place. They cannot, then, determine the direction in which the helix winds.

However, the propylene oxide, by consuming the HI, prevents this elimination from occurring, and in its presence the product is essentially the optically pure bis-siloxyhelicene **14** (Scheme I). The elimination of benzylic ethers was similarly prevented in related syntheses of optically active **6** and **8**.[7c] Of course when propylene oxide is present in excess, stoichiometric, rather than catalytic, amounts of iodine are required, for HI that has been consumed cannot regenerate I_2 by reacting with oxygen in the air. It turns out that although the combination of propylene oxide and iodine was conceived to avert the elimination of ethers, this mixture confers on photocyclizations additional benefits, which are set forth elsewhere.[29]

[9]Helicene Cobaltocenium Oligomers. The helicene cobaltocenium oligomers **9** were obtained when **14** was combined with 2 equiv of *t*-BuLi, to which $CoBr_2{\cdot}DME$[30] was later added. The product was oxidized with $FeCl_3$ in aqueous HCl and precipitated with NH_4PF_6. The procedure was optimized for the synthesis of bis(indenyl)cobalt hexafluorophosphate (**25**) by varying the bases, solvents, and cobalt salts. The optimal procedure produces **25** in 75% yield and **9** in 87% yield. When the base was LiTMP, KHMDS, or LiOBA and THF was the solvent, the yields of **25** were ca. 70%.[31] If LiTMP was the base and diethyl ether the solvent, the yield decreased to 39%.[32] A variety of other solvents failed completely. These included 1,2-dimethoxyethane and 1,4-dioxane (which were studied because they dissolve **14** well), dimethylformamide and dimethyl sulfoxide (which dissolve **9** and **25** well), and THF mixed with hexamethylphosphoramide (which should increase the reactivities of the anions).[32] Other hindered bases when used in THF gave yields of only 16–41%: $(TMP)_2Mg$, TMPMgBr, LiHMDS, and NaHMDS.[31] When the cobalt salt was $CoCl_2$ or $CoI_2{\cdot}DME$, the yields were 66 and 50%, respectively. Other cobalt salts, $Co(acac)_2$, $Co(acac)_3$, and $Co(NH_3)_6Cl_3$, gave no product.



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An interesting procedure we explored was first to combine indene with $CoBr_2{\cdot}DME$ and then to add a base that reacts with the hydrocarbon but not with the metal salt.[33] Clearly the base cannot be *t*-BuLi. However, potassium hexamethyldisilazide (KHMDS) meets the requirements.[34,35] Indeed, when indene was combined in THF with $CoBr_2{\cdot}DME$ and then treated with KHMDS, it yielded, after oxidation and precipitation by ammonium hexafluorophosphate, bis(indenyl)cobalt hexafluorophosphate (**25**) in 68–82% yield. Unfortunately, this procedure did not work well with **14**. It gave only a 36% yield of material whose elemental analysis for C, H, and Co showed only two $C_{36}H_{20}$ units per cobalt atom and 15% of material other than $H_2(C_{36}H_{20})_2CoPF_6$.

The ^1H NMR spectrum of **9** exhibits very broad resonances between δ 5.4 and 9.0, 3.6 and 5.2, and 2.4 and 3.6. Except that the width accords with a polymeric structure, the spectrum provides little information. The ^{13}C NMR spectrum (Figure 1) shows the obligatory peaks between δ 117 and 134, attributable to the aromatic carbons. However, there are also peaks between δ 100 and 70 that are significant because they show the cobalts to be bonded to the cyclopentadienyl rings. They are analogous to resonances in **25**.[36] Table I shows how similar the chemical shifts of the cyclopentadienyl carbons are in the two molecules. As expected, because of the overhanging benzene rings, these carbons are all ca. 2.5 ppm more shielded in helix **9** than in **25**. The magnitude of the effect should be and is similar to the difference between chemical shifts of similarly situated carbons (carbons 1 and 2)[37] in [7]- and [4]helicenes (1–4 ppm).[38] There is also a small peak at δ 39.45 attributable to the indene–CH_2s that should terminate each of **9**'s chains. In **14** the indene methylene carbon resonates at δ 40.13.[39] The intensity of this resonance is greater in the samples of oligomer (Table II, entries 1–4) that appear to be particulary short. In those that are long the peak is barely observed (entries 5 and 6).

The UV spectrum (Figure 2) is similar to that of **25**.[40] It shows three strong absorptions at ca. 483, 335, and 255 nm (log ϵ = 4–5.5), with the wavelengths of maxima and extinction coefficients seemingly slightly smaller in shorter oligomers (e.g., entry 2, in Table II). The CD spectrum (Figure 2) shows two positive Cotton effects at ca. 480 and 380 nm and a negative one at ca. 260 nm. All the circular dichroisms ($\Delta\epsilon$ = ±300–1200) are very large.

The mass spectrum of **9** (the sample used was that described in entry 6 of Table II) is displayed in Figure 3. The most prominent peaks correspond to oligomers of [9]helicene ($C_{36}H_{20}$, abbreviated here as "Ar") and cobalt. They extend from $HArCo^+$ through $CoArCo^+$ and $HArCoArH^+$ to $CoArCoArCoArCoArCo^+$. In addition, oligomers carrying a PF_6^- anion were detected (e.g., 1622, $HArCoArCoArH^+$ PF_6^-). Although this spectrum identifies a variety of oligomers, we could not separate them using reversed-phase TLC, size-exclusion, or ion-exchange chromatography.

A possibility we investigated was whether cobalt bromide, instead of combining with the indenyl anions to give cobaltocene structures, coupled the anions to biindenyls. There are two indications that this does not occur to an appreciable extent. One is that in the ^{13}C NMR spectra (Figure 1) there are no significant signals near the positions at which *dl*- and *meso*-1,1′-bi-1*H*-indene

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[28] This sample was prepared by combining ketone **18** with $LiAlH_4$, ethanol, and (+)-binaphthol in THF at −78 °C, according to the procedure of Noyori, R.; Tomino, I.; Tanimoto, Y.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6709.

[29] Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769.

[30] Kölle, U.; Khouzami, F. *Chem. Ber.* **1981**, *114*, 2929. DME ≡ 1,2-dimethoxyethane.

[31] LiTMP = lithium 2,2,6,6-tetramethylpiperidide, KHDMS = potassium hexamethyldisilylazide, LiOBA = lithium *tert*-octyl-*tert*-butylamide, $(TMP)_2Mg$ = bis(2,2,6,6-tetramethylpiperidino)magnesium, TMPMgBr = (2,2,6,6-tetramethylpiperidino)magnesium bromide, LiHMDS = lithium hexamethyldisilylazide, NaHMDS = sodium hexamethyldisilylazide.

[32] Poindexter, M. K. Ph.D. Dissertation, Columbia University, New York, 1988.

[33] This thought relates to the discovery by Eaton et al. that lithium tetramethylpiperidide deprotonates cubane in the presence of zinc, cadmium, and mercury chlorides. (a) Eaton, P. E.; Cunkle, G. T.; Marchioro, G.; Martin, R. M. *J. Am. Chem. Soc.* **1987**, *109*, 948. (b) Eaton, P. E.; Higuchi, H.; Millikan, R. *Tetrahedron Lett.* **1987**, 1055.

[34] (a) Wannagat, U.; Niederprüm, H. *Chem. Ber.* **1961**, *94*, 1540. (b) Warf, J. C. *Inorg. Chem.* **1982**, *21*, 4125. (c) Tanabe, M.; Crowe, D. F. *J. Chem. Soc., Chem. Commun.* **1969**, 1498. (d) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913.

[35] The yield of **25** was slightly lower (67%) when lithium tetramethylpiperidide was used in place of KHMDS (82%).

[36] Köhler, F. H. *Chem. Ber.* **1974**, *107*, 570.

[37] The first and second protonated carbons counting from the inside of the end of the helix.

[38] (a) Martin, R. H.; Defay, N.; Figeys, H. P.; Flammang-Barbieux, M.; Cosyn, J. P.; Gelbcke, M.; Schurter, J. J. *Tetrahedron* **1969**, *25*, 4985. (b) Defay, N.; Zimmermann, D.; Martin, R. H. *Tetrahedron Lett.* **1971**, 1871.

[39] Indene in $CDCl_3$ shows it at δ 38.7.[36]

[40] In this case the perchlorate salt. Fischer, E. O.; Seus, D. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **1953**, *8*, 694.

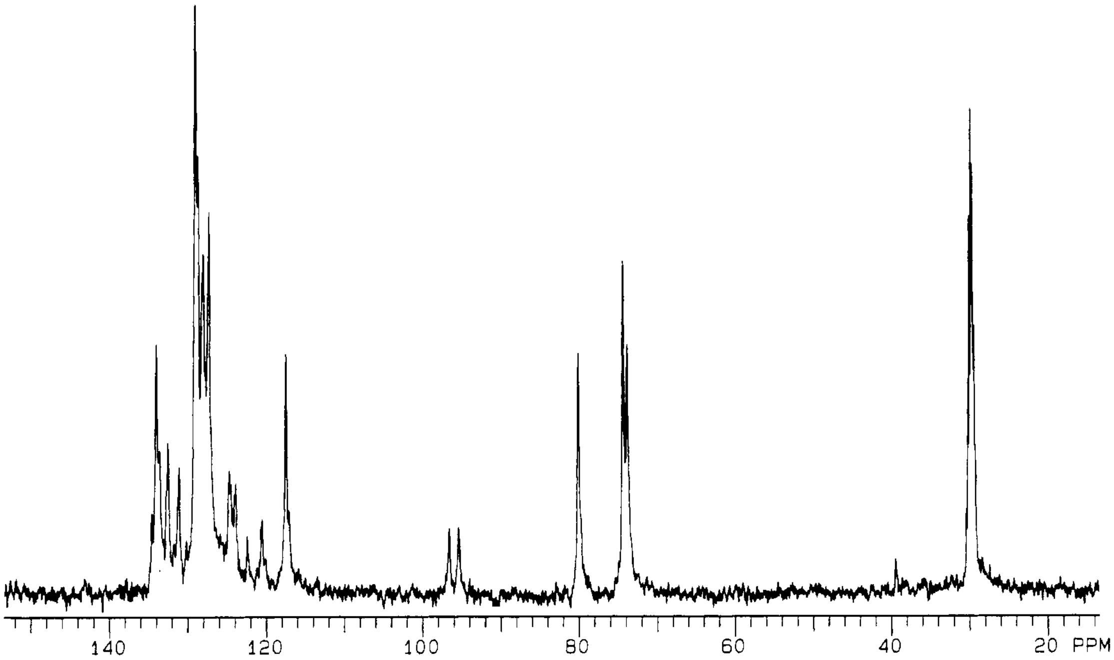

Figure 1. 75-MHz proton-noise decoupled ^{13}C NMR spectrum of 9 in CD_3COCD_3. The spectrum was measured using 90° pulses and no relaxation delay and is displayed with 7-Hz line broadening. The chemical shifts are measured assuming that of CD_3COCD_3 to be 29.8 ppm.

Table I. Comparison of the Chemical Shifts of the Cyclopentadienyl Carbons in **9** and **25**[a]

carbons	chemical shifts (δ) 9	25[b]	difference (ppm)
1, 3	74.37, 73.85	76.7	2.3, 2.9
2	80.08	83.0	3
4, 5	96.95, 95.40	98.3	1.3, 2.9

[a] In acetone-d_6. [b] See ref 36.

Table II. Dependence of the Yields, Lengths, and Specific Rotations of Samples of **9** on the Solvents Used to Prepare Them

entry	solvent	formula[a]	yield (%)	$[\alpha]_D$[b,c]
1	THF	$H_2Ar_{3.9}(Co^+PF_6^-)_{2.9}$	51	*d*
2	$PhNEt_2$	$H_2Ar_{2.6}(Co^+PF_6^-)_{1.6}$	58	25 500°
3	PhOPh	$H_2Ar_{4.9}(Co^+PF_6^-)_{3.9}$	79	29 800°
4	$PhOCH_3$	$H_2Ar_{4.9}(Co^+PF_6^-)_{3.9}$	69	31 700°
5	$PhCH_3$	$H_2Ar_{7.2}(Co^+PF_6^-)_{6.2}$	84	33 900°
6	$PhCH_3$	$H_2Ar_{6.7}(Co^+PF_6^-)_{5.7}$	87	29 600°

[a] Derived from the C, H, and Co element analyses. The experimental section includes the somewhat different formulas derived if the samples are assumed to contain small amounts of water. [b] Determined using solutions in acetone whose concentration was ca. 0.002 g/dL. [c] ±300°. [d] For a sample prepared from (*M*)-**14** whose enantiomeric excess (ee) was 50%, $[\alpha]_D$ = −20 600°.

absorb (δ 51.1 and 50.7).[41] The second is that in the mass spectrum (Figure 3) there are no appreciable signals at positions like *m/z* 1418, where $HArArCoArH^+$ should be observed. It is noteworthy that the sample described above that was prepared by simultaneously combining **14**, $CoBr_2$·DME, and KHMDS, and which had a number of other deficiencies, also showed a significant peak in its FAB mass spectrum at *m/z* 1418.

The lengths of the oligomer chains seem to depend on the solvent used in their preparation (Table II). Elemental compositions analyze these lengths, for they easily distinguish degrees of polymerization that are this small. Thus a simple complex of two helicenes with one cobalt $[(C_{36}H_{21})_2CoPF_6]$ requires an analysis (C, 77.84; H, 3.81; Co, 5.30) that is very different from that of an infinite polymer (C, 65.89; H, 3.07; Co, 8.97). When the solvent is THF (entry 1), the oligomers on average are tetrameric. When it is aromatic, with the exception of diethylaniline (entry 2), the oligomers are larger, possibly because aromatic solvents dissolve the growing oligomers better or because they contain less water. Diphenyl ether (entry 3) produces on average a pentamer. Anisole (entry 4) and toluene (entry 5) produce oligomers that are larger yet. They have the highest specific rotations, between 32 000 and 34 000°, which correlates possibly with their greater length. Toluene produced the oligomer with the longest chain of all (entries 5 and 6).

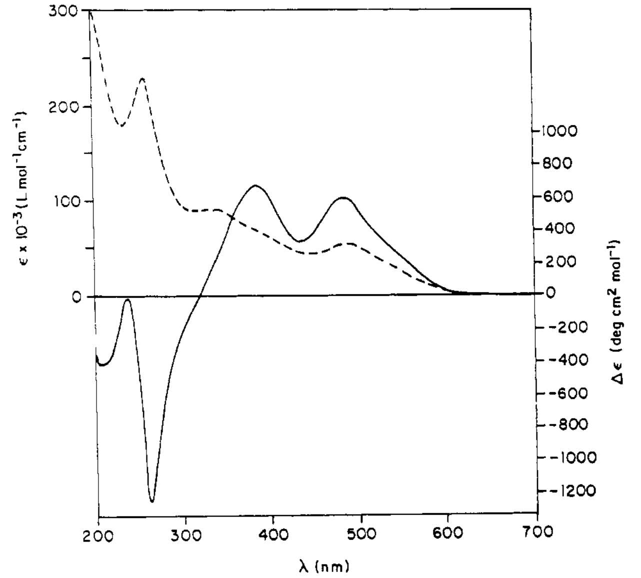

Figure 2. UV and CD spectra of 9 in CH_3CN.

Trimethylsilyl-Substituted Helical Cobaltocenium Oligomers. During the preparation of the materials described above, precipitates were seen to form after ca. 1 h. This suggested that precipitation might be terminating growth and that the molecular weights of the oligomers could increase if solubilizing nonaromatic groups were attached to **14**. The substituted helicene **26** was therefore synthesized by lithiating **12** with *n*-BuLi, adding TMSCl, and eliminating the ether functions under acid catalysis. (This helicene, after purification by chromatography on basic alumina, was a mixture of double-bond isomers.) With *t*-BuLi in toluene and then with $CoBr_2$·DME (followed by oxidation with $FeCl_3$ in aqueous HCl and precipitation with ammonium hexafluorophosphate), it, like the unsubstituted helicene **14**, produced an

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[41] Heimer, N. E.; Hojjatie, M.; Panetta, C. A. *J. Org. Chem.* **1982**, *47*, 2593.

