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Synthesis and Properties of an Optically Active Helical Bis-cobaltocenium Ion

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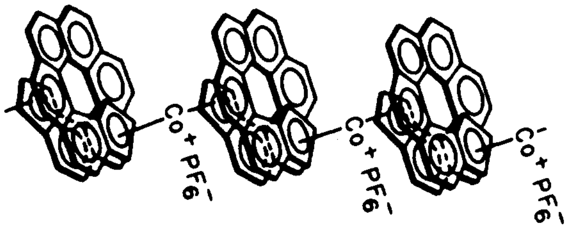
Abstract: The optically active helical bis-cobaltocenium salt **6** is synthesized, as are two related monocobaltocenium salts, **29** and **30**. The structure of **6** is analyzed by X-ray diffraction, which shows that the metals are separated by 8.49 Å. Reducing **6** either electrochemically or with K(Hg) produces species that absorb near 920 nm, but the absorption is not an intervalence transition. It originates instead from isolated Co(II) centers. This is demonstrated by the reduction product of **29**, which has only one cobalt, also absorbing at a similar wavelength (λ_{max} = 957 nm). The optical and ESR spectra imply that the unpaired electron in monoreduced **6** is largely localized on cobalt and that direduced **6** is essentially a Co(II)Co(II) diradical. The difference between two Co(III)/Co(II) reduction potentials of **6**, 130 mV, is shown to be appropriate for a conjugated dimetallocene with metals so distant. Crystal data for **6**: $M = 1275.02$; orthorhombic, space group $P2_12_12_1$; $Z = 4$; $a = 11.560(4)$, $b = 12.244(3)$, and $c = 41.349(17)$ Å; $V = 5852.5$ Å^3; $R = 0.1137$ for 4653 reflections having $F_o \geq n\sigma(F_o)$ ($n = 7.5$).

Introduction



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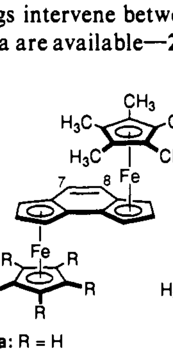
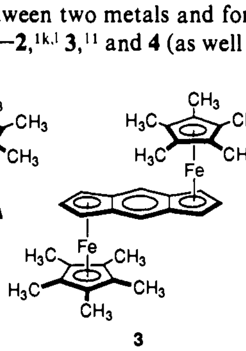
Bridges of unsaturated hydrocarbons are thought to provide paths for electrons to transfer between metals in different oxidation states.[1] In the case of the helical bridged cobaltocenium oligomers **1**, cyclic voltammetry and (after partial reduction) circular dichroic spectroscopy and near-IR spectroscopy suggest that the helicene is a weakly effective agent for such transmission.[2] However, because they could not be separated, the individual components of the oligomeric mixture could not be analyzed. We describe here a way to surmount this difficulty by synthesizing a dimer (**6**) in which two cobalts are connected by a helicene and capped by pentamethylcyclopentadienyl (Cp*) groups. We report the dimer's electrochemistry and the ESR and near-IR spectra of its reduction products. These imply that among the few structures in which a pair of cyclopentadienyls linked by benzene rings intervene between two metals and for which any relevant data are available—**2**,[1k,l] **3**,[11] and **4** (as well as some homologues of **4**),[1m,n]—the cobalts in **1** and **6** interact more weakly than those in **2b** and probably more weakly than those in **3**. The extent of the interaction seems to depend more on the distance between the metals than on the details of the linking group's structure.



2 a: R = H
b: R = CH$_3$
c: R = H, 7,8-dihydro



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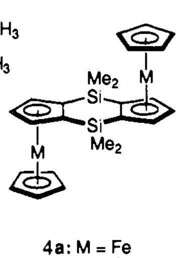

4a: M = Fe
b: M = Cr

The reduction products of **6** absorb maximally in the near-IR at 920 nm, but this absorption is shown not to arise from an

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(1) Bis(fulvalenyl)diiron and related molecules: (a) Morrison, W. H., Jr.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 2331. (b) 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. (c) Levanda, C.; Bechgaard, K.; Cowan, D. W. *J. Org. Chem.* **1976**, *41*, 2700. (d) Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 956. Ferrocene diynes: (e) Kramer, J. A.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 3330. (f) Motoyama, I.; Watanabe, M.; Sano, H. *Chem. Lett.* **1978**, 513. Temperature dependence: (g) Hendrickson, D. N.; Oh, S. M.; Dong, T.-Y.; Kambara, T.; Cohn, M. J.; Moore, M. F. *Comments Inorg. Chem.* **1985**, *4*, 329 and references therein. (h) Dong, T.-Y.; Hendrickson, D. N.; Iwai, K.; Cohn, M. J.; Geib, S. J.; Rheingold, A. L.; Sano, H.; Motoyama, I.; Nakashima, S. *J. Am. Chem. Soc.* **1985**, *107*, 7996. (i) Nakashima, S.; Katada, M.; Motoyama, I.; Sano, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2253. Biferrocenes: (j) Webb, R. J.; Geib, S. J.; Staley, D. L.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1990**, *112*, 5031 and references cited in its footnote 9. Indacene derivatives: (k) Iijima, S.; Motoyama, I.; Sano, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3180. (l) Reiff, W. M.; Manriquez, J. M.; Ward, M. D.; Miller, J. S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 423. Reiff, W. M.; Manriquez, J. M.; Miller, J. S. *Hyperfine Interact.* **1990**, *53*, 397. Metallocenes linked by two silyl groups: (m) Atzkern, H.; Hiermeier, J.; Köhler, F. H.; Steck, A. *J. Organomet. Chem.* **1991**, *408*, 281. (n) Atzkern, H.; Hiermeier, J.; Kanellakopulos, B.; Köhler, F. H.; Müller, G.; Steigelmann, O. *J. Chem. Soc., Chem. Commun.* **1991**, 997. Benzenecyclopentadienyliron cations: (o) Lacoste, M.; Desbois, M.-H.; Astruc, D. *Nouv. J. Chim.* **1987**, *11*, 561. (p) Lacoste, M.; Varret, F.; Toupet, L.; Astruc, D. *J. Am. Chem. Soc.* **1987**, *109*, 6504. (q) Bligh, R. Q.; Moulton, R.; Bard, A. J.; Piórko, A.; Sutherland, R. G. *Inorg. Chem.* **1989**, *28*, 2652. Review: (r) Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985**, *24*, 87.

(2) (a) Katz, T. J.; Sudhakar, A.; Teasley, M. F.; Gilbert, A. M.; Geiger, W. E.; Robben, M. P.; Wuensch, M.; Ward, M. D. *J. Am. Chem. Soc.* preceding paper in this issue. (b) Preliminary communication: Sudhakar, A.; Katz, T. J.; Yang, B.-W. *J. Am. Chem. Soc.* **1986**, *108*, 2790.

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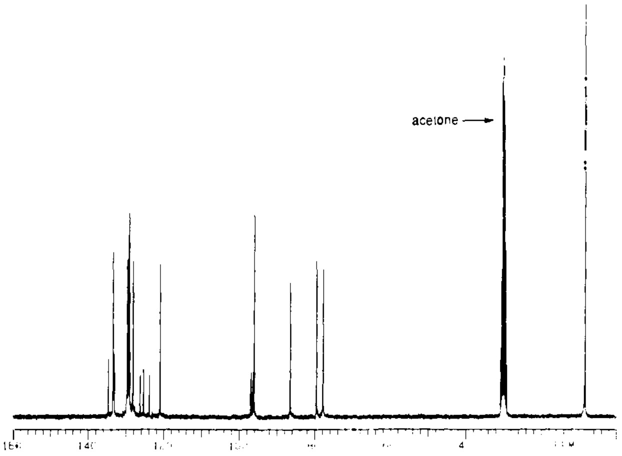


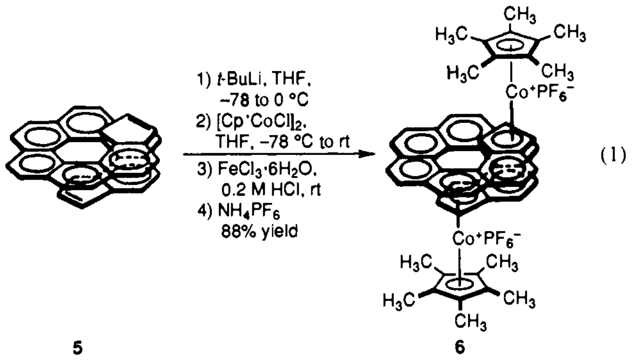
Figure 1. 75-MHz proton-noise decoupled ^{13}C NMR spectrum of 6 in CD_3COCD_3. The spectrum was measured using 90° pulses and no relaxation delay. It is displayed with 1.3-Hz line broadening. The chemical shifts are measured assuming that of CD_3COCD_3 to be 29.8 ppm.

intervalence transfer,[3] for similar absorption is also exhibited by the reduction products of the related helicene **29**, which has only one Cp*-capped cobalt attached to it.

In this article, we describe first the syntheses of **6** and **29** and then their electrochemistry (as well as that of other cobaltocenium ions whose cyclopentadienyls are fused to helicenes) and the ESR, visible, and near-IR spectra of their reduction products. The X-ray diffraction analysis of **6** identifies its absolute configuration, the distance between its metals, and the details of the helicene's shape.

Results

A. Syntheses. Synthesis of a Helicene Capped by Two Cp* Groups. The (*P*)-(+)-enantiomer of **6**, an orange crystalline solid, was synthesized from (*P*)-(+)-helical bis(indene) **5**[2] in 88% yield (eq 1). The procedure was previously optimized to give the simpler structure **7** from indene (the base in this case was *n*-butyllithium and the yield 58%), and it was learned that if the $[Cp^*CoCl]_2$[4] is not purified, substantial amounts of $Cp^*{}_2Co^+PF_6^-$ and bis(indenyl)$Co^+PF_6^-$ (**8**) form.



(1)

The ^{13}C NMR signals of **6** (Figure 1) between δ 100 and 76, like similar resonances in the helicene cobaltocenium oligomers **1**, as well as in **7** (see below) and **8**,[5] show that the cobalts are bonded to cyclopentadienyl rings (Table I). Notice, incidentally, that as in the case of **1**,[2] in **6** the helicene's cyclopentadienyl carbons are 2–3 ppm more shielded than those in **7**, an expected consequence of the ring currents of the superimposed benzenes.