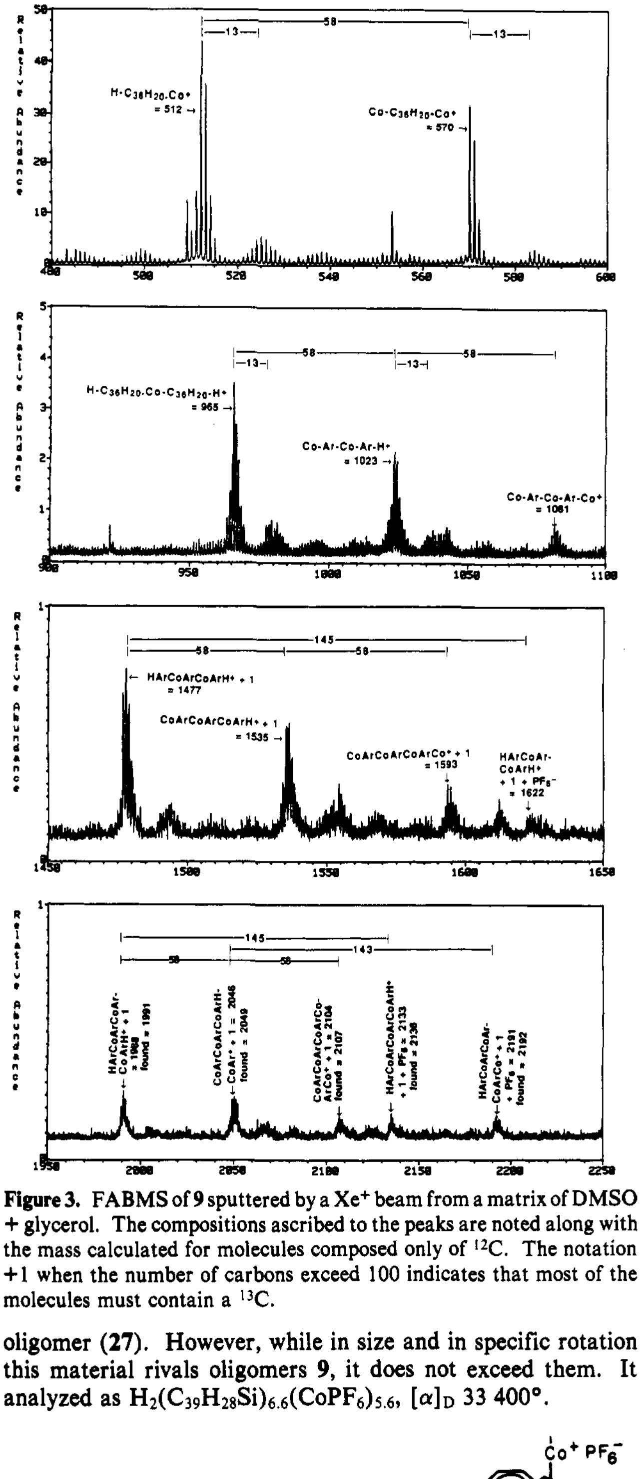
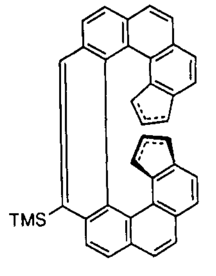


Figure 3. FABMS of **9** sputtered by a Xe^+ beam from a matrix of DMSO + glycerol. The compositions ascribed to the peaks are noted along with the mass calculated for molecules composed only of ^{12}C. The notation +1 when the number of carbons exceed 100 indicates that most of the molecules must contain a ^{13}C.

oligomer (**27**). However, while in size and in specific rotation this material rivals oligomers **9**, it does not exceed them. It analyzed as $H_2(C_{39}H_{28}Si)_{6.6}(CoPF_6)_{5.6}$, $[\alpha]_D$ 33 400°.



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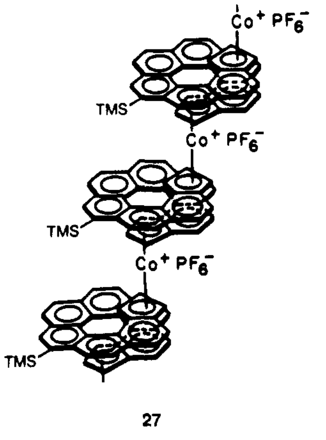

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The spectra of the substituted oligomer are similar to those of the unsubstituted ones, but they have the following additional

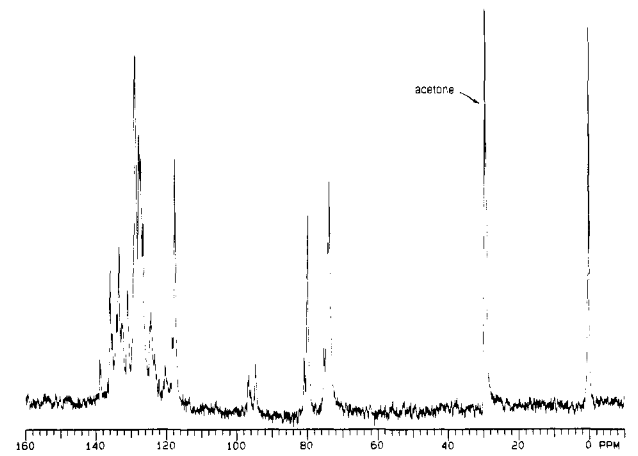

Figure 4. 75-MHz proton–noise decoupled ^{13}C NMR spectrum of **27** in CD_3COCD_3. The spectrum was measured using 90° pulses and no relaxation delay and is displayed with 10-Hz line broadening. The chemical shifts are measured assuming that of CD_3COCD_3 to be 29.8 ppm.

characteristics. In the NMR spectra of **27**, TMS resonances appear at δ 0.60 in the proton spectrum and (see Figure 4) at δ 1.0 in the carbon spectrum. No terminal methylene resonance is seen at ca. δ 40, which agrees with the greater length of the oligomer. The FAB mass spectrum, displayed in the supplementary material, shows oligomers of the trimethylsilyl-substituted helicene, $C_{39}H_{28}Si$, abbreviated here as "Ar", and cobalt from $ArCoAr^+$ through $ArCoArCoArCoArCoArCoArCoAr^+$. The size of the largest oligomer observed in this spectrum is larger than that in the spectrum (Figure 3) of the unsubstituted material **9**. Moreover, the peaks due to the large ions are much more intense.

The cobaltocenium oligomers **9** and **27** are extraordinarily robust materials. Storage for years in the air at ambient temperature has not affected them. They thus share the oxidative stability both of cobaltocenium salts[42] and of aromatic hydrocarbons. Their solutions also require no special protection during periods of a few hours to a few days.

[9]Helicene Ferrocene Oligomer. Bis(indenyl)iron,[43] unlike bis(indenyl)cobalt salts,[42,44] is very easily destroyed by oxidation. To prepare and isolate the iron analogue of **9** should therefore be difficult. The procedure we tried used *t*-BuLi in toluene to deprotonate **14** and $FeBr_2 \cdot DME$[45] in THF to introduce the iron.[46] Benzene extracted a product from this mixture that contained both iron and hydrocarbon and displayed ^{13}C resonances similar to those shown by the cyclopentadienyl carbons in bis(indenyl)iron.[47] It showed high specific rotations, $[\alpha]_D$ 27 000° (*c* 0.1, benzene), and large circular dichroisms.[48] However, it proved impossible for us to obtain pure.

Voltammetry. Assignment of the CV Peaks. Figure 5 shows cyclic voltammograms of three samples of the oligomers in DMF. Each sample contained chains of varying lengths, including some with only a single metal, and the average lengths were different. Two cathodic features (I and II in Figure 5) and two anodic features (III and IV) are observed. Of these, feature II is assigned to the reduction of the mononuclear portion of each sample. This is because its peak potential (−1.22 V) is similar to that measured

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(42) Fischer, E. O.; Herberich, G. E. *Chem. Ber.* **1961**, *94*, 1517.

(43) Osiecki, J. H.; Hoffman, C. J.; Hollis, D. P. *J. Organomet. Chem.* **1965**, *3*, 107.

(44) Fischer, E. O.; Seus, D.; Jira, R. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **1953**, *8*, 692.

(45) Kölle, U.; Fuss, B.; Khouzami, F.; Gersdorf, J. *J. Organomet. Chem.* **1985**, *290*, 77.

(46) We found that *n*-BuLi in THF followed by $FeBr_2 \cdot DME$ gives bis(indenyl)iron in 97% yield.

(47) For C-1 and C-3: 62.18, 61.67, and 60.81 ppm vs 61.9 ppm in bis(indenyl)iron; C-2: 67.51 and 67.13 ppm vs 69.9 ppm; C-4 and C-5: 85.68 and 84.00 ppm vs 87.0 ppm.

(48) CD (PhH) λ_{max} ($\Delta\epsilon$): 557 (103), 394 (485), 278 nm (−303).

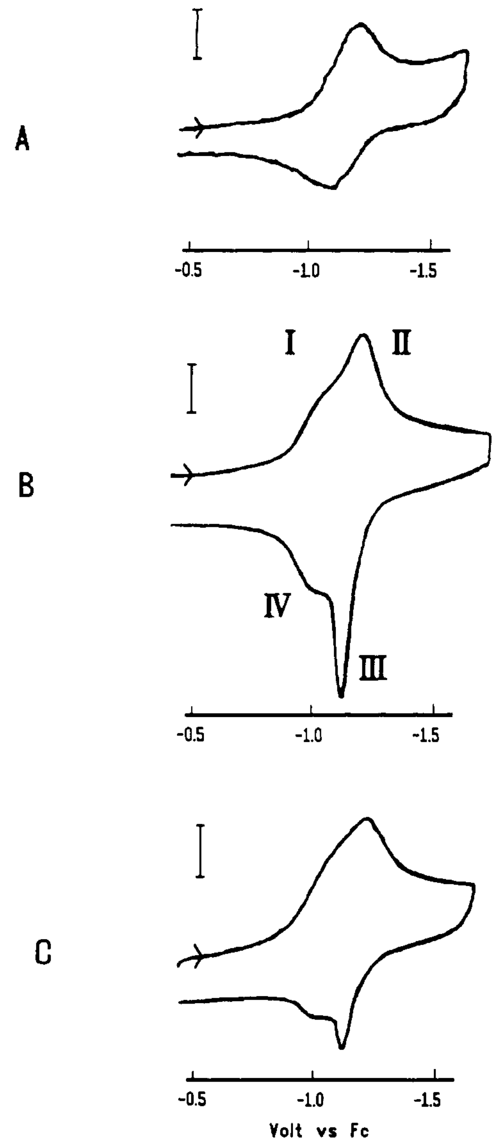
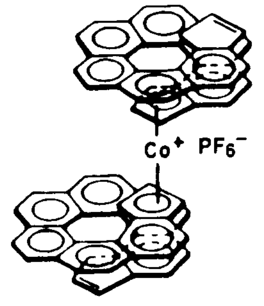


Figure 5. CV scans of samples of **9** and **27** at Pt electrodes in DMF, v = 0.5 V/s, ambient temperature: (A) short-chain sample **9**, entry 2, Table II, 2.4 mg in 25 mL; (B) medium-length sample **9**, entry 5, Table II, 2.2 mg in 25 mL; (C) long-chain sample **27**, 3.2 mg in 25 mL. The current marker represents 200 pA for (A) and (B), 500 pA for (C).

for **28**,[49,50] because it increases in size as the average degree of polymerization increases (compare Figures 5A, B, and C), and because interactions between adjacent metals should facilitate reductions and therefore shift the first reduction potential of the polynuclear complexes to values more positive than that of the mononuclear complex.[51] The magnitude of the shift (0.12 V) is approximately that expected considering the reduction potentials of four cobalt complexes: **29**, the analogue of **29** in which the cobaltocenium ion constituting the helix's last ring is missing, **28**, and the analogue of **28** in which both terminal five-membered rings are missing.[50,52]



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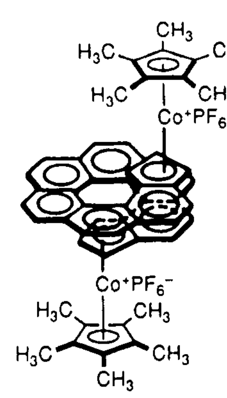

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The multinuclear materials should accept additional electrons at potentials separated by less than ca. 130 mV, the difference between the first two reduction potentials of **29**.[50] Like the system of four successive electron transfers separated in potential by ca. 120 mV, whose theory was considered by Evans et al.,[57] such reductions should lead to broad waves instead of individual peaks.[58] Although the cathodic features have the form required if transport to the electrode is controlled by diffusion ($i_{pc} \propto v^{1/2}$, "diffusional shape"), the main anodic feature does not. The shape of peak III is characteristic of redox couples in which the reduced form is insoluble and the oxidized form soluble (a "stripping" peak).[59] It is sharp because diffusion to the electrode does not determine the current–time relationship. Its size relative to peak II increases at slower scan rates. These characteristics suggest that the oligomer forms a poorly soluble film, which is stripped from the electrode when the original polycation re-forms on the return sweep.

Peak IV, a minor anodic feature whose shape is diffusional, may arise from that part of the reduced polymer whose solubility is appreciable or whose rate of precipitation is slow. That the reduced material dissolves slightly was confirmed, as described below, using a quartz crystal microbalance. That the reduced polymer precipitates in a measurable time was shown by cyclic voltammograms in which the scan rates were varied. In CH_3CN, slowly scanned CVs look like those seen in DMF (Figure 6A), and the stripping peak (III) is observed even for the short-chain sample. However, when $v > 0.5$ V/s, peak III for this sample assumes a diffusional shape, implying that precipitation is negligible during ca. 10 s. Possibly the solution temporarily supersaturates. For the samples with longer chains, diffusional shape is also noted, but only when the scan rates are much higher. For the sample of **9** described in Table II, entry 5, this rate must exceed 100 V/s (a time scale of ca. 20 ms) before the shapes of both anodic features are diffusional.

A third, irreversible peak appears at considerably more negative potentials (E_p = −2.4 V, Figure 6B, the solvent is CH_3CN), consistent with the observation that other neutral cobaltocenes are reduced at 1.2–1.3 V negative of the +/0 couple (see Table III). Thus, cobaltocenium (Cp_2Co^+) in CH_3CN undergoes two reversible reductions: $E°$ = −1.34 [+/0 or Co(III)/Co(II) couple] and −2.28 V [0/− or Co(II)/Co(I) couple].[60] As described in the accompanying paper, three mononuclear cobalt complexes that

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[49] $E°_1$ = −1.16 V, E_{pc} = −1.20 V (ref 50).

[50] Gilbert, A. M.; Katz, T. J.; Geiger, W. E.; Robben, M. P.; Rheingold, A. L. *J. Am. Chem. Soc.* Following paper in this issue.

[51] Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.

[52] The difference between the reduction potentials of the [8]helicene derived from **29** by deleting the last cobaltocenium ion and **29** itself is −0.05 V. The addition of half the difference (−0.06 V) between the reduction potential of **28** and of the bis[8]helicene derived from **28** by deleting both terminal five-membered rings (−0.03 V) suggests that the shift should be ca. 0.08 V.

[53] Bunel, E. E.; Campos, P.; Ruz, J.; Valle, L.; Chadwick, I.; Santa Ana, M.; Gonzalez, G.; Manriquez, J. M. *Organometallics* **1988**, *7*, 474.

[54] Bunel, E. E.; Valle, L.; Jones, N. L.; Carrol, P. J.; Barra, C.; Gonzalez, M.; Munoz, N.; Visconti, G.; Aizman, A.; Manriquez, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 6596.