Table I. Chemical Shifts of Cyclopentadienyl Carbons in 6, 1, 7, and 8[a]

	chemical shifts (δ)			
carbons[b]	6	1[c]	7	8[c]
1, 3	77.72, 79.42	74.37, 73.85	79.77	76.7
2	86.33	80.08	89.12	83.0
4, 5	96.73, 96.17	96.95, 95.40	99.39	98.3

[a] All in acetone-d_6. [b] See the numbering on structure **8**. [c] See ref 2. [c] Reference 3.

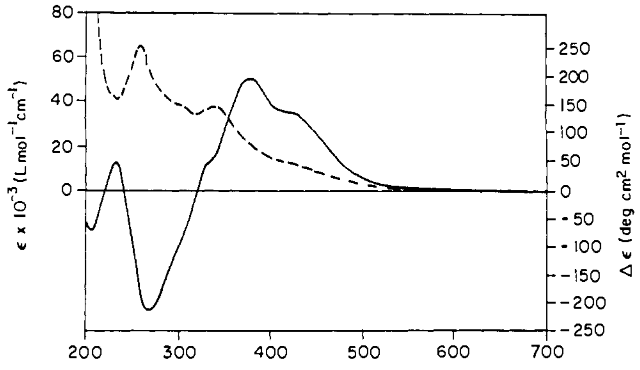
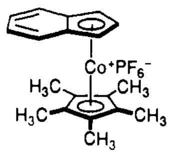
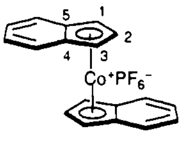
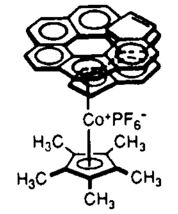


Figure 2. UV and CD spectra of (*P*)-(+)-6 in CH_3CN.







The UV and CD spectra of **6** (Figure 2) are also similar to those of **1**.[2] In the UV spectrum there are three strong absorptions at 419, 339, and 259 nm (log ε = 4.2–4.8), and in the CD spectrum there are two strong positive Cotton effects at 430 and 382 nm and one negative at 270 nm (Δε = ±140–215). Compared to those of **1**, the extinction coefficients and circular dichroisms for **6** are much smaller, and the long wavelength peaks in its UV and CD spectra are at shorter wavelengths. In **1** the CD at longest wavelength appears at ca. 483 nm, presumably because the conjugation is more extended. The specific rotation of **6**, $[\alpha]_D$ 8200°, is similar to that of **5** (7800°).[2] Unlike **1**, which failed to crystallize after a number of attempts, **6** crystallized when its solution in THF was evaporated at room temperature, and the structure of the crystals (Figure 3) was determined by X-ray diffraction analysis. Relevant features are summarized in Table II.

Syntheses of Helicenes Bonded to Only One Cobalt. To provide standards against which the properties of the helicene bonded to two Cp*Cos could be compared, two structures were synthesized that have helicenes bonded to only one cobalt atom. In the first attempt, helicene **5** was deprotonated with only 1 equiv of lithium diisopropylamide, reacted with $[Cp^*CoCl]_2$, oxidized with $FeCl_3{\cdot}6H_2O$ in aqueous HCl, and precipitated with NH_4PF_6. This, however, did not produce the monocapped helicene. Instead it gave **6** in 45% yield! The reason might be that the indenyl protons in the Co(II) derivative of **9** are more acidic than those in **5**.

To circumvent this problem we synthesized the [8]helicene **28** (see below), which when combined with $[Cp^*CoCl]_2$ can produce only a monocapped analogue of **6**. The synthesis was effected by photocyclizing **21** (see Scheme I), a transformation modeled

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[3] (a) Allen, G. C.; Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 357. (b) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (c) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247. (d) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (e) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 4393.

[4] Kölle, U.; Khouzami, F.; Fuss, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 131. Cp* = pentamethylcyclopentadienyl.

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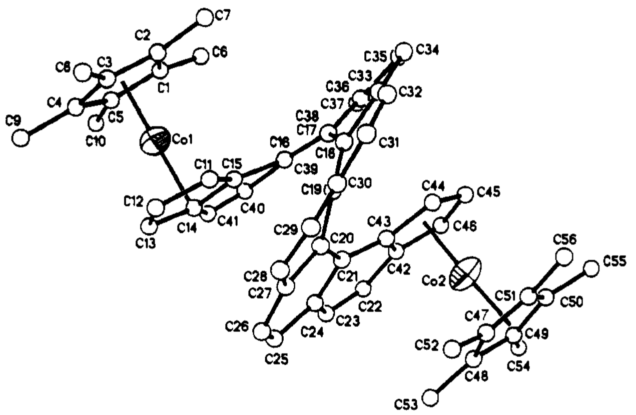