[55] Morrison, W. H., Jr.; Krogsrud, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998.

[56] (a) McManis, G. E.; Nielson, R. M.; Weaver, M. J. *Inorg. Chem.* **1988**, *27*, 1827. (b) Davison, A.; Smart, J. C. *J. Organomet. Chem.* **1973**, *49*, C43.

[57] Sokol, W. F.; Evans, D. H.; Niki, K.; Yagi, T. *J. Electroanal. Chem.* **1980**, *108*, 107.

[58] Although the "inner" cobalts in these oligomers (those bonded to two helicenes, both of which are attached to another metal) should, because of the electron-withdrawing effect of the Co(III), reduce more easily than the "outer" cobalts (those bonded to two helicenes, only one of which is attached to another metal), the difference is likely to be small because the helices are so long.

[59] Brainina, K. Z. *Talanta* **1971**, *18*, 513.

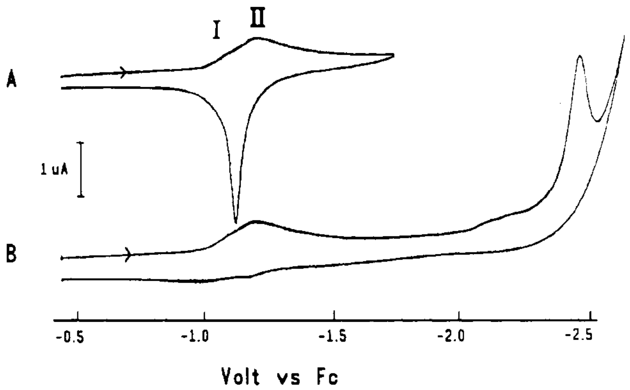

Figure 6. CV scans of medium-length sample **9**, entry 5, Table II, in CH_3CN at Pt electrode, v = 0.1 V/s, ambient temperature, 2.4 g in 10 mL: (A) potential region similar to that of Figure 5; (B) more negative scan, showing irreversible wave at −2.4 V and the absence of the stripping peak on return.

have one or more arene rings fused to a cobalt-bound cyclopentadienyl show the same pattern, a reversible Co(III)/Co(II) process at −0.9 to −1.1 V and a second reduction, of limited chemical reversibility, at −2.1 to −2.3 V.[50]

Deposition of Oligomer Films. When the cationic oligomers are reduced in CH_3CN at potentials of −1.6 to −1.7 V, black films form rapidly on the Pt gauze electrode. When potentials to the positive side of −1.2 V are applied to the coated electrodes, large currents pass as the films oxidize and strip away. Pt bead voltammograms of the reoxidized solutions were essentially unchanged from those prior to the deposition. Thus, films appear to form quantitatively and reversibly. Throughout the reduction, and despite the formation of the films, *the electrolyses continue smoothly* ($\log i \propto t$) to completion (current <2% of original). At this point the originally red solutions are very lightly colored, and voltammograms at a freshly inserted Pt bead show that electroactivity at potentials at which the starting oligomers reduce is greatly diminished. The implications are two: the fully reduced oligomers accumulate as films on the Pt electrode and *the films are conductive*. An alternative explanation that the films are insulating but porous would not appear to account for the implication of the linear dependence of $\log i$ on t,[61] that the mass transfer parameter throughout the electrolysis is constant. However, stronger evidence that the films are conductive is their ability to mediate other reductions.

Mediator Properties of Oligomer-Modified Electrodes. The potential range in which the oligomer-coated electrodes are stable is −1.2 to −2.4 V, the negative limit arising from the irreversible cathodic process that appears to decompose the films (Figure 6). To confirm that the oligomer films are conductive, voltammograms at a coated electrode were recorded for a test substrate. The mixed sandwich complex $CpFe(C_6Me_6)^+$ was chosen because it undergoes a reversible one-electron reduction within the range of potentials at which the films are stable.[62] At a bare Pt electrode, a Nernstian-shaped one-electron wave with $E°$ = −2.01 V was observed, consistent with earlier measurements by Astruc in a different solvent.[62] After the electrode had been coated with a thick film of the oligomer, the shape and $E°$ values of the iron complex's voltammograms were unchanged, showing that the film did not decrease the electrode's effective area or conductive properties.

The cyclic voltammograms at a Pt electrode of solutions containing both **9** and the Fe complex show waves for both components (Figure 7), and although the shapes of the Fe complex's voltammograms are the same whether **9** is present or not, when it is, the cathodic peak heights are enhanced. This effect is accentuated when the films deposited on the Pt electrode are first thickened by poising the potential at −1.4 V for several minutes or when the scan rate is diminished. In the first scan through the Fe(II/I) wave, the cathodic currents at the coated electrodes are as much as four times larger than at bare Pt, but the corresponding anodic Fe(I)/Fe(II) wave is unenhanced. A likely explanation for the increase is that the Fe(I) complex, which as Figure 7 shows has an appropriate reduction potential, reduces the film. This would partially destroy the film and regenerate Fe(II), accounting for both the diminution of the anodic Fe(I)/Fe(II) wave compared to its cathodic counterpart (Figure 8, initial scan) and the lack of a stripping peak (III) on the return sweep (Figure 7). This is an example of homogeneous redox catalysis.[63]

The oligomer films were shown to catalyze electron-transfer processes that are slow at bare Pt electrodes. An example is the two-electron couple $(\eta^6\text{-}C_6Me_6)_2Ru(II)/(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)Ru(0)$, which at Pt and certain other solid electrodes proceeds by slow heterogeneous charge transfer ($E_{1/2}$ = −1.42 V).[64,65] If Pt electrodes have oligomer deposited on them, the charge-transfer rate appears to increase appreciably, as evidenced by the decreasing values of ΔE_p (Figure 9). At v = 0.1 V/s, the decrease was from 90 mV in the absence of oligomer to 49 mV in its presence. This catalytic effect is being studied quantitatively.

Coulometric Estimation of Polymer Length. A. Bulk Electrolysis. In a polymer composed of repeating identical redox-active units, the ratio m/q should be independent of polymer length (m is the mass deposited when q coulombs are passed). An exception is expected if the chains are short and the capping groups are not electroactive. In such cases it should be possible to analyze the degree of polymerization (x), which is proportional to the number of electroactive centers in the sample, by measuring m/q. The precision depends on the chain length and on the relative molecular weights of the end and repeating groups. To be high for **9** or **27**, samples of more than 10 mg, larger than desirable, must be analyzed. Nevertheless, as described in the Experimental Section, meaningful results can be obtained with smaller samples if proper care is taken. It can be shown that in the case of **9**, eq 2 holds. In this equation, n is the number of electrons (1)

$$x = 455/(nFm/q - 656) \qquad (2)$$

transferred per electroactive group, F is the Faraday constant, and 455 and 656 are the formula weights of the capping helicene and the repeating unit $[([9]\text{helicene})Co^+PF_6^-]$.[66]

The degree of polymerization analyzed in this way, using CH_3CN as the solvent to decrease the solubility of the film, was 1.1 for a 5.2-mg sample of **9**, entry 2 in Table II, and 3.3 for a 3.3-mg sample of **9**, entry 5 in Table II (Table IV). The precision cannot be specified because we did not have enough of each sample to repeat the analyses. The shorter sample was also analyzed by reversing the electrolysis to strip the electrode. This is advantageous because the increased speed of electrolysis for samples that are preconcentrated on the electrode[67] reduces corrections for background currents. Thus electrolyses to 95% completion took 30 min for the reduction and 3 min for the oxidation. The chain length measured by the stripping electrolysis was 1.3. The agreement with the degree of polymerization analyzed by elemental analysis (1.6) is good (Table IV).

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(60) (a) Geiger, W. E. *J. Am. Chem. Soc.* **1974**, *96*, 2632. Other references to the electrochemistry of cobaltocene and its derivatives: (b) Geiger, W. E. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 156.

(61) Bard, A. J.; Santhanam, K. S. V. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1970; Vol. 4, pp 218–222.

(62) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758.

(63) Andrieux, C. P.; Savéant, J. M. *J. Electroanal. Chem.* **1986**, *205*, 43.

(64) Pierce, D. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 7636.

(65) Pierce, D. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 6063.

(66) The corresponding figures for **27** are 527 and 729.

(67) Heineiman, W. R.; Mark, H. B., Jr.; Wise, J. A.; Roston, D. A. In *Laboratory Techniques in Electroanalytical Chemistry*; Kissinger, P. T.; Heineman, W. R., Eds.; Marcel Dekker, Inc.: New York, 1984; Chapter 19.

Table III. Electrochemical Potentials (vs Ferrocene) for Cobaltocenium Oligomers and Related Mononuclear Complexes

sample	x^a	solvent	E_{pc}(I)	E_{pc}(II)	$E°(+/0)$	$E°(0/-)$	ref
9, entry 2, Table II	1.5	DMF	*b*	−1.22			this work
9, entry 5, Table II	3.5	DMF	−1.10	−1.23			this work
27	5.3	DMF	−1.10	−1.21			this work
$(C_5H_5)_2Co^+$		CH_3CN			−1.34	−2.28	*c*
$(indenyl)_2Co^+$		CH_3CN			−0.92	−2.14	*d*, this work
$(C_5H_5)Fe(C_6Me_6)^+$		DMF			−2.01		*e*, this work
$(C_6Me_6)_2Ru^{2+}$		CH_3CN	(2+/0 couple: $E_{1/2} = -1.42$)				*f*, *g*

[a] Nominal number of Co atoms per oligomer, based on elemental analysis. [b] This feature is small in the short-chain-length sample. [c] Reference 60a. [d] Originally reported as −0.53 V in DMF/0.2 M $NaClO_4$: Hsiung, H.-S.; Brown, G. H. *J. Electrochem. Soc.* **1963**, *110*, 1085. [e] Reference 62. [f] Reference 64. [g] Reference 65.

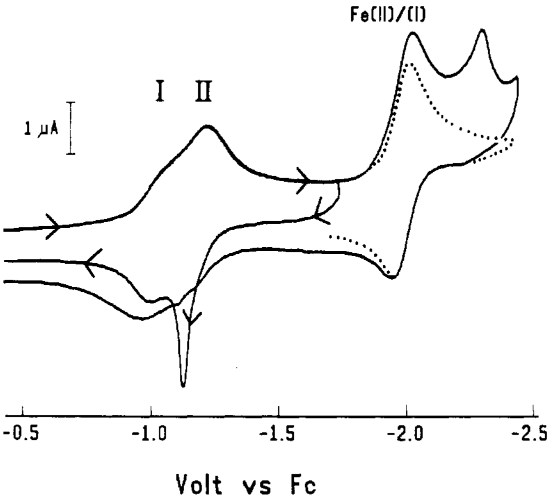

Figure 7. CV scans of Fe(II)/Fe(I) couple of $CpFe(C_6Me_6)^+$ in 25 mL of DMF at a Pt electrode, v = 0.1 V/s, ambient temperature. Dotted line: response of 1.1 × 10^{-4} M Fe complex without oligomer added. Solid line: after addition of 2.2 mg of **9**, entry 5, Table II. If the scan is discontinued prior to the Fe wave (arrows), the usual stripping takes place. Note that the zero current levels for the dotted and solid lines have been adjusted to match at −1.7 V in order to facilitate comparison of the Fe(II)/(I) peak heights.

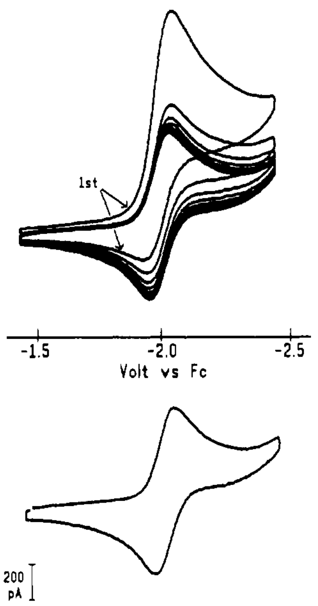

Figure 8. Repetitive CV scans of Fe(II)/(I) couple of $CpFe(C_6Me_6)^+$ at Pt electrode coated with **9**, entry 5, Table II. Same conditions as in Figure 7. The top shows the first through tenth cycles, and the bottom shows the twelfth, when the steady state has been reached.

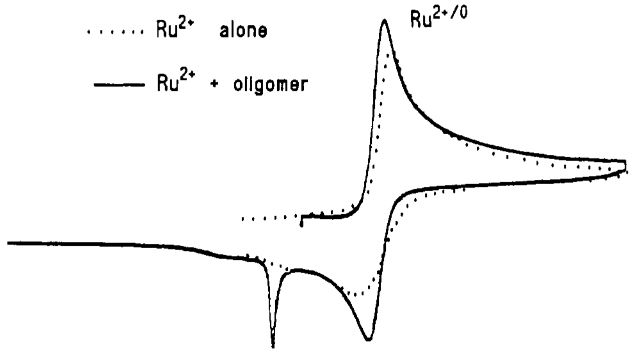

Figure 9. CV scans of $(C_6Me_6)_2Ru^{2+/0}$ at a bare Pt electrode (dotted line) and in presence of oligomer deposit (solid line). Conditions: 3 × 10^{-4} M Ru complex, as BF_4^- salt; 3 mg of **27** in 25 mL of DMF; v = 0.1 V/s; ambient temperature; full potential limits −0.45 to −2.15 V. The scan in the presence of oligomer was initiated after E_{appl} had been held at −1.3 V for 30 s.

Table IV. Chain Lengths Measured by Elemental Analysis and Electrochemically

sample	no. of Co	method
9, entry 2, Table II	1.6	C, H, Co anal.
	1.1	coulometric redn.
	1.3	QCM[a]
9, entry 5, Table II	6.2[b]	C, H, Co anal.
	3.3	coulometric redn.
	3.1	QCM

[a] Quartz Crystal Microbalance. [b] An alternative interpretation of the elemental analysis $[H_2(C_{36}H_{20})_{4.5}(CoPF_6)_{3.5}·4.8H_2O]$ implies that this figure is 3.5.

For the longer sample (entry 5) the degree of polymerization analyzed by coulometry (x = 3.3) did not agree with that obtained by elemental analysis (x = 6.2). However agreement was good if the elemental analyses were interpreted under the assumption that the sample of oligomer contained some water. Then x was analyzed to be 3.5. (That is, the analysis could be interpreted to correspond to $H_2Ar_{4.5}(Co^+PF_6^-)_{3.5}·4.8H_2O$ instead of $H_2Ar_{7.2}(Co^+PF_6^-)_{6.2}$.) The elemental analyses for all the oligomer samples are interpreted in the Experimental Section under both assumptions, that they contain water and that they do not.

B. Measurements Using a Quartz Crystal Microbalance. Because these experiments demonstrated the need for higher precision when sample sizes are small, we turned for further measurements to the piezoelectric quartz crystal microbalance (QCM), which determines the weight of a quartz crystal by analyzing its resonant frequency.[68] The change in the weight of a quartz crystal on which electroactive material was deposited could be monitored during electrolysis by the Sauerbrey relationship[69] while coulometric charge was also being recorded.

Typical data are shown in Figure 10. The top shows how the change in frequency (Δf), which is proportional to the change in mass (Δm), varies as **9** is repeatedly electrolyzed (downward arrow) and then back-electrolyzed (upward arrow). The values of m/q may be analyzed during either the forward or backward electrolysis since the weight of the sample is known at all times. However, the measurements of charge during the experiments

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(68) Ward, M. D.; Buttrey, D. A. *Science (Washington, DC)* **1990**, *249*, 1000.

(69) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206. $\Delta f = -2(\Delta m)nf_0^2/[A(\mu_q\rho_q)^{1/2}]$, where n is the overtone number, f_0 is the crystal resonant frequency, A is area, μ_q is the sheer modulus of quartz, and ρ_q is the density of quartz.