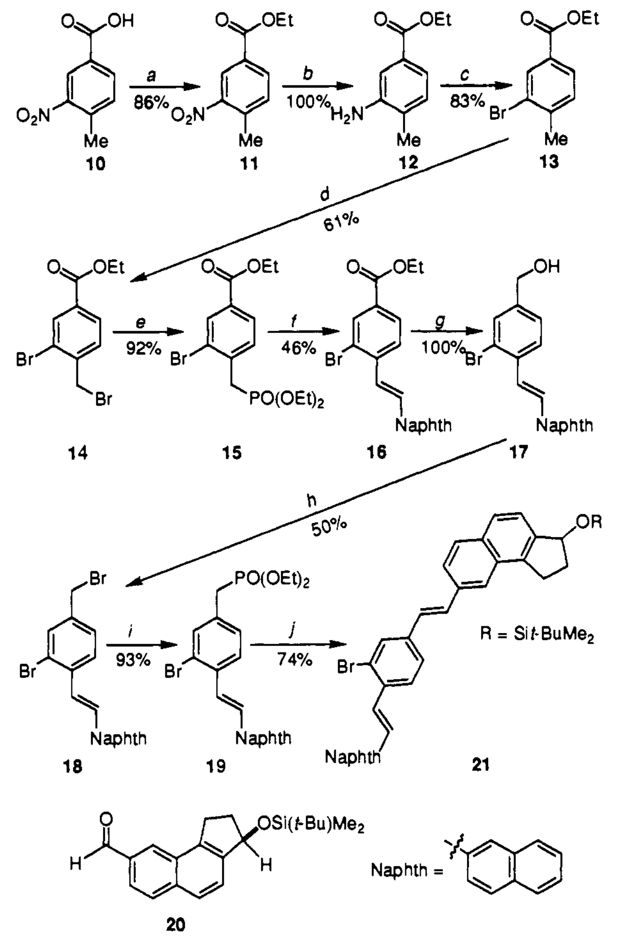
Figure 3. Structure of 6 as analyzed by X-ray diffraction.

Table II. Selected Bond Distances and Bond Angles for $[C_{56}H_{50}Co_2][PF_6]_2{\cdot}2THF$ (6)

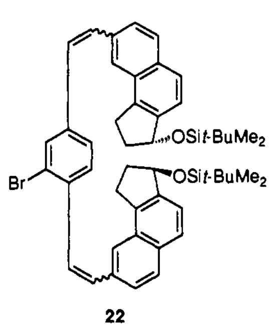
	Bond Distances (Å)		
Co(1)–CNT1[a]	1.643(15)	Co(1)–CNT2[b]	1.671(15)
Co(2)–CNT2[c]	1.668(15)	Co(1)–CNT4[d]	1.669(15)
C(16)–C(17)	1.397(20)	C(16)–C(39)	1.417(21)
C(17)–C(18)	1.496(23)	C(18)–C(19)	1.352(24)
C(18)–C(33)	1.472(24)	C(19)–C(20)	1.449(22)
C(19)–C(30)	1.493(25)	C(30)–C(31)	1.350(27)
C(31)–C(32)	1.196(29)	C(32)–C(33)	1.437(29)
C(33)–C(34)	1.410(30)	C(34)–C(35)	1.240(31)
C(35)–C(36)	1.508(27)	C(36)–C(37)	1.405(27)
C(37)–C(38)	1.241(25)	C(38)–C(39)	1.405(27)
C(39)–C(40)	1.440(23)	Co(1)–Co(2)[e]	8.49
	Bond Angles (deg)		
CNT1–Co(1)–CNT2	178.9(6)	CNT3–Co(2)–CNT4	177.6(6)
C(16)–C(17)–C(18)	123.8(13)	C(16)–C(17)–C(36)	116.0(14)
C(18)–C(17)–C(36)	120.1(14)	C(17)–C(16)–C(39)	119.6(12)
C(17)–C(18)–C(19)	125.8(15)	C(17)–C(18)–C(33)	113.9(14)
C(19)–C(18)–C(33)	120.2(16)	C(18)–C(19)–C(20)	125.9(15)
C(20)–C(19)–C(30)	119.7(14)	C(19)–C(30)–C(29)	110.7(17)
C(18)–C(19)–C(30)	114.3(15)	C(31)–C(32)–C(33)	127.7(21)
C(32)–C(33)–C(34)	128.2(18)	C(33)–C(34)–C(35)	124.7(21)
C(34)–C(35)–C(36)	122.4(20)	C(35)–C(36)–C(37)	124.0(16)
C(36)–C(37)–C(38)	123.5(17)	C(37)–C(38)–C(39)	119.6(12)

[a] CNT1 = centroid of atoms C(1) to C(5). [b] CNT2 = centroid of atoms C(11) to C(15). [c] CNT3 = centroid of atoms C(42) to C(46). [d] CNT4 = centroid of atoms C(47) to C(51). [e] Nonbonded Co–Co distance.