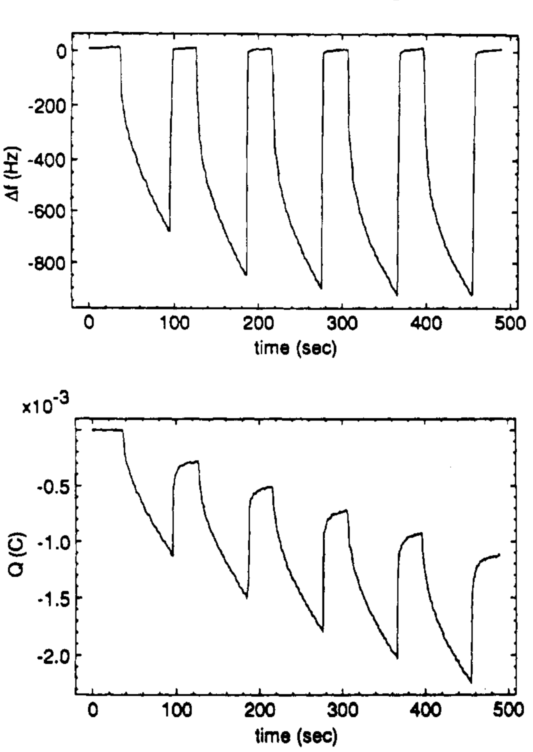

Figure 10. Quartz crystal microbalance data for 2 mg of **9**, entry 2, Table II, in CH_3CN. (Top) change in frequency and (bottom) accumulated charge in repetitive swings between $E_{appl} = -1.6$ (downward arrow) and -0.8 V (upward arrow).

(Figure 10, bottom) suggest that the latter should provide more reliable values. Note in the figure that although on back-electrolysis the value of Δf returns to 0 (top, implying that a clean electrode is reformed), the charge (bottom) is not fully regained. The probable reason is that not all of the reduced oligomer precipitates. (That reduced polymer is slightly soluble was also noted above in accounting for peak IV in Figure 5, and that it precipitates slowly when the chains are short was noted in accounting for the disappearance of the stripping peaks when scan rates were increased.) The failure of all the oligomer to precipitate is not a serious complication, for, as noted, the mass of each sample is known from the change in Δf prior to back-electrolysis. If data like those in Figure 10 are analyzed in the same way as the data from the bulk electrolyses described above, they give the x-values presented in Table IV.

Circular Dichroism. An interesting question was whether, because of the increased electron mobility in mixed-valence species, partially reducing **9** would greatly increase the circular dichroism.[70] An acetonitrile solution of **9** (entry 6, Table II) was reduced in a CD cell with excess cobaltocene (4.7 times as much as needed to reduce every Co^+ in **9**), and then the CD spectrum was monitored while the reduced species was oxidized back to **9**. The oxidation was brought about by air diffusing through the septum that sealed the cell.[71] The CD spectra of **9** and its reduction product are shown in Figure 11. While **9** shows two positive Cotton effects and one that is negative [482 ($\Delta\epsilon = 663$), 382 (757), 262 nm (−1350)], its reduction product shows only one that is positive and one that is negative [407 ($\Delta\epsilon = 733$), 269 nm (−610)]. We presume that cobaltocene reduces **9** to the helical cobaltocene, in which each Co^+ is replaced by a Co. The reason is that when **25** is combined with 1 equiv of cobaltocene in THF at room temperature, it produces in 97% yield bis(indenyl)cobalt, identified by its UV spectrum.[40] After the sample was oxidized for 2 h (Figure 11), the peak at 407 nm observed in the reduced helical material decreased in intensity and split into two, at 483 and 389 nm, characteristic of **9**, while the peak at 269 nm in the reduced material increased in intensity and moved to 264 nm, a position also characteristic of **9**. After one cycle of reduction and oxidation, the CD spectrum was identical with the initial spectrum, but the intensities were all 9% lower, presumably because the experiment destroyed this amount of the starting material. The isosbestic points at ca. 525 and 280 nm imply that two species, **9** and its reduction product, are interconverting but without passing through a recognizable intermediate. Thus, either no appreciable amount of mixed-valent product forms or the properties of mixed-valence materials are intermediate between those of the fully oxidized and fully reduced oligomers.

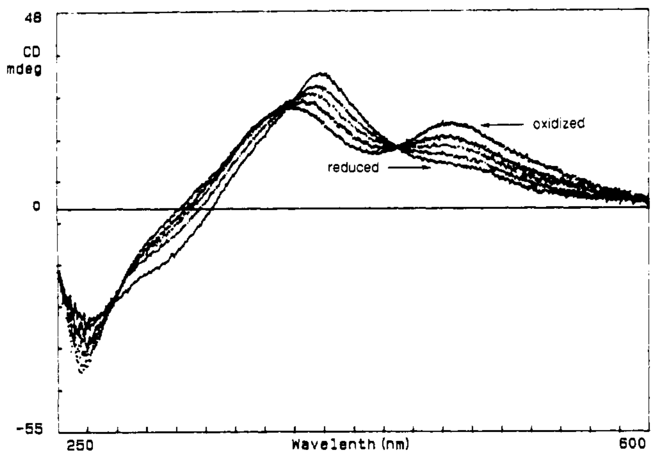

Figure 11. CD spectra in CH_3CN of **9** that has been reduced by cobaltocene and is being oxidized by air.

Discussion

Absolute Configuration of Bromo Alcohol 19. The absolute stereochemistry is assigned to **19** on the basis of analogies with reductions of other indanones and analyses of the ^1H NMR spectra of its *O*-methylmandelate esters. Thus the combination of (−)-diphenylvalinol and borane, which reduces **18** to (+)-**19**, reduces both acetophenone and α-tetralone to the (*R*)-carbinols.[15,16] This suggests that (+)-**19** has the *R*-configuration. In early experiments to synthesize **19** optically active,[7c,72] we found that ether solutions of $LiAlH_4$, (+)-*N*-methylephedrine, and 2 equiv of 3,5-dimethylphenol[19] reduce **18** to (−)-**19**. (The enantiomeric excess was 67%.) Accordingly, the enantiomer of this reagent must reduce **18** to (+)-**19**, and since it reduces both acetophenone and α-tetralone to (*R*)-carbinols,[19] the implication again is that (+)-**19** has *R*-stereochemistry. This last reagent when prepared from (−)-*N*-methylephedrine also reduces other benzindenones (5-bromo- and 8-bromo-1*H*-benz[*e*]inden-1-ones) to (*R*)-carbinols.[31,68] In those cases the stereochemical assignments are supported by analyses of the CD spectra of their *p*-bromobenzoates. In the case of **19**, although the *p*-bromobenzoate was prepared, attempts to assign the stereochemistry using the exciton splitting in its CD spectrum[73] failed.

The ^1H NMR spectra of **19**'s *O*-methylmandelate esters also confirm the assignment. The assumption is that Dale and Mosher's hypothesis is correct, that the ^1H NMR spectra of diastereomeric *O*-methylmandelates can be understood if **30** is the dominant conformation of the esters of (*S*)-(+)-*O*-methylmandelic acid.[74] The esters of this acid with (*R*)- and (*S*)-**19** can

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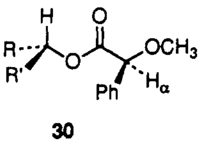
(70) That the circular dichroism might not increase is suggested by an experiment carried out 20 years ago by Weissman and Chang. They found that the optical activities of hexahelicene's anions are not notably large. Throughout the UV, they are less than those of hexahelicene itself. See Weissman, S. I.; Chang, R. *J. Am. Chem. Soc.* **1972**, *94*, 8683.

(71) Oxygen is effective in oxidizing cobaltocene to cobaltocenium. Kojima, H.; Takahashi, S.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1973**, 230.

(72) Sudhakar, A. R. Ph.D. Dissertation, Columbia University, New York, 1985.

(73) (a) Koreeda, M.; Akhtar, M. N.; Boyd, D. R.; Neill, J. D.; Gibson, D. T.; Jerina, D. M. *J. Org. Chem.* **1978**, *43*, 1023. (b) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy*; University Science Books: New York, 1983.

(74) (a) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512. (b) Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, 4929.



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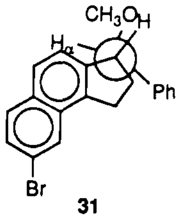

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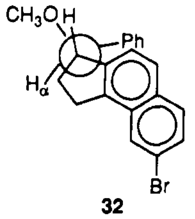

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then be represented as **31** and **32**, respectively. The analysis developed by Dale and Mosher implies that the ester of the (+)-alcohol is **31**, for the protons of the CH_2 adjacent to its ester function resonate at higher fields in this isomer than in its diastereomer, which must then be **32**. In the former the resonances are at δ 2.02 and 2.58, and in the latter they are at δ 2.24 and 2.75. The double resonance experiments demonstrating these facts are described in the Experimental Section and in the supplementary material. The observation that the spectrum of the (–)-alcohol's ester exhibits an aromatic proton resonance, a doublet at δ 7.14, at higher fields than the resonance of any aromatic proton in the spectrum of the (+)-alcohol's ester (presumably **31**) also accords with the (–)-alcohol's ester being **32**. This structure, unlike **31**, has a naphthalene proton that is eclipsed by the phenyl.

Dale and Mosher's explanation for their effect is that the ring currents of phenyl groups preferentially shield overlying protons. If we assume that naphthalene has a similar effect, then the positions of the resonances due to H_a also confirm the assignment. Since the ring current in naphthalene should shield H_a in **31**, and since the resonance of H_a in the ester of the (+)-alcohol (δ 4.77 in $CDCl_3$) is at higher field than that in the ester of its enantiomer (δ 4.80), the (+)-alcohol should be the one whose ester is **31**. It is the (*R*)-enantiomer.

The Winding Direction of Helix 14. The right-handed or (*P*)-helical configuration[26] was assigned to the dextrorotatory helicene on the basis of analogies with the chiroptical properties of helicenes whose configurations have been assigned in a variety of ways.[75] Thus this configuration was assigned to **14** because it appears that all dextrorotatory carbohelicenes have the (*P*) configuration[75a] and more significantly because the CD spectrum of **14** (Figure 12) between 275 and 450 nm is remarkably like that of all the carbohelicenes from pentahelicene to nonahelicene, especially heptahelicene.[76] This assignment was confirmed when the absolute configuration of **29** was analyzed by X-ray crystallography.[50]

It follows that since **13** in Scheme I has the *R*,*R*-configuration (because it was made from (*R*)-(+)-**19**), the helix **14** winds in the direction that excludes the two siloxy groups from its interior. Indeed, this was the strategic thought underlying the plan for the synthesis. It means that the asymmetry of alcohol **19** should determine the direction in which the helix winds, and the observation that, within experimental error, 100% enantiomerically pure *R*-alcohol does give 100% enantiomerically pure (*P*)-helix indicates the correctness of the hypothesis.

We note, incidentally, that although there is no X-ray structural analysis to show that the two siloxy groups in **13** are on the exo-face of the helix, if they were both on the endo face, then the helix formed from (*R*,*R*)-**12** would have (*M*) helicity. We reject this possibility because steric considerations make it implausible for the helix to wind preferentially so as to place these siloxys on the inside and because the relationship between the direction in which the helicene winds and the sign of its circular dichroism would be violated.

Another point about the induction of helical asymmetry concerns the choice of siloxyaldehyde **10**. Related research resulting in the synthesis of optically active **6** and **8**[7c] showed that the stereochemistry of precursor **33**, an isomer of **10**, determined the direction in which the helix winds. Since **33** is easier to prepare, we experimented to see whether it could be used in place of **10**.[68] However, it was found that, unlike **11** in Scheme I, **34** reacts very slowly when photoirradiated, and it gives no easily characterizable product. The ^1H NMR spectrum of the reaction mixture included resonances characteristic of stilbenes (an AB quartet, $J = 12.5$ Hz, at δ 6.7–7.0) and of nonhelical structures (δ 9, see structure **22** above), and its optical activity barely increased. In contrast, when **11** was photoirradiated, the optical activity of the reaction mixture increased 20-fold in 1 h as the highly active helix was produced. The conclusion is that while **10** is a highly effective precursor to optically pure **14**, **33** is not.

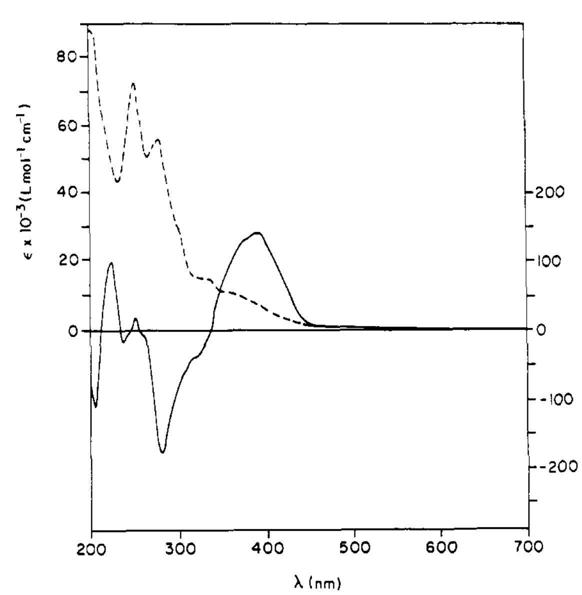
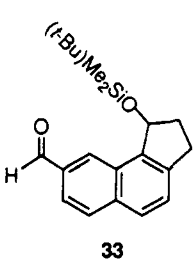


Figure 12. UV and CD spectra of **14** in CH_3CN.



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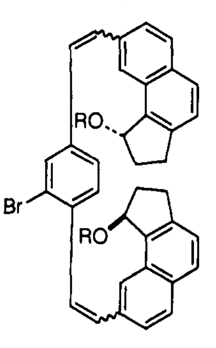

34 [R = Si(*t*-Bu)Me_2]

Blocking by Bromine. We show above that if the bromine is removed in Scheme I from structure **11**, the photocyclization does not give appreciable amounts of helicene **12**. It gives instead dinaphthanthracene **22**. The bromine thus directs the photocyclization to give the helix, and since the bromine is easily removed afterward, it is indispensable in making the synthesis possible. The effect of the bromine is not just to resist cyclization at the position it occupies; it resists cyclization also at the position adjacent. This effect has proven instrumental in the synthesis of a number of other molecules: the parent hydrocarbons [5]- and [7]helicene[77] and their bis-quinone derivative.[74b,78]

The chemical literature contains numerous examples of bromine blocking photocyclizations to positions it occupies.[79,80] We have

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(75) (a) Laarhoven, W. H.; Prinsen, W. J. C. *Top. Curr. Chem.* **1984**, *125*, 63 and references cited therein. See p 91. (b) Bestmann, H. J.; Both, W. *Chem. Ber.* **1974**, *107*, 2923.

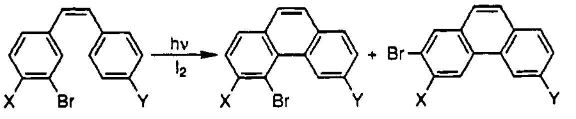
(76) Martin, R. H.; Marchant, M. J. *Tetrahedron* **1974**, *30*, 343.

(77) (a) Sudhakar, A.; Katz, T. J. *Tetrahedron Lett.* **1986**, *27*, 2231. (b) Liu, L.; Katz, T. J. *Tetrahedron Lett.* **1991**, *32*, 6831.

(78) Yang, B.; Liu, L.; Katz, T. J.; Liberko, C. A.; Miller, L. L. *J. Am. Chem. Soc.* **1991**, *113*, 8993.

(79) (a) Reference 18. Experiments that appear to contradict those reported here appear in (b) Mallory, F. B.; Mallory, C. W.; Sen Loeb, S. E. *Tetrahedron Lett.* **1985**, *32*, 3773. (c) Gorsane, M.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1985**, *94*, 205. (d) Mervic, M.; Ghera, E. *J. Am. Chem. Soc.* **1977**, *99*, 7673. (e) Martin, R. H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 649.