Scheme I [a]



[a] (a) EtOH, benzene, catalytic HCl, 80 °C, 48 h. (b) $SnCl_2{\cdot}2H_2O$, EtOH, 70 °C, 30 min. (c) $NaNO_2$, HBr, H_2O, −5 °C, 5 min; CuBr, HBr, H_2O, 70 °C, 1 h. (d) *N*-Bromosuccinimide, catalytic benzoyl peroxide, CCl_4, 82 °C, 10 h. (e) $P(OEt)_3$, 150 °C, 20 h. (f) NaH, THF, rt, 1.5 h; 2-naphthaldehyde, THF, rt, 18 h, 65 °C, 18 h; Girard's reagent T, 77 °C, 1 h. (g) $(i\text{-}Bu)_2AlH$, toluene 0 °C to rt, 1 h. (h) PBr_3, pyridine, benzene, 0 °C, 1.5 h. (i) $P(OEt)_3$, DME, 85 °C, 114 h. (j) NaH, DME, rt, 1 h; **20**, DME, 10 h.



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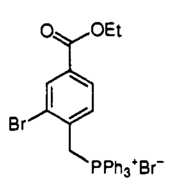

23

on the cyclization of **22** that ultimately leads to **1**.[2] The synthesis of **21**, in turn, was realized as shown in Scheme I. Commercially available 3-nitro-*p*-toluic acid (**10**) was converted to its ethyl ester **11**,[6] reduced to the amine **12**[7] by Bellamy's procedure,[8] diazotized, and converted to the known aryl bromide **13**.[9] Before the procedure in Scheme I was developed, **13** was brominated with *N*-bromosuccinimide to give **14**, which with PPh_3 in CH_3CN gave phosphonium salt **23** (pictured outside the scheme). LiOEt in ethanol, followed by 2-naphthaldehyde, produced the desired stilbene **16** as a cis–trans mixture,[10] but it was contaminated by 2-naphthaldehyde and **13**. The last was troublesome because **16**, 2-naphthaldehyde, and **13** could not be separated by flash chromatography. Among the other base/solvent combinations tried, diazabicyclo[4.3.0]non-5-ene/CH_3CN and NaH/THF (both at room temperature) also produced **13**, and potassium hexamethyldisilylazide/THF (at −78 °C to room temperature) returned starting materials. It was to circumvent this problem that phosphonate **15** was used in place of **23**. With NaH,[12] followed by 2-naphthaldehyde, this produced a mixture of *trans*-stilbene **16**[13] and 2-naphthaldehyde. No **13** formed. The aldehyde was removed by Girard's Reagent T,[14] leaving pure **16** in 46% yield. Stilbene **16** was reduced with $(i\text{-}Bu)_2AlH$,[15] and alcohol **17** was converted to **18** by PBr_3/pyridine.[16] Reaction with $P(OEt)_3$ in DME then gave phosphonate **19**, which was converted

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(6) Kermack, W. O. *J. Chem. Soc., Mem. Proc.* **1924**, *125*, 2285.

(7) Seka, R. *Chem. Ber.* **1925**, *58*, 1778.

(8) (a) Bellamy, F. D.; Ou, K. *Tetrahedron Lett.* **1984**, *25*, 839. (b) Bellamy, F. D.; Ou, K. *Tetrahedron Lett.* **1985**, *26*, 1362.

(9) Auwers, K. v.; Harres, L. *Z. Phys. Chem. (Leipzig)* **1929**, *143*, 1.

(10) Stilbene **16**, when synthesized from phosphonium salt **23**, shows two ethyl resonances in a 1/1.1 ratio, due to *cis*-**16** at δ 3.61 (m, 2 H) and 1.26 (t, 3 H) and *trans*-**16** at δ 4.38 (q, 2 H) and 1.39 (t, 3 H). The cis and trans isomers were identified by heating their mixture in benzene with a catalytic amount of I_2,[11] which enriches the trans isomer.

(11) Yamashita, S. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 487.

(12) Wadsworth, W. S., Jr.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 1733.

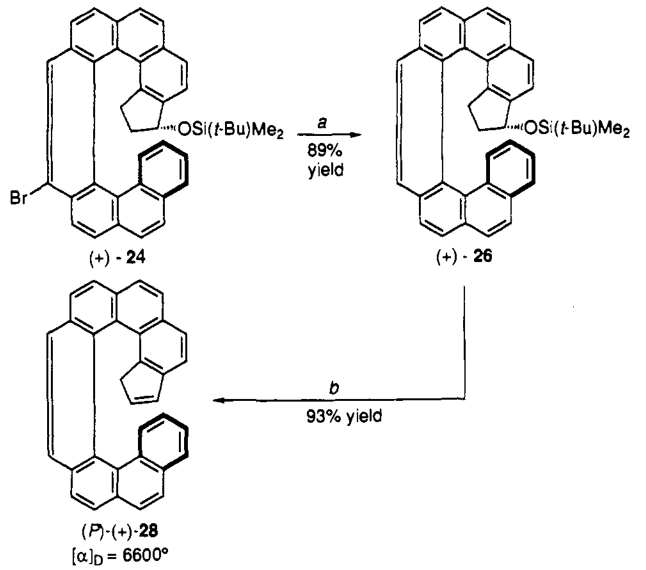
(13) Only ethyl group splittings at δ 4.38 (q, 2 H) and 1.39 (t, 3 H) are seen.

(14) Girard, A.; Sandurlesco, G. *Helv. Chim. Acta* **1936**, *19*, 1095.

(15) Yoon, N. M.; Gyoung, Y. S. *J. Org. Chem.* **1985**, *50*, 2443.

(16) Smith, L. H. *Org. Synth., Collect. Vol. III* **1955**, 793.

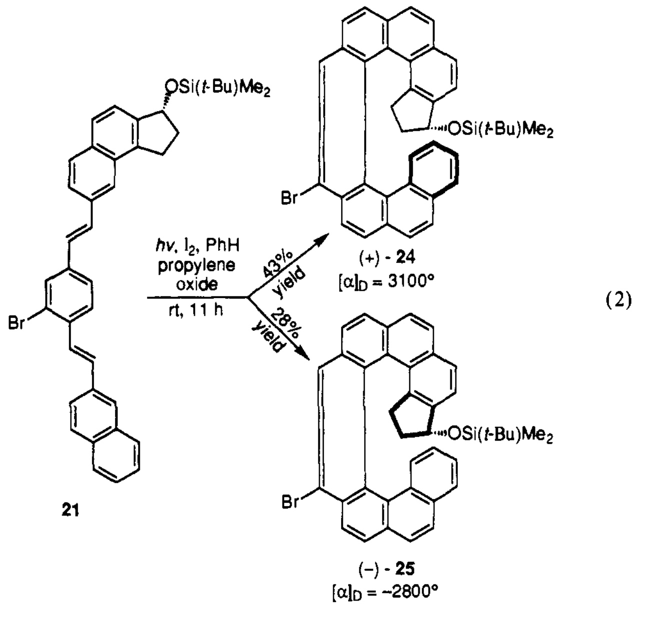
Scheme II [a]



[a] (a) n-BuLi, THF, −78 °C, 30 min; NH_4Cl, H_2O, −78 °C to rt. (b) p-TsOH·H_2O, benzene, 80 °C, 30 min.

to **21**[17] by combining it in DME with NaH[12] and then with aldehyde **20**.[2]

Photocyclizing **21** using a stoichiometric amount of I_2 and propylene oxide in benzene[18] produced two products, helicenes (*P*)-(+)-**24** ([α]D 3100°) and (*M*)-(−)-**25** ([α]D −2800°) in 43 and 28% yields, respectively (eq 2). Note that, in contrast, **22**

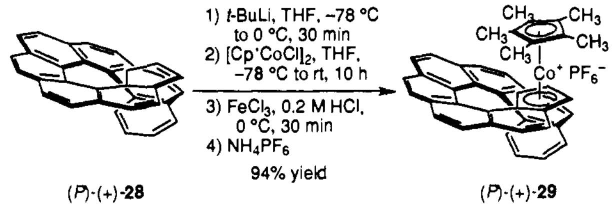


(2)

gives only one helical isomer.[2] Helicene (*P*)-(+)-**28** ([α]D 6600°) was obtained by removing the Br atom from (*P*)-(+)-**24** with n-BuLi, quenching with water, and eliminating the siloxy group with p-TsOH·H_2O in benzene (Scheme II). (*M*)-(−)-**28** ([α]D −6300°) was obtained similarly from (*M*)-(−)-**25**. The first step gave (−)-**27**, the analogue of (+)-**26**, in 76% yield, and the second gave (−)-**28** in 100% yield.

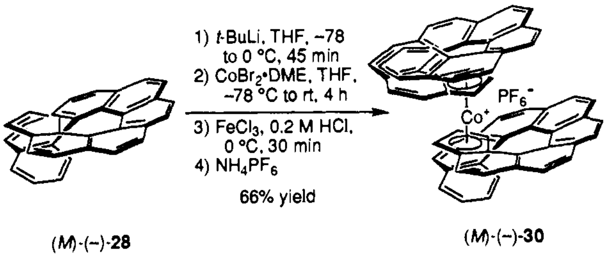
The UV spectra of (*P*)-(+)-**28** (displayed in the supplementary material) and (*M*)-(−)-**28** show four strong absorptions at 342, 315, 269, and 247 nm (log ε = 4.0–4.7). They are identical. The specific rotations differ essentially only in sign, [α]D +6600° and −6300°. The CD spectra of the enantiomers are mirror images of one another, that of (*P*)-(+)-**28** (also displayed in the supplementary material) showing Cotton effects at 372 (Δε = +173), 314 (−95), 276 (−215), and 242 nm (+118). [The figures measured for (*M*)-(−)-**28** are 370 (Δε = −160), 314 (+88), 276 (+203), and 242 nm (−108).] These spectra are essentially identical to the CD spectrum of [7]helicene,[19] which, together with the observation that all dextrorotatory carbohelicenes have the *P* configuration[20] and the X-ray structural analysis reported here for (*P*)-(+)-**6**, is the basis for the assignments of structures (*P*)-(+)-**24** and (*M*)-(−)-**25**.

The helicene capped by Cp*Co, (*P*)-(+)-**29**, was finally obtained when (*P*)-(+)-**28** was deprotonated with 1 equiv of t-BuLi, reacted with $[Cp^*CoCl]_2$, oxidized with $FeCl_3$/HCl, and precipitated with NH_4PF_6. The yield was 94% (eq 3). A similar procedure, in which $CoBr_2$·DME[21] was substituted for $[Cp^*CoCl]_2$,



(3)

produced the helical cobaltocenium dimer (*M*)-(−)-**30**. The yield was 66% (eq 4). The specific rotation of (*P*)-(+)-**29** is 4500°, while that of (*M*)-(−)-**30** is −13 600°, slightly more than twice the specific rotation of helicene (*M*)-(−)-**28**.