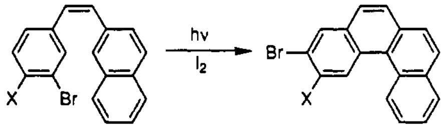
noticed, however, that there is one exception: these cannot be the α-positions of naphthalenes.[74b,81] At these positions reactions do occur, presumably because electronic effects prevail.



(3)

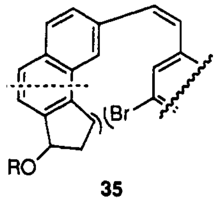
X = Y = H
X = H, Y = F
X = CH_3, Y = H

Consider now the position adjacent to the bromine. There the bromine does not block attack by unencumbered benzenes. Thus the transformations in eq 3 give mixtures of both possible photocyclization products.[82] However, if the attacking benzene is encumbered, bromine does block the adjacent position. Equation 4 records two examples.[83] The explanation we put forward and illustrate with the cyclization of **12** is that the steric interaction indicated on structure **35** is the origin of the effect.



(4)

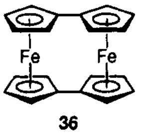
X = H and CH_3



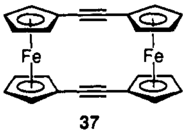
35

Thus in the absence of either the bromine or the lower left portion of the molecule, there should be no appreciable steric interference, and the effect therefore should, and seemingly does, vanish. But if the ring system at the left is a naphthalene and the bromine is present, cyclization at the position adjacent to the bromine is repulsed.

Interaction between the Components. The helical cobaltocenium oligomers synthesized here are not only the first optically active polymetallocenes, but they are also the first polymeric metallocenes whose metals are linked by conjugated aromatic ligands. Their closest relative is poly(1,1′-ferrocenylene),[84] but in this structure rotation about the σ-bonds between the ferrocenes disrupts conjugation. Also related are two structures in which interaction of metallocenes might be achieved by forcing their proximity,[85,86] and last, there is a chromium–naphthalene polymer.[87] None, however, behaves as though the metals interact strongly. In partially oxidized short poly(1,1′-ferrocenylene), the intervalence transfer (IT) bands observed in the near-IR spectrum, at ca. 1800 nm (ϵ = 1080–1720), indicate that the constituent iron atoms interact only modestly.[88] In longer poly(1,1′-ferrocenylene), partial oxidation by DDQ increases conductivity somewhat (from $8 \times 10^{-12}\ \Omega^{-1}\ cm^{-1}$ to $2 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$), but the near-IR band (ca. 1900 nm) is said to be weak.[89] By contrast, in dinuclear ferrocenes that are fully delocalized, like the cations of **36**[90] and **37**,[91] the IT bands, both at 1550 nm, are stronger (ϵ = 2100 and 3100, respectively), while in poly(vinylferrocene), whose iron centers are insulated from one another, there is no peak in the near-IR.[89] For **38**, one of the two structures in which metallocenes are forced to be proximate—there are no physical studies of the other—the difference between the first two oxidation potentials ($\Delta E°$ = 116–208 mV for n = 1–3) and a weak near-IR absorption at 1600 nm (ϵ = 200 when n = 1) show that the metals interact only weakly.[82] The similarity between the values of $\Delta E°$ reported for these oligomers and those measured here for **9** (ca. 100 mV), and in the accompanying manuscript for **29** (130 mV)[50] implies that the metals in these structures interact to a similar extent.



36



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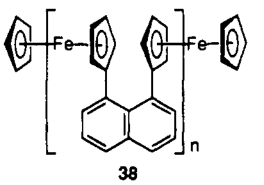

38

The specific rotation of **9**, $[\alpha]_{577}$ 37 000° (entry 5, Table II), is appreciably larger than that of simple helicenes.[92] However, its rotational strengths, measured by the CD spectra, are not significantly enhanced by union of the helical metallocene units. Consider Table V. This compares the rotational strengths and molar ellipticities for similar peaks in two cobaltocenium ions, oligomer **9** and monomer **8**, and in the corresponding hydrocarbons **7** and **6**. The ratio of **9**:**8** shows that the rotational strength is higher in the oligomer than in the monomer, and the ratio of **7**:**6** shows that it is slightly higher in the hydrocarbon with nine rings (**7**) than in the hydrocarbon with only seven (**6**). If the ratio of the ratios is examined, it is seen to be similar to, and even less than, the average number of monomers linked in the oligomer, ca. 6. The absence of enhancement by the union of the monomers is also evidenced by the data in Table VI, which compares the rotational strengths at two wavelengths of CD peaks in **9** and in **29**. Again their ratio, ca. 7, is similar to the number, 6, of helical units in the oligomer.

Experimental Section

General Information. The reagents were combined under nitrogen or argon. Diethyl ether and tetrahydrofuran were distilled under argon from sodium or potassium benzophenone ketyl. Benzene (Fisher, spectranalyzed grade) for photocyclization reactions was used without purification. All other solvents were purified according to Perrin[93] and distilled under nitrogen or argon. n-Butyllithium/hexanes (Aldrich) and t-BuLi/pentane (Aldrich) were titrated according to Eastham.[94] Potassium hexamethyldisilylazide (Callary) was titrated according to Brown.[95] Borane/THF (Aldrich) was titrated according to Brown.[96] Preparative silica gel (Woelm 32–62, 32–63 μm) column chromatography

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(80) The following papers record cyclizations that avoid positions occupied by bromine, but they do not record whether these positions are attacked when the bromines are absent: (a) Gorsane, M.; Defay, N.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1985**, *94*, 215. (b) Unpublished results of experiments with 2-(2-bromo-5-fluorostyryl)naphthalene recorded by Mallory, F. B.; Mallory, C. W. in ref 26, p 173. (c) Joly, M.; Defay, N.; Martin, R. H.; Declerq, J. P.; Germain, G.; Soubrier-Payen, B.; Van Meerssche, M. *Helv. Chim. Acta* **1977**, *60*, 537.

(81) (a) Brison, J.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1983**, *92*, 893. (b) Blackburn, E. V.; Loader, C. E.; Timmons, C. J. *J. Chem. Soc. (C)* **1970**, 163.

(82) (a) Gore, P. H.; Kamonah, F. S. *Synth. Commun.* **1979**, *9*, 377. (b) Martin, R. H.; Schurter, J. J. *Tetrahedron* **1972**, *28*, 1749. (c) Unpublished results of experiments with 3-bromo-4′-fluorostilbene recorded by Mallory, F. B.; Mallory, C. W. in ref 27, p 136.

(83) (a) Le Guen, J.; Taylor, R. *J. Chem. Soc., Perkin Trans. II* **1974**, 1274. (b) Martin, R. H.; Schurter, J. J. *Tetrahedron Lett.* **1969**, 3679.

(84) Neuse, E.; Bednarik, L. *Macromolecules* **1979**, *12*, 187.

(85) Hopf, H.; Dannheim, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 701.

(86) (a) Lee, M.-T.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1985**, *4*, 539. (b) Arnold, R.; Matchett, S. A.; Rosenblum, M. *Organometallics* **1988**, *7*, 2261.

(87) Bush, B. F.; Lagowski, J. J. *Organometallics* **1988**, *7*, 1945.

(88) Brown, G. M.; Meyer, T. J.; Cowan, D. O.; LeVanda, C.; Kaufman, F.; Roling, P. V.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 506.

(89) Cowan, D. O.; Park, J.; Pittman, C. V., Jr.; Sasaki, Y.; Mukherjee, T. K.; Diamond, N. A. *J. Am. Chem. Soc.* **1972**, *94*, 5110.

(90) LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhoff, U. T.; Eilbracht, P.; Candela, G. A.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181.

(91) Levanda, C.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* **1976**, *41*, 2700.

(92) Up to 9600°. Ref 75a.

(93) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon: New York, 1988.

(94) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

(95) Brown, C. A. *Synthesis* **1974**, 427.

Table V. Rotational Strengths of Similar CD Peaks in **9**, **8**, **7**, and **6**

structure	λ (nm)	[θ]	rotational strength[a]
9, ca. 6 units	263	-5.21×10^6	-5.06×10^{-37}
8	243	5.51×10^5	1.03×10^{-37}
7	282	-6.89×10^5	-6.91×10^{-38}
6	282	7.55×10^5	5.60×10^{-38}
		ratio of **9**:**8** = –5	
		ratio of **7**:**6** = –1.2	
		ratio of ratios = 4	

[a] cgs units. Calculated according to ref 100.

Table VI. Rotational Strengths of Similar CD Peaks in **9** and **29**

structure	λ (nm)	[θ]	rotational strength[a]
9, ca. 6 units	263	-5.21×10^6	-5.06×10^{-37}
29	270	-7.06×10^5	-6.43×10^{-38}
		ratio = 8	
9, ca. 6 units	484	2.46×10^6	4.08×10^{-37}
29	430	4.55×10^5	6.71×10^{-38}
		ratio = 6	

[a] cgs units. Calculated according to ref 100.

was conducted according to Still.[97] The plates used for thin-layer chromatography (TLC) were E. Merck's silica gel 60 F-254 (0.25-mm thickness), precoated on glass, and they were visualized under both long (365 nm) and short (254 nm) UV light. Circular dichroic (CD) spectra were obtained on a JASCO J-500A spectrometer with a DP-500N data processor. Elemental analyses were performed by Galbraith Laboratories in Knoxville, TN or at Columbia University using a Perkin-Elmer 2400 CHN elemental analyzer.

2,7-Dibromonaphthalene (15). This was prepared from 2,7-dihydroxynaphthalene according to the procedure of Porzi and Concilio[13] with some modification. The modification recorded here was developed by Dr. Michael Poindexter and is reproduced with his permission.[32] The residue left after acetonitrile had been removed was heated at 310–320 °C for 80 min instead of at 250 °C for 1 h. Upon being cooled to ca. 80 °C, the mixture was poured into 2 L of 70% ethanol and stored in a cold room (4 °C) overnight. The filtered solid was dissolved in CH_2Cl_2, treated with Norit, brought briefly to a boil, and then filtered through Celite. The dark red filtrate when concentrated and cooled overnight formed crystals, which were filtered and washed with petroleum ether. The yield of tan plates from 400 g of diol was 393 g (55%), mp 139–140 °C.

2-Bromo-7-(trimethylsilyl)naphthalene (16). 2,7-Dibromonaphthalene (**15**, 114.4 g, 0.4 mol) in 1 L of THF contained in an oven-dried 2-L 3-necked round-bottomed flask, fitted with a mechanical stirrer and dropping funnel, was cooled under argon to –78 °C. *n*-Butyllithium in hexanes (175 mL, 2.4 M, 0.42 mol) was added in drops over 30 min, and the mixture was stirred at –78 °C for another 20 min. Dry chlorotrimethylsilane (81 mL, 69.5 g, 0.64 mol, distilled from CaH_2) was added from the dropping funnel over 10 min, whereupon the mixture began to warm and the color turned orange. After the evolution of heat subsided (ca. 15 min), the mixture was warmed to room temperature and stirred for 2 h. Concentration to ca. 250 mL, addition of 1 L of water, extraction with ether (1 × 600 mL, 3 × 100 mL), washing the extract with 200 mL of brine, drying ($MgSO_4$), and evaporation of solvent gave 126 g (112%) of yellow-orange liquid, which when stored at –15 °C solidified to a pale yellow mass, which was recrystallized from ethanol, mp 38–39 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.36 (s, 9 H), 7.53 and 7.67 (AB q, *J* = 8.7, 1.9 Hz, 2 H), 7.60 and 7.77 (AB q, *J* = 8.1, 1.1 Hz, 2 H), 7.89 (s, 1 H), 8.00 (d, *J* = 1.3 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ –1.17, 119.65, 126.78, 129.35, 129.51, 130.05, 130.23, 131.94, 132.72, 133.94, 139.44. HRMS (EI): *m/z* 278 (M^+, 2), 263 (M – CH_3, 2), 73 (M – $C_{10}H_6$, 100). HRMS: calcd for $C_{13}H_{15}BrSi$ 278.0126, found 278.0135 (and the observed and calculated pattern of parent peak intensities match).

2-Bromo-7-(3-chloropropionyl)naphthalene (17). A solution of 61 g (0.48 mol) 3-chloropropionyl chloride in 50 mL of CH_2Cl_2 was added under nitrogen from a dropping funnel to stirred anhydrous $AlCl_3$ (70 g, 0.526 mol) and CH_2Cl_2 (100 mL) contained in a 1-L 3-necked flask. After the mixture was cooled in dry ice/acetone, a solution of 126 g of **16** in 200 mL of CH_2Cl_2 was added over 35 min. The mixture was stirred for 10 min at –78 °C, allowed to warm to room temperature over 45 min, and then poured into ca. 1 L of ice plus 100 mL of concentrated HCl. After being extracted with CH_2Cl_2 (1 × 1 L, 3 × 200 mL), the combined organic solutions were washed once with 1.5 L of water, dried ($MgSO_4$), filtered, and evaporated to give 135 g of crude **17**, an off-white solid. This was either cyclized without further purification or purified by shaking it with 500 mL of petroleum ether and filtering, which gave 90 g (76%) of pure **17**, mp 120 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.35 (br s, 0.79 H), 8.12 (d, *J* = 8.6 Hz, 1.05 H), 7.75 (d, *J* = 8.9 Hz, 1.05 H), 7.66 (dd, *J* = 8.8, 1.8 Hz, 1.05 H), 3.96 (t, *J* = 6.9 Hz, 2.10 H), 3.56 (t, *J* = 6.9 Hz, 2.10 H). Other experiments gave yields of 86 ± 5%.

8-Bromo-1,2-dihydrobenz[*e*]inden-3-one (18). Method 1: Using $AlCl_3$–H_2SO_4. Crude **17** (65 g, 0.218 mol) was added over 20 min in small portions to a vigorously stirred suspension of $AlCl_3$ (35 g) and concentrated H_2SO_4 (325 mL) cooled in an ice–water bath. The reaction mixture became yellow and then orange. The flask was heated, and when the internal temperature was 65 °C, the rate of stirring was increased and the rate of heating decreased to control the foaming. When this subsided, the mixture was held at 98 °C for 1 h. It was then cooled to ca. 70 °C and cautiously poured into 4 L of ice and water. The mixture was stirred for 2 h and then extracted with CH_2Cl_2 (2 × 1 L, 2 × 500 mL). The organic solutions were washed with water (1 L), dried ($MgSO_4$), filtered, and evaporated, giving 45 g of yellow solid. This, in 1 L of CH_2Cl_2, was filtered through a 6-in. × 5-cm column of neutral alumina and washed with more CH_2Cl_2. Evaporation gave 38.7 g of **18** (68% from **17**, 76% from **15**), a pale yellow solid, mp 131–132 °C (lit.[7a,b] mp 132–134 °C). The ^{1}H NMR spectrum was identical with that of a sample prepared according to a previously published procedure, and the IR spectrum was identical to that published.[7b] The material can be recrystallized as described below.

Method 2: Using Concentrated H_2SO_4. Purified **17** (89.5 g, 0.300 mol) was added over 40 min to 300 mL of stirred concentrated H_2SO_4 contained in a 2-L 3-necked flask. The mixture was heated to 90 °C and maintained at this temperature for 80 min. After cooling, the reaction mixture was poured into ice–water, extracted with CH_2Cl_2 (15 × 200 mL), washed with 2 L of water, dried ($MgSO_4$), filtered, and evaporated. Crystallization from CH_2Cl_2–ether gave 61 g of off-white solid. A second crop, 15 g, was obtained by chromatographing the mother liquor. The total yield, 76 g (97%), represents one of 73% from **15**.