(4)

B. Electrochemistry. Electrochemistry of 6 and 29. The electrochemistry of these cobaltocenium salts was analyzed using acetonitrile solutions and a Pt electrode. At −1.46 V relative to the ferrocene/ferrocenium couple, the mononuclear complex **29** undergoes a diffusion-controlled, reversible reduction by one electron (confirmed by coulometry). A second reversible reduction occurs at −2.62 V, and a third, this time irreversible and consuming several electrons, at a cathodic peak potential, E_{pc}, of −3.1 V. The first two redox reactions are identified as Co(III)/Co(II) and Co(II)/Co(I) couples by the similarity of their $E°$ values to those of bis(cyclopentadienyl)cobalt(III).[22] The third is likely to be associated with reduction of the helicene's aromatic backbone. At E_{appl} = −2.0 V, a red-orange 0.5 mM solution of **29** consumes 1.1 F/mol and gives a green solution of the Co(II) complex, samples of which were withdrawn for ESR spectroscopic analysis (see below). Reelectrolysis at −1.0 V quantitatively regenerated **29**.

The dinuclear complex **6** displayed two closely spaced reduction waves in the vicinity of −1.5 V, as well as two at more negative potentials. The latter are both irreversible in CH_3CN (E_{pc} = −2.62 and −2.84 V), while in THF only the last is ($E°$ = −2.76 V and E_{pc} = −3.05 V, Figure 4). For the purpose of this paper, it is the former, poorly resolved pair that is significant. Its features were reproduced mathematically (Figure 5), assuming that the reductions are reversible, mass transport is diffusion-controlled,

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[17] Like other Wadsworth-Emmons reactions, this is presumed to give the trans double bond.[12]

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

[19] Martin, R. H.; Marchant, M. J. *Tetrahedron* **1974**, *30*, 343.

[20] (a) Laarhoven, W. H.; Prinsen, W. J. C. *Top. Curr. Chem.* **1984**, *125*, 63. (b) Bestmann, H. J.; Both, W. *Chem. Ber.* **1974**, *107*, 2923.

[21] Kölle, U.; Khouzami, F. *Chem. Ber.* **1981**, *114*, 2929.

[22] See Table III and leading references in (a) Geiger, W. E. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1985; p 156. (b) Strelets, V. V. *Coord. Chem. Rev.* **1992**, *114*, 1.

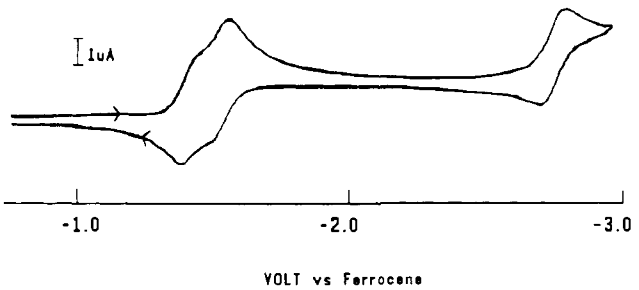


Figure 4. CV scan of 0.5 mM 6 in THF/0.1 M n-Bu_4NPF_6 at a Pt electrode, ambient temperature, $v = 0.10$ V s^{-1}.

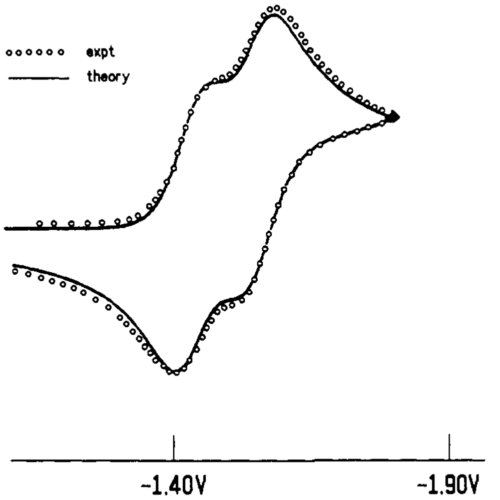


Figure 5. Comparison of the first two electrochemical waves for 6 according to theory (line) and experiment (circles). Theory: EE mechanism, $k_{s1} = k_{s2} = 0.8$ cm s^{-1}; $\alpha_1 = \alpha_2 = 0.5$; $E°_1 = -1.41$ V, $E°_2 = -1.54$ V. Experiment: 0.32 mM 6 in CH_3CN/0.1 M n-Bu_4NPF_6, Pt electrode, $v = 0.1$ V s^{-1}, ambient temperature.

and no chemical reaction intervenes between the two electron additions. The separation between the formal potentials ($E°_1 = -1.41$ V and $E°_2 = -1.54$ V) was found to be 130 mV, indicating that interaction between the two redox centers is weak but finite. If the metals were electronically isolated from one another, the value of $\Delta E°$ would have been 36 mV.[23] Another indication of interaction between the metals is the more positive value of $E°$ for **6** (-1.41 V) than for **29** (-1.46 V), a reflection of electron withdrawal by the second Cp*Co(III) group.

Bulk coulometry in CH_3CN (2.0 F/mol) at $E_{appl} = -2.0$ V (Pt basket, ambient temperature) transformed **6** into its two-electron reduction product **31**, whose solutions are deep green (eq 5). The

$$[Cp^*Co^+\ PF_6^-]_2C_{36}H_{20} \xrightarrow[\text{or K(Hg), THF, rt, 4h}]{\text{Electrolysis in } CH_3CN} [Cp^*Co^+]_2C_{36}H_{20} \quad (5)$$

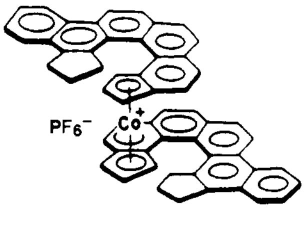
yield, measured by analyzing the solutions of reactant and product by voltammetry at a rotating platinum electrode, was >95%. Reelectrolysis quantitatively regenerated the starting material, showing that the first two reductions of **6** are nearly completely reversible. Solutions of **31** were also prepared (see below) by reducing **6** with K(Hg).

Table III. Electrochemical Potentials vs Ferrocene for Cobalt Complexes in CH_3CN/0.1 M n-Bu_4NPF_6

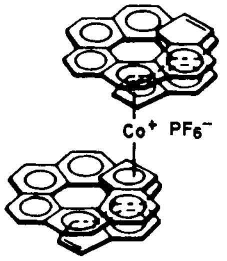
complex	number	$E°_1$[a]	$E°_2$	other waves (ir)[b]
$Cp^*_2Co^+_2(\mu$-[9]helicene)	6	-1.41	-1.54	-2.62,[c] -2.84[d]
Cp^*Co^+([8]helicene)	**29**	-1.46	-2.62	-3.1
Cp_2Co^+		-1.34	-2.28[f]	
bis(indenyl)Co^+	**8**	-0.92[e]	-2.1(ir)	
bis(benzo[6]helicene)Co^+	**32**	-0.98		
bis([8]helicene)Co^+	**30**	-1.10	-2.1(ir)	
bis([9]helicene)Co^+	**33**	-1.16		

[a] First reduction process: Co(III)/Co(II) couple for mononuclear complexes. [b] ir = chemically irreversible; peak potential reported at scan rate of 0.1 V s^{-1}. [c] Reversible in THF, $E° = -2.76$ V. [d] In THF $E_{pc} = -3.05$ V. [e] Reported previously in DMF as $E_{1/2} = -0.53$ V vs SCE, see Hsiung, H.-S.; Brown, G. H. *J. Electrochem. Soc.* **1963**, *110*, 1085. [f] Data from Geiger, W. E. *J. Am. Chem. Soc.* **1974**, *96*, 2632.

Electrochemistry of Other Helical Cobaltocenium Salts. We also briefly investigated the voltammetry at Pt of four additional monocobaltocenium salts in aqueous acetonitrile: the hexafluorophosphates of bis(indenyl)cobalt (**8**), bis(benzo[6]helicene)-cobaltocenium (**32**),[24] bis([8]helicene)cobaltocenium (**30**), and bis([9]helicene)cobaltocenium (**33**).[25] Each underwent a diffusion-controlled one-electron reduction in the expected potential range (Table III). For **8**, bulk coulometry at potentials more negative than its $E°$ (-0.92 V) confirmed that the number of electrons taken up was one per molecule (0.95 F/mol).



32



33

The reduction of the bis(benzo[6]helicene)-Co(III) complex **32** ($E° = -0.98$ V in DMF) was confirmed to be a reversible, one-electron process by the standard diagnostics of cyclic voltammetry, chronoamperometry, and rotating disc voltammetry. Its diffusion coefficient, 3.4×10^{-6} cm^2 s^{-1}, is lower than that of Cp_2Co^+ in the same medium, reflecting the larger size of the bis-helicene. Its electrochemistry at Pt, unlike that of Cp_2Co^+ and **8**, is not Nernstian. The separation of the cathodic and anodic peak potentials suggests that for **32** the Co(III)/Co(II) electron-transfer is quasireversible, with a standard heterogeneous rate constant k_s ca. 5×10^{-3} cm s^{-1}.[26] Bulk reduction consumed 1.0 F/mol and gave solutions that, like all the other Co(II) solutions studied except that from **8**, were dark green. Those from **8** were red-brown.

Complexes **30** and **33** displayed Co(III)/Co(II) couples with only limited chemical reversibility. The ratio i_a/i_c for **30** when the CV scan rate was 0.1 V s^{-1} was about 0.7, suggesting that the Co(II) species undergoes a chemical reaction.[27] Its nature, however, was not investigated.

We note in Table III that among the four mononuclear cobaltocenium salts in which each cyclopentadienyl ring is fused to an arene, namely **8**, **30**, **32**, and **33**, the $E°$ values become steadily more negative as the number of unsaturated rings increases. Thus, the larger the aromatic backbone, the more the Co(III) oxidation state is favored over that of the Co(II). It may be inferred that the larger helicenes mix less effectively with the e_1 pair of the Co.

C. Spectroscopic Properties of the Reduction Products of 6 and 29. Near-Infrared Spectra. Many di- and