(*R*)-(+)-8-Bromo-1,2-dihydrobenz[*e*]inden-3-ol (19). Method 1: Using Catalytic Amounts of Diphenylvalinol. (*S*)-(–)-Diphenylvalinol (1.82 g, 7.14 mmol) and 10 mL of THF in a 500-mL round-bottomed flask containing a stirring bar was purged with Ar and cooled to –78 °C, and 68 mL of 1.26 M BH_3–THF (86 mmol) was added slowly by syringe. The flask was allowed to warm to room temperature, heated to 40 °C until no more gas evolved, and then cooled to 0 °C. Ketone **18** (18.8 g, 71.4 mmol) in 225 mL of THF was added by cannula, and an additional 10 mL of THF was used to wash over residual amounts. After the solution was stirred overnight at room temperature, 10 mL of 15% NaOH was cautiously added, and then 40 mL of water was added, giving a homogeneous solution, from which the solvent was evaporated. The residue was extracted with CH_2Cl_2 (2 × 200 mL), water (2 × 200 mL), and ether (3 × 200 mL). The combined extracts were shaken, and the aqueous phase was discarded. The organic phase was extracted with water (2 × 200 mL) and brine (200 mL), dried ($MgSO_4$), filtered, and evaporated, giving a mixture of diphenylvalinol and **19**. Flash chromatography, with CH_2Cl_2 as eluant, gave 18.8 g of (+)-**19**, a 99% yield, $[\alpha]_D$ 58.3° and $[\alpha]_{577}$ 61.9° (*c* 0.530, CH_2Cl_2), corresponding to an ee of 99%, mp 150–151 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.87 (d, *J* = 7 Hz, 1 H), 2.09 (m, 1 H), 2.70 (m, 1 H), 3.06 (m, 1 H), 3.36 (m, 1 H), 5.42 (m, 1 H), 7.54 and 7.73 (two overlapping AB quartets, *J* = 9 Hz, 4 H), 7.99 (br s, 1 H). This spectrum is identical with that of the racemic alcohol.[7a,b]

Method 2: Using Stoichiometric Amounts of Diphenylvalinol. (*S*)-(–)-Diphenylvalinol (12.77 g, 50 mmol) in 50 mL of THF was purged with N_2 and cooled to –78 °C, whereupon 84 mL of 1.26 M BH_3–THF (106 mmol) was added slowly by syringe. The flask was warmed to 0 °C and maintained at this temperature overnight. Ketone **18** (10.45 g, 40 mmol) in 100 mL of THF was added by cannula, and the reaction was stirred overnight at room temperature. After 10 mL of 15% NaOH, then 10 mL water were cautiously added, solvent was evaporated from the homogeneous solution, and the residue in 1 L of ether was extracted with 15% NaOH (2 × 100 mL), water (5 × 100 mL), and brine (100 mL). Drying with K_2CO_3, filtration, and evaporation gave a mixture of alcohol **19** and diphenylvalinol. Flash chromatography with CH_2Cl_2

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(96) Brown, H. C. *Organic Synthesis via Boranes*; Wiley: New York, 1975; pp 241–245.

(97) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

gave 10.4 g of (+)-**19**, a 99% yield, $[\alpha]_{577}$ 60.9° (*c* 0.542, CH_2Cl_2), corresponding to a 98% ee.

Method 3: Using $LiAlH_4$, *N*-Methylephedrine, and 3,5-Dimethylphenol. (+)-*N*-Methylephedrine (35.8 g, 0.2 mol) in 350 mL of dry ether was added over 20 min to a stirred suspension of $LiAlH_4$ (8.05 g, 0.2 mol) in 100 mL of dry ether. After the mixture refluxed for 1 h and cooled, 3,5-dimethylphenol (48.9 g, 0.4 mol) was added over 225 min in 220 mL of dry ether. After the mixture refluxed for 1 h and cooled in a salt–ice bath (internal temperature 0 °C), 20 g of **18** (77 mmol) were added in one portion. After the mixture was stirred overnight, water (10 mL) was added in drops, followed by 400 mL of 1 M HCl. The aqueous layer was washed with ether (200 mL), and the ether layers were washed with 1 M HCl (300 mL), water (300 mL), 10% NaOH (3 × 200 mL), and brine (500 mL). After the solution was dried ($MgSO_4$) and the volume of solvent reduced, crystals of **19** were filtered: 11.5 g, $[\alpha]_{578}$ −43° (*c* 0.40, CH_2Cl_2). A second crop, 4.1 g, $[\alpha]_{578}$ −0.56° (*c* 0.36, CH_2Cl_2), was obtained by adding pentane to the filtrate. Evaporating the solvent gave 4.3 g more, $[\alpha]_{578}$ −9.2° (*c* 0.76, CH_2Cl_2).

Determination of the Enantiomeric Excess in 19. (*S*)-(+)-*O*-Methylmandelic acid (76 mg, 0.46 mmol) and 0.23 mL of $SOCl_2$ (3.19 mmol) in a 10-mL round-bottomed flask equipped with a condenser was purged with N_2 and heated to 80 °C for 5 min, during which time gas evolved. The solution was cooled to room temperature, 5 mL of benzene was added, and the solvent was evaporated on the Rotovap. This was repeated with 2 mL of benzene to remove excess $SOCl_2$.[98] The clear oil was dissolved in 2 mL of benzene and added by pipet to a slurry of (+)-**19** (40 mg, 0.15 mmol, prepared according to method 2 above), pyridine (0.08 mL, 0.9 mmol), and benzene (1 mL). After the mixture was stirred for several hours, the reaction was quenched with water, and the mixture was extracted with ether and 0.1 M HCl. The ether extracts were further extracted with water, saturated Na_2CO_3, and brine and dried with K_2CO_3. Filtration and evaporation gave a milky oil, which was flash chromatographed with CH_2Cl_2, giving 60 mg of the *O*-methyl mandelate ester, a quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.02 (m, 1 H), 2.58 (m, 1 H), 3.08 (m, 1 H), 3.27 (m, 1 H), 3.43 (s, 3 H), 4.77 (s, 1 H), 6.43 (dd, J = 7.2, 3.2 Hz, 1 H), 7.37 (m, 3 H), 7.44 (m, 2 H), 7.51 and 7.75 (AB q, J = 8.8 Hz, 2 H), 7.58 and 7.70 (AB q, J = 8.7 Hz, 2 H), 7.98 (d, J = 1.7 Hz, 1 H). Double resonance experiments show that the resonances at δ 2.02 and 2.58 are due to the protons on the five-membered ring adjacent to the carbon bearing the ester. Thus, the resonance at δ 6.43 collapses to a doublet with J = 7.1 Hz when the former is irradiated and to a doublet with J = 3.5 Hz when the latter is irradiated and remains unaffected while those at δ 3.08 and 3.27 are irradiated. A comparison of the spectrum of this ester with the 400-MHz ^{1}H NMR spectrum of the mixture of *O*-methyl mandelates prepared from the racemic alcohol shows that the ester of the enantiomeric alcohol exhibits these resonances: δ 2.24 (m, 1 H), 2.75 (m, 1 H), 4.80 (s, 1 H), 6.43 (m, 1 H), 7.14 (d, J = 8.2 Hz, 1 H). The intensities show the ee to be 98%. The sample of (+)-**19** used for the experiment was prepared using stoichiometric amounts of diphenylvalinol. It exhibited $[\alpha]_D$ 57.6° and $[\alpha]_{577}$ 60.4°. This implies values for optically pure **19** of $[\alpha]_D$ 58.8° and $[\alpha]_{577}$ 61.6°. Some relevant spectra are displayed in the supplementary material.

(*R*)-(+)-(8-Bromo-1,2-dihydrobenz[*e*]inden-3-oxy)-*tert*-butyldimethylsilane (20). To 18.8 g of **19** (99% ee, 71.4 mmol) and 15.1 g of imidazole (221 mmol) in 300 mL of DMF was added 16.2 g of *tert*-butylchlorodimethylsilane (107 mmol).[99] The mixture under nitrogen was stirred overnight, diluted with 500 mL of ether, poured into 500 mL of cold water, and extracted with 500 mL of ether. The organic phase was extracted with water (6 × 250 mL), the combined aqueous phases were extracted with 500 mL of ether, and the ether solution was extracted with 500 mL of water. The combined organic phases were dried ($MgSO_4$), filtered, and evaporated, giving 28.3 g of crude **20**. This, dissolved in petroleum ether, was filtered through a short column of silica gel and eluted further with petroleum ether. The yield of **20** was 24.3 g (90%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.20 (s, 3 H), 0.22 (s, 3 H), 0.98 (s, 9 H), 2.08 (m, 1 H), 2.63 (m, 1 H), 2.99 (m, 1 H), 3.33 (m, 1 H), 5.45 (m, 1 H), 7.42–7.55 (m, 2 H), 7.65–7.75 (m, 2 H), 7.97 (br s, 1 H). This spectrum was identical with that of the racemic material.[7a,b] Other experiments gave yields of 85–99%. One, using the enantiomer of **19**, whose $[\alpha]_{578}$ was −41°, gave **20**, whose $[\alpha]_{578}$ was −50° (*c* 0.3, CH_2Cl_2).

(*R*)-3-[((*tert*-Butyldimethyl)silyl)oxy]-2,3-dihydro-1*H*-benz[*e*]indene-8-carboxaldehyde (10). Bromoether **20** (24.3 g, 64.4 mmol) in 500 mL of THF and 350 mL of ether was purged with N_2 and cooled to −78 °C. *n*-Butyllithium in hexanes (70 mL, 2.4 M, 167 mmol) was dropped in syringe over 10 min. After the solution was stirred for 30 min, 50 mL of DMF (644 mol) was added over 10 min by syringe to the yellow-orange solution (exotherm), which was stirred for 2 h. After the mixture was warmed to room temperature, the reaction was quenched with saturated NH_4Cl, and the mixture was extracted with water (4 × 250 mL) and then 250 mL of brine, dried with $MgSO_4$, filtered, and evaporated. Flash chromatography with petroleum ether and CH_2Cl_2 (1:0 to 2:1) and rechromatography gave 18.0 g of pure **10**, an 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.20 (s, 3 H), 0.22 (s, 3 H), 0.98 (s, 9 H), 2.12 (m, 1 H), 2.65 (m, 1 H), 3.12 (m, 1 H), 3.44 (m, 1 H), 5.47 (t, J = 7 Hz, 1 H), 7.60 and 7.79 (AB quartet, J = 8 Hz, 2 H), 7.94 (br s, 2 H), 8.32 (s, 1 H), 10.17 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −4.75, −4.49, 18.04, 25.71, 27.91, 35.73, 76.37, 122.60, 125.70, 127.40, 129.55, 129.70, 130.55, 133.96, 136.59, 140.56, 143.78, 192.37. The ^{1}H NMR spectrum was identical with that of the racemic material.[7a,b] Other experiments gave 85–92% yields. One, using the enantiomer of **20**, whose $[\alpha]_{578}$ was −50°, gave **10**, whose $[\alpha]_{578}$ was −42.7° (*c* 0.3, CH_2Cl_2). The melting point, measured using a sample that was ca. 67% optically pure, was 51–52 °C.

1-Bromo-2,5-bis(bromomethyl)benzene. 2-Bromo-*p*-xylene (46.2 g, 0.25 mol) was refluxed for 100 min with *N*-bromosuccinimide (98 g, 0.55 mol) and dibenzoyl peroxide (500 mg) in 500 mL of CCl_4. Cooling, filtering, evaporating, and triturating with pentane crystallized the product, 18.5 g of white solid, mp 86 °C. A second crop of 20.5 g was obtained from the mother liquor. The total yield, 39.0 g, was 45.5%, mp (uncorrected) 87–90 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.40 (s, 2 H), 4.57 (s, 2 H), 7.31 (dd, J = 7.8, 1.8 Hz, 1 H), 7.42 (d, J = 7.8 Hz, 1 H), 7.61 (d, J = 1.8 Hz, 1 H) [H_2O peak is seen at δ 1.54]. ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.28, 32.64, 124.42, 128.51, 131.45, 133.63, 137.07, 138.89. MS (CI, CH_4): m/z 263 (M + 1, 100), 182 (M − Br, 25), 103 (M − 2Br, 35).

(2-Bromo-1,4-phenylene)bis(methylene) bis(triphenylphosphonium) dibromide. The tribromide above (39 g) and triphenylphosphine (63 g) were refluxed for 3 h in 300 mL of dry DMF. After the mixture was cooled, the addition of 200 mL of ether precipitated a solid, which was washed with ether and dried. The yield was 89.2 g (91%) of white fluffy solid, mp 260 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.46 (d, J_{PH} = 14.4 Hz, 2 H), 5.67 (d, J_{PH} = 14.1 Hz, 2 H), 6.92 (m, 2 H), 7.30 (m, 1 H), 7.60–7.81 (m, 30 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.60 (d, J_{PC} = 47.9 Hz), 30.31 (J_{PC} = 52.2 Hz), 116.26, 117.40, 129.99, 130.04, 130.16, 133.90, 134.07, 134.21, 134.96, 135.07. (Many of the ^{13}C NMR signals overlap.)

Bis-stilbene 11. *n*-Butyllithium in hexanes (23.5 mL, 2.46 M, 57.9 mmol) was added under N_2 in drops to 250 mL of cold (−78 °C) dry EtOH. After it had been warmed to room temperature and stirred until homogeneous, the solution was transferred by cannula to a slurry of 18.0 g of aldehyde **10** (55.1 mmol) and 23.9 g of (2-bromo-1,4-phenylene)bis(methylene)bis(triphenylphosphonium) dibromide (27.6 mmol) in 450 mL of dry EtOH under N_2. After the mixture was stirred overnight, the reaction was quenched with 700 mL of water, which precipitated bis-stilbene **11** as a yellow solid but left the Ph_3PO in solution. The product was filtered through Celite, washed with water, and then washed from the filter with CH_2Cl_2. The solution was dried with $MgSO_4$, filtered, and evaporated, giving 20.1 g of **11**, a yellow solid. Flash chromatography with petroleum ether/CH_2Cl_2 (6:1 to 4:1) and rechromatography of impure fractions gave 17.2 g (a 78% yield) of **11**, a yellow powder. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.15–0.23 (s, 12 H), 0.9–1.01 (s, 18 H), 2.06 (m, 2 H), 2.61 (m, 2 H), 2.8–3.5 (m, 4 H), 5.41 (m, 2 H), 6.5–7.9 (m, 17 H). IR (KBr, cm^{-1}): 2955, 2928, 2889, 2855, 1420, 1461, 1360, 1252, 1105, 1051, 1037, 985, 955, 884, 861, 836, 775. HRMS (EI): calcd 800.30807, found 800.3166, and the pattern of intensities is correct.

(*P*)-*exo,exo*-3,18-di((*tert*-Butyldimethylsilyl)oxy)-13-bromo-[9]helicene 12. A solution of bis-stilbene **11** (500 mg, 0.623 mmol), I_2 (350 mg, 2.76 mmol), and propylene oxide (10 mL, 143 mmol) in 1300 mL of benzene was degassed by bubbling Ar through for 30 min and irradiated through Pyrex for 14 h with a medium-pressure Hg lamp. The orange solution was extracted with 500 mL of dilute aqueous $NaHCO_3$ and $Na_2S_2O_3$, dried with $MgSO_4$, filtered, and concentrated to a small volume. The solution was filtered through a short column of alumina and eluted further with benzene until the filtrate was colorless, and the solvent was evaporated. This was repeated 20 times so that a total of 10.0 g of **11** was transformed. ^{1}H NMR and TLC analyses revealed the presence of a trace of the endo,exo isomer (a tiny singlet at δ 1.1 for one of two diastereotopic *tert*-butyl groups; the other at δ 0.9 is obscured by the *tert*-butyl group of the exo,exo isomer) and other minor impurities. Flash chromatography with petroleum ether and CH_2Cl_2 (6:1 to 5:1), rechromatography of less-pure fractions, and rechromatography of the

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[98] Jacobus, J.; Raban, M.; Mislow, K. *J. Org. Chem.* **1968**, *33*, 1142.

[99] The method is that of Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

combined purified material gave 4.94 g (50% yield) of pure (*P*)-*exo,exo*-**12**, a yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.08 (s, 6 H), 0.18 (s, 6 H), 0.23 (m, 2 H), 0.92 (s, 18 H), 0.99 (m, 2 H), 1.17 (m, 2 H), 1.71 (m, 2 H), 4.87 (m, 2 H), 6.99 and 7.17 (AB q, J = 8.0 Hz, 4 H), 7.25–7.35 (m, 2 H), 7.44 and 7.48 (Ab q, J = 8.5 Hz, 2 H), 7.81–7.94 (m, 3 H), 8.31 (s, 1 H), 8.42 (d, J = 8.0 Hz, 1 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ –4.68, –4.38, 18.28, 25.94, 29.47, 29.56, 36.93, 37.03, 77.21, 120.50, 120.67, 122.96, 123.17, 125.63, 125.68, 125.92, 125.96, 126.26, 126.66, 126.68, 127.93, 128.19, 128.67, 129.26, 129.47, 131.05, 131.34, 131.39, 132.29, 132.43, 134.68, 134.72, 145.04, 145.10. HRMS (EI): calcd 796.2767, found 796.2726 and the pattern of intensities is correct; $[\alpha]_D$ 3160° and $[\alpha]_{577}$ 3420° (c 0.204, CH$_2$Cl$_2$).

(*P*)-*exo,exo*-3,18-di((*tert*-Butyldimethylsilyl)oxy)[9]helicene 13. *n*-Butyllithium in hexanes (10 mL, 2.5 M, 25 mmol) was added by syringe to **12** (4.90 g, 6.14 mmol) in 700 mL of THF that had been purged with Ar and cooled to –78 °C. After being stirred for 30 min, the orange-colored solution was quenched with 50 mL of saturated NH$_4$Cl, warmed to room temperature, diluted with 700 mL of ether, extracted with water (4 × 250 mL) and then brine (250 mL), dried with MgSO$_4$, filtered, and evaporated. Flash chromatography with petroleum ether and CH$_2$Cl$_2$ (8:1 to 5:1) gave 4.07 g (92% yield) of pure **13**. ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.09 (s, 6 H), 0.19 (s, 6 H), 0.29 (m, 2 H), 0.88 (m, 2 H), 0.92 (s, 18 H), 1.13 (m, 2 H), 1.69 (m, 2 H), 4.90 (m, 2 H), 6.97 and 7.17 (Ab q, J = 8.1 Hz, 4 H), 7.30 and 7.48 (Ab q, J = 8.5 Hz, 4 H), 7.83 and 8.00 (AB q, J = 8.1 Hz, 4 H), 8.01 (s, 2 H). $[\alpha]_D$ 3490° and $[\alpha]_{577}$ 3770° (c 0.204, CH$_2$Cl$_2$).

(*P*)-(+)-[9]Helical Bis-indene 14. A solution of **13** (1.11 g, 1.54 mmol) and *p*-toluenesulfonic acid (59 mg, 0.31 mmol) in 150 mL of benzene was purged with N$_2$ and refluxed for 30 min. The solution was cooled, extracted with saturated Na$_2$CO$_3$, dried with MgSO$_4$, filtered, and concentrated. The yellow fractions eluted by benzene from a flash chromatography column were combined and evaporated, giving 680 mg (97% yield) of powdery yellow **14**. ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.04 (dt, J = 23.8, 1.8 Hz, 2 H), 1.93 (dt, J = 23.8, 1.7 Hz, 2 H), 5.83 (dt, J = 5.5, 1.9 Hz, 2 H), 6.47 (dt, J = 5.5, 1.8 Hz, 2 H), 7.11 and 7.18 (Ab q, J = 8.1 Hz, 4 H), 7.18 and 7.25 (Ab q, J = 8.5 Hz, 4 H), 7.70 and 7.95 (AB q, J = 8.2 Hz, 4 H), 8.00 (s, 2 H). ^{13}C NMR (75 MHz, CDCl$_3$): 40.13, 119.56, 122.88, 125.87, 126.01, 126.10, 126.28, 126.40, 126.54, 128.10, 128.26, 130.19, 130.44, 130.85, 132.17, 132.44, 137.62, 142.83. $[\alpha]_D$ 7820° and $[\alpha]_{577}$ 8480° (c 0.106, CH$_2$Cl$_2$). MS (CH$_4$, CI): m/z 455 (M + 1), 483 (M + 29). Mp: darkens at 245 °C, melts at 273–275 °C. CD (CH$_3$CN) $\lambda_{\max}$ ($\Delta\epsilon$, rotational strength[100]): 392 (170, 7.04 × 10^{-38}), 279 (–226, –6.24 × 10^{-38}), 252 (23, –), 239 (–29, –), 225 (129, 1.86 × 10^{-38}), 205 nm (–137, –1.63 × 10^{-38}). Anal. Calcd for C$_{36}$H$_{22}$: C, 95.12; H, 4.88. Found: C, 95.01; H, 4.98. The UV/CD spectrum of this sample is displayed in Figure 6.

Photocyclization in the Absence of Propylene Oxide and Preparation of 23. The experiment was performed with racemic **11**, prepared like the optically active material. Its solution (280 mg, 0.35 mmol) in 1.9 L of benzene was degassed, and, after I$_2$ (9 mg, 0.035 mmol) had been added, irradiated for 2.3 h. Removing the benzene left a yellow solid (145 mg, 77% yield), the cyclized bis-indene (^{1}H NMR and MS analyses). This was dissolved in dry ether (50 mL) and treated at –78 °C with *n*-BuLi (5 mL, 2.6 M). After the mixture was stirred at –78 °C for 10 min and at 0 °C for 5 min, the reaction was quenched with water and worked up with ether. Chromatography on neutral alumina, with CH$_2$Cl$_2$–pentane (1:1) as the eluant, gave 205 mg (86%) of yellow solid whose ^{1}H NMR spectrum shows it to be a mixture of **23** and the isomer in which one double bond had moved. This was converted predominantly to **23** by stirring for 4 h with a solution of LiOEt (prepared by adding 1 mL of 2.6 M *n*-BuLi to 4 mL of EtOH) in benzene (1 mL). Work up and chromatography (alumina) gave 20 mg of yellow solid, assigned structure **23** because like **14** it has a ^{1}H NMR spectrum that shows, besides the resonances of aromatic protons, only one pair of resonances characteristic of indenes in helicenes [δ 5.77, 5.65, 3.01 (d, J = 24 Hz), and 2.68 (d, J = 24 Hz)]. The mass spectrum (CI, NH$_3$) showed M + 1 = 455, as required.

The photocyclization was also carried out using bis-stilbene (60 mg) that had been prepared from **19**, $[\alpha]_D$ 46.7°.[27] Argon was passed for 10 min through its solution in benzene (185 mL), and I$_2$ (3 mg) was added. After this had been irradiated for 70 min, the solvent was stripped, and the product in CH$_2$Cl$_2$–petroleum ether (1:2) was passed through a short column of alumina. The yellow product showed $[\alpha]_D$ 82° (c 0.1, CHCl$_3$).

Bis-stilbene 21. This was prepared according to the procedure used in the preparation of bis-stilbene **11**, using 1.04 g (3.19 mmol) of aldehyde **10**, 1.32 g (1.68 mmol) of 1,4-phenylenebis(methylene)bis(triphenylphosphonium) dibromide,[101] 1.57 mL (4.02 mmol) of a 2.57 M solution of *n*-BuLi/hexanes, and 100 mL of absolute ethanol, to yield 460 mg (0.64 mmol, 40% yield) of **21**, a yellow solid. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.18–0.22 (s, 12 H), 0.97–1.02 (s, 18 H), 2.08 (m, 2 H), 2.63 (m, 2 H), 2.92 (m, 1 H), 3.07 (m, 1 H), 3.24 (m, 1 H), 3.42 (m, 1 H), 5.46 (m, 2 H), 6.60–6.80 (m, 2 H), 7.10–7.45 (m, 8 H), 7.60–7.90 (m, 8 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ –4.52, –4.28, 18.29, 25.95, 27.91, 28.06, 35.86, 35.92, 122.43, 122.92, 123.26, 123.31, 124.53, 126.32, 126.44, 126.55, 126.90, 127.00, 127.10, 128.03, 128.13, 128.50, 128.80, 129.37, 130.20, 130.25, 130.35, 130.46, 130.64, 132.54, 132.59, 133.05, 134.89, 134.97, 136.23, 136.31, 136.67, 136.79, 138.61, 138.73, 142.44, 142.83. MS (CI, NH$_3$): m/z 740 (M + 18, 75), 608 (M – t-Bu(CH$_3$)$_2$SiOH + 18, 100), 591 (M – t-Bu(CH$_3$)$_2$SiO, 90), 459 (M – [t-Bu(CH$_3$)$_2$SiO]$_2$H, 100).

Photocyclization of 21 to 22. Bis-stilbene **21** (150 mg, 0.21 mmol) and 120 mg of I$_2$ (0.47 mmol) in 450 mL of spectroscopic grade benzene was degassed with argon. Propylene oxide (4 mL) was added, and the solution was irradiated for 6 h. The residue left after the solvent had been evaporated was dissolved in benzene (20 mL), and *p*-toluenesulfonic acid (10 mg) was added. The solution was heated to ca. 70 °C for 10 min. After being cooled to room temperature, the reaction mixture was extracted with ether, washed with brine, dried, and evaporated, giving a yellow solid (62 mg, 65% yield). The ^{1}H NMR spectrum is displayed in the supplementary material and analyzed in text above.

Isolation of 24. The experiment was performed using bis-stilbene stereoisomeric with **11** in Scheme I. This was prepared in Schemes I and II from (–)-**19**, $[\alpha]_D$ –37.3°, which had been made by reducing **18** with LiAlH$_4$, (+)-*N*-methylephedrine, and 3,5-dimethylphenol. This bis-stilbene (0.34 g) was irradiated overnight (9 h) in benzene as in the preparation of **12**. It was done, however, in three 240-mL batches. The residue left when the solvent was stripped was chromatographed on a 6-in. × 3-cm column of silica. Elution with petroleum ether/CH$_2$Cl$_2$ (6:1 to 3:1) gave two main fractions. The second was the exo,exo helicene enantiomeric with **13**, $[\alpha]_{578}$ –2940°, obtained in 27% yield. The first was its endo,exo isomer **24**, $[\alpha]_{578}$ –75 ± 25°, obtained in 12% yield. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.10 (s, 3 H), 0.15 (s, 3 H), 0.16 (s, 3 H), 0.19 (s, 3 H), 0.28 (m, 2 H), 0.72–1.30 (m, 4 H), 0.93 (s, 9 H), 1.10 (s, 9 H), 1.63 (m, 1 H), 1.71 (m, 1 H), 4.58 (m, 1 H), 4.89 (m, 1 H), 6.99 and 7.17 (AB q, J = 8.1, 2.6 Hz, 4 H), 7.28–7.36 (dd, 2 H), 7.44 and 7.48 (AB q, J = 86.7 Hz, 2 H), 7.81–7.94 (m, 3 H), 8.31 (s, 1 H), 8.42 (d, J = 8.4 Hz, 1 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ –4.67, –4.39, –4.21, 18.21, 18.30, 25.95, 25.99, 29.59, 29.83, 35.95, 37.06, 75.29, 77.14, 77.21, 120.29, 120.78, 122.36, 123.86, 124.80, 125.51, 125.80, 125.90, 126.41, 126.49, 126.72, 126.79, 127.13, 128.00, 128.37, 128.48, 128.65, 128.98, 129.20, 129.60, 129.70, 131.16, 131.60, 131.87, 132.27, 132.53, 134.81, 135.94, 142.59, 144.82. HRMS (FAB): calcd 796.2767, found 796.2768.

Cobalt Dibromide 1,2-Dimethoxyethane. As Kölle did not provide experimental details,[30] we give our procedure. Care was taken to keep the flask and argon atmosphere dry. Bromine (14 mL, 0.27 mol) was added to dry cobalt powder (325 mesh, 16 g, 0.27 mol) in 250 mL of 1,2-dimethoxyethane, and the mixture was stirred and refluxed for several hours. The solvent was stripped, leaving a gummy blue solid, which was transferred inside a glovebox to a Soxhlet thimble. After extraction with 1,2-dimethoxyethane for two days, removal of solvent, transfer to an appropriate vessel, and pumping to dry it, the resulting blue solid was transferred within a glovebox to vials for storage. Anal. Calcd for C$_4$H$_{10}$CoBr$_2$O$_2$: C, 15.55; H, 3.25; Co, 19.08. Found: C, 15.87; H, 3.49; Co, 18.53. The procedure is a modification of one used first in our laboratory by Poindexter. His sample analyzed as follows: C, 15.79; H, 3.28; Co, 19.32.[32]

Synthesis of 25 by Combining Indene, CoBr$_2$·DME, and KHMDS in THF. As KHMDS in toluene (4.3 mL, 0.62 M, 2.7 mmol) was added in drops to a cold (0 °C) solution of CoBr$_2$·DME (400 mg, 1.29 mmol) and indene (0.30 mL, 2.57 mmol) in 25 mL of THF that had been purged with Ar, the blue solution changed to an opaque dark green and then to red-orange. The solution was stirred overnight (but the yield was identical when this time was 4 h), quenched with 2 mL of water, and oxidized with 390 mg of FeCl$_3$·6H$_2$O (1.44 mmol) in 20 mL of 0.2 M HCl. After the solution was stirred for 30 min, 630 mg of NH$_4$PF$_6$ (3.87 mmol) was

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(100) Rotational strength = 1.234 × $10^{-42}[\theta]_i^\circ\Delta_i^\circ/\lambda_i^\circ$, where $[\theta]_i^\circ$ is the elipticity and λ_i° the wavelength at the band maximum, and Δ_i° is the wavelength interval between λ_i° and the wavelength at which $[\theta]$ falls to $[\theta]_i^\circ/e$. See Moscowitz, A. In *Optical Rotatory Dispersion*; *Applications to Organic Chemistry*; Djerassi, C., Ed.; McGraw Hill: New York, 1960; Chapter 12.

(101) Friedrich, K.; Henning, H.-G. *Chem. Ber.* **1959**, *92*, 2756.

added, and then acetone was added until the solution was homogeneous. The organic solvents were evaporated, and a bronze precipitate was filtered and washed with water. It was washed from the filter with acetone, and the solvent was evaporated. The bronze residue was washed with ether and filtered until the filtrate was colorless. It was then washed from the filter with acetone, which was evaporated, giving 460 mg (an 82% yield) of **25**, a bronze solid. Similar experiments using lithium and sodium hexamethyldisilazides gave yields of 50 and 41%, respectively. When lithium tetramethylpiperidide was used as the base, the yield was 68%.

Helical Cobaltocenium Oligomer 9. *tert*-Butyllithium in pentane (0.68 mL, 1.73 M, 1.18 mmol) was added in drops to 253 mg of **14** (0.557 mmol) in 50 mL of toluene that had been purged with Ar and cooled to 0 °C. The yellow solution turned orange, and an orange precipitate formed. After being stirred for 30 min, the mixture was warmed to room temperature and stirred for 30 min more. A solution of $CoBr_2 \cdot DME$ (172 mg, 0.557 mmol) in 10 mL of THF that had been purged with Ar was added in drops by cannula. The precipitate disappeared, and the reaction mixture turned a dark brown color. After the mixture was stirred overnight, a dark precipitate and dark orange supernate formed. Water (1 mL) and $FeCl_3 \cdot 6H_2O$ (170 mg, 0.61 mmol) in 20 mL of 0.2 M HCl were added, and the mixture was agitated by ultrasound. The dark red precipitate was filtered through Celite and washed with water and ether. The material washed from the filter with DMF and acetone was treated with NH_4PF_6 (908 mg, 5.57 mmol) and diluted with water. The acetone was evaporated. Addition of more water precipitated the oligomer, which was filtered through Celite and washed with water. After the precipitate was washed from the filter with acetone and DMF, 908 mg of NH_4PF_6 was added. The acetone was evaporated, and the solution was diluted with water. This precipitated the oligomeric salt, a red solid, which was filtered through Celite, washed with water and ether, and washed from the filter with acetone. The solvent was concentrated to 50 mL and diluted with sufficient ether to precipitate the oligomer. This was filtered, washed with ether, and then dried at 160 °C and 0.05 Torr. The yield of **9**, a brick-red powder, was 280 mg (81%). ^{13}C NMR (75 MHz, acetone-d_6): δ 39.42, 73.80, 74.42, 80.08, 95.46, 96.54, 117.36, 120.52, 122.45, 124.07, 124.74, 125.34, 125.69, 127.35, 128.18, 129.06, 130.72, 131.12, 131.70, 131.94, 132.54, 133.06, 134.02. IR (KBr, cm^{-1}): 3658 w, 3117 w, 2954 w, 1917 w, 1607 m, 1429 w, 1383 m, 1351 w, 1302 w, 1245 w, 1206 w, 957 w, 851 s, 784 m, 680 m, 600 m, 559 s, 470 m. $[\alpha]_D$ 29 600° and $[\alpha]_{577}$ 32 300° (*c* 0.002 41, acetone). UV (CH_3CN) λ_{max} (log ϵ): 486 (4.79), 342 (5.00), 258 nm (5.48). CD (CH_3CN) λ_{max} ($\Delta\epsilon$, rotational strength): 485 (746, 4.18×10^{-37}), 386 (846, 4.1×10^{-37}), 263 (−1580, -5.85×10^{-37}), 209 nm (−623, -2.79×10^{-37}). Anal. Calcd for $H_2(C_{36}H_{20})_{6.7}(CoPF_6)_{5.7}$: C, 69.05; H, 3.27; Co, 8.00. Calcd for $H_2(C_{36}H_{20})_{6.0}(CoPF_6)_{5.0} \cdot 1.5H_2O$: C, 68.93; H, 3.35; Co, 7.83. Found: C, 68.99; H, 3.83; Co, 7.90. The mass spectrum of this sample is displayed in Figure 3.

The DMF used for the extractions in this preparation is not required. Pure acetone works as well and was used for all the other samples.

Helical Cobaltocenium Oligomer 9, Table II, Entry 5. ^1H NMR (300 MHz, acetone-d_6): δ 2.4–3.6 (complex br m), 3.6–5.2 (complex br m), 5.4–9.0 (complex br m). ^{13}C NMR (75 MHz, acetone-d_6): δ 39.45, 73.85, 74.37, 80.08, 95.40, 96.59, 117.07, 117.48, 120.55, 122.43, 123.91, 124.07, 124.54, 124.75, 127.34, 127.79, 128.06, 128.74, 129.08, 130.20, 131.14, 132.54, 133.06, 133.63, 134.00, 134.56. IR (KBr, cm^{-1}): 3117 w, 3050 w, 2955 w, 1608 m, 1430 w, 1385 m, 1302 w, 1262 w, 1245 w, 1150 w, 1081 w, 841 s (PF_6^-), 784 w, 680 w, 600 w, 558 m (PF_6^-). MS (FAB, *m*-nitrobenzyl alcohol, "Ar" = $C_{36}H_{20}$): *m/z* 512 (HArCo, 50), 570 (CoArCo, 40), 965 (HArCoArH, 4), 1023 (CoArCoArH, 3), 1081 (CoArCoArCo, 1), 1477 (HArCoArCoArH + 1, 0.8), 1535 (CoArCoArCoArH + 1, 0.5), 1593 (CoArCoArCoArCo + 1, 0.2), 1622 (HArCoArCoArH + PF_6 + 1, 0.1), 1990 (HArCoArCoArCoArH + 3, 0.2), 2048 (CoArCoArCoArCoArH + 3, 0.2), 2107 (CoArCoArCoArCoArCo + 4, 0.05), 2136 (HArCoArCoArCoArH + PF_6 + 4, 0.05), 2192 (CoArCoArCoArCoArH + PF_6 + 1, 0.05). No higher oligomers could be detected. $[\alpha]_D$ 33 900° and $[\alpha]_{577}$ 36 700° (*c* 0.001 52, acetone). UV (CH_3CN) λ_{max} (log ϵ): 487 (4.84), 337 (sh, 5.03), 257 nm (5.39). CD (CH_3CN) λ_{max} ($\Delta\epsilon$): 482 (594), 383 (685), 262 (−1297), 208 nm (467). Anal. Calcd for $H_2(C_{36}H_{20})_{7.2}(CoPF_6)_{6.2}$: C, 68.80; H, 3.25; Co, 8.08. Calcd for $H_2(C_{36}H_{20})_{4.5}(CoPF_6)_{3.5} \cdot 4.8H_2O$: C, 68.55; H, 3.61; Co, 7.27. Found: C, 68.53; H, 3.65; Co, 7.27.

Helical Cobaltocenium Oligomer 9, Table II, Entry 1. The ^{13}C NMR spectrum is displayed in ref 8.

Helical Cobaltocenium Oligomer 9, Table II, Entry 2. UV (CH_3CN) λ_{max} (log ϵ): 477 (4.51), 319 (4.74), 255 nm (5.13). Anal. Calcd for $H_2(C_{36}H_{20})_{2.6}(CoPF_6)_{1.6}$: C, 74.82; H, 3.62; Co, 6.23. Calcd for $H_2(C_{36}H_{20})_{2.5}(CoPF_6)_{1.5} \cdot 0.4H_2O$: C, 74.73; H, 3.68; Co, 6.11. Found: C, 74.76; H, 3.91; Co, 6.05.

Helical Cobaltocenium Oligomer 9, Table II, Entry 3. Anal. Calcd for $H_2(C_{36}H_{20})_{4.9}(CoPF_6)_{3.9}$: C, 70.30; H, 3.34; Co, 7.62. Calcd for $H_2(C_{36}H_{20})_{4.0}(CoPF_6)_{3.0} \cdot 2.4H_2O$: C, 70.10; H, 3.55; Co, 7.17. Found: C, 70.14; H, 4.12; Co, 7.24.

Helical Cobaltocenium Oligomer 9, Table II, Entry 4. Anal. Calcd for $H_2(C_{36}H_{20})_{4.9}(CoPF_6)_{3.9}$: C, 70.30; H, 3.34; Co, 7.62. Calcd for $H_2(C_{36}H_{20})_{4.6}(CoPF_6)_{3.6} \cdot 0.8H_2O$: C, 70.23; H, 3.40; Co, 7.49. Found: C, 70.26; H, 3.74; Co, 7.56.

(*P*)-(+)-11-(Trimethylsilyl)[9]helical Bis-indene 26. *n*-Butyllithium (1.36 mL, 2.59 M, 3.51 mmol) was added in drops to a solution of **12** (701 mg, 0.88 mmol) in 100 mL of THF at −78 °C. The orange-brown solution was stirred at −78 °C for 30 min, and then TMSCl (5.57 mL, 43.92 mmol) was added in drops. After the solution was stirred at room temperature for 3 h, water and ether were added. The ether solution, after being washed, dried ($MgSO_4$), and stripped, left a yellow oil, which after repeated flash chromatography on silica gel, with petroleum ether/CH_2Cl_2 (7:1 to 4:1) as the eluant, yielded 400 mg (0.53 mmol, 61%) of *exo,exo*-3,18-di((*tert*-butyldimethylsilyl)oxy)-11-(trimethylsilyl)[9]helicene, a yellow solid (TLC: R_f = 0.17, 4/1 petroleum ether/CH_2Cl_2). ^1H NMR (200 MHz, $CDCl_3$): δ 0.06 (s, 6 H), 0.16 (s, 6 H), 0.22 (m, 2 H), 0.63 (s, 3 H), 0.84 (t, 2 H), 0.90 (s, 18 H), 1.10 (m, 2 H), 1.69 (m, 2 H), 4.89 (m, 2 H), 6.99 and 7.17 (AB q, *J* = 8.1, 3.0 Hz, 4 H), 7.26 (m, 2 H), 7.43 and 7.45 (m, 2 H), 7.81 and 7.98 (AB q, *J* = 8.1 Hz, 3 H), 8.17 (s, 1 H), 8.22 (d, *J* = 8.4 Hz, 1 H).

After 320 mg (0.43 mmol) of the above solid had refluxed for 30 min in 100 mL of benzene with 16 mg (0.09 mmol) of *p*-toluenesulfonic acid, pouring the mixture into saturated aqueous Na_2CO_3 solution, extraction, drying ($MgSO_4$), filtration, and evaporation gave a yellow solid. Chromatography on basic Al_2O_3, with benzene as the eluant, yielded 200 mg (0.38 mmol, 89%) of mixed isomers **26**, a yellow solid (TLC: R_f = 0.95, benzene). ^1H NMR (300 MHz, $CDCl_3$): δ 0.66 (s, 9 H), 0.79–1.30 (m, 1 H), 1.91 (d, *J* = 23.6 Hz, 1 H), 2.93 (m, 2 H), 5.42 (m, 1 H), 5.68 (m, 1 H), 5.82 (m, 1 H), 6.42 (m, 1 H), 7.02–7.3 (m, 9.5 H), 7.65 (m, 2 H), 7.90 (m, 1.5 H), 8.18 (m, 2 H).

Helical Cobaltocenium Oligomer 27. The procedure was the same as that used to synthesize **9**, but the following quantities of reagents were used: 200 mg (0.38 mmol) of (*P*)-(+)-11-(trimethylsilyl)[9]helical bis-indene **26**, 0.34 mL (0.80 mmol) of a 2.36 M solution of *tert*-BuLi/pentane, 117 mg (0.38 mmol) of $CoBr_2 \cdot DME$,[30] 100 mL of toluene, 20 mL of THF, 113 mg (0.42 mmol) of $FeCl_3 \cdot 6H_2O$ in 20 mL of 0.2 M HCl, and 625 mg (3.83 mmol) of NH_4PF_6. Yield: 205 mg (0.29 mmol, 77% yield) of **27**, a red solid. ^1H NMR (300 MHz, acetone-d_6): δ 0.47 (s), 0.51 (s), 0.55 (s), 0.58 (s), 0.60 (s), 2.5–3.0 (complex br m), 3.7–5.3 (complex br m), 5.4–8.4 (complex br m). ^{13}C NMR (75 MHz, acetone-d_6): δ 0.12, 73.25, 73.69, 74.15, 75.20, 94.62, 96.51, 96.80, 117.45, 118.18, 123.21, 124.17, 124.48, 126.48, 127.05, 127.56, 128.68, 130.83, 132.17, 132.48, 133.28, 133.96, 134.38, 135.19, 135.75, 138.69. IR (KBr, cm^{-1}): 3120 w, 2954 w, 1606 w, 1254 w, 1205 w, 1089 w, 924 w, 838 s, 758 w, 690 w, 630 w, 602 w, 557 m, 471 w. MS (FAB, *m*-nitrobenzyl alcohol, "Ar" = $C_{39}H_{28}Si$): *m/z* 1108 (ArCoAr, 83), 1693 (ArCoArCoAr + 1, 60), 1751 (CoArCoArCoAr + 1, 20), 1838 (ArCoArCoAr + PF_6 + 1, 20), 1897 (CoArCoArCoAr + PF_6 + 1, 10), 2276 (ArCoArCoArCoAr, 18), 2422 (ArCoArCoArCoAr + PF_6, 10), 2568 (ArCoArCoArCoAr + $2PF_6$, 7), 2861 (HArCoArCoArCoArCoArH, 3), 3006 (HArCoArCoArCoArCoArH + PF_6, 3), 3152 (HArCoArCoArCoArCoArH + $2PF_6$, 3), 3297 (HArCoArCoArCoArCoArH + $3PF_6$, 2), 3443 (ArCoArCoArCoArCoArCoAr, 1), 3588 (ArCoArCoArCoArCoArCoAr + PF_6, 0.5), 3736 (HArCoArCoArCoArCoArCoArH + $2PF_6$, 1.1), 3880 (HArCoArCoArCoArCoArCoArH + $3PF_6$, 1), 4027 (ArCoArCoArCoArCoArCoArCoAr, 1). $[\alpha]_D$ 33 400° and $[\alpha]_{577}$ 35 900° (*c* 0.0018, acetone). UV (2.98×10^{-7} M, CH_3CN) λ_{max} (log ϵ): 491 (5.16), 340 (sh, 5.37), 266 nm (5.94). CD (2.98×10^{-7} M, CH_3CN) λ_{max} ($\Delta\epsilon$): 480 (1039), 386 (1376), 264 (−2342), 210 nm (−764). Anal. Calcd for $H_2(C_{39}H_{28}Si)_{6.6}(CoPF_6)_{5.6}$: C, 67.12; H, 4.09; Co, 7.16. Calcd for $H_2(C_{39}H_{28}Si)_{6.3}(CoPF_6)_{5.3} \cdot 0.5H_2O$: C, 67.11; H, 4.11; Co, 7.10. Found: C, 67.11; H, 4.00; Co, 7.10.

Electrochemistry. Solvents were purified, as previously described, by distilling them in a vacuum from drying agents.[65] The supporting electrolyte (0.1 M) was *n*-Bu_4NPF_6, recrystallized from ethanol and vacuum-dried. Although all potentials are referred to the ferrocene/ferrocenium couple, the internal standard used in each experiment was either an aqueous SCE or a Ag/AgCl electrode, against which the ferrocene couple was measured. The values reported in this paper may be referred back to the SCE by adding +0.40 (CH_3CN) or +0.45 V (DMF). Voltammetry and coulometry experiments were performed in a drybox under nitrogen at ambient temperatures with commercial instruments as described previously.[65] A small cell (5–10 mL) was used to reduce the amount of oligomer required. Concentrations of electroactive cationic compounds, limited by their solubilities, were generally below 3×10^{-4} M.

Coulometry. Because the samples were diluted, some effort was required to minimize background corrections. The electrolyte was exhaustively preelectrolyzed at −1.5 V before the test compound was added. Model systems with similar redox potentials were investigated until we were confident that an accuracy of better than 5% relative error could be achieved. One systematic error of concern, since the redox potentials of **9** and **27** are close to those of oxygen, was the regeneration of the cations by reaction of the reduced complexes with oxygen. The one-electron reduction of Cp_2Co^+ and $(indenyl)_2Co^+$ gave $n = 1.02$ and 0.95, respectively, under our conditions. Oligomer sample sizes of 2–5 mg were employed. In a typical experiment, 10 mL of $CH_3CN/n\text{-}Bu_4NPF_6$ was preelectrolyzed at a Pt gauze cylinder at $E_{appl} = -1.6$ V until the current had fallen to 1.7% of the initial value. Oligomer **9** (5.2 mg, entry 2, Table II) was introduced, and the electrolysis was reinitiated. After 33 min, when the current had fallen to 2.7% of its initial value, 0.50 coulombs had passed. A correction of 0.06 coulombs was applied for background, and eq 2 then showed that $x = 1.1$. During the electrolysis, the solution turned from deep red to light yellow-brown and the electrode turned black. Reoxidation at −0.8 V returned both the solution and the electrode to their original appearances.

Quartz Crystal Microbalance. These experiments were conducted under nitrogen employing bench-top Schlenk techniques at gold electrodes. Sample sizes of about 2 mg were used. The basic procedures are those reported earlier.[102]

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Supplementary Material Available: NMR spectra of materials synthesized and the mass spectrum of **27** (27 pages). Ordering information is given on any current masthead page.

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[102] Ward, M. D. *J. Electroanal. Chem.* **1989**, *273*, 79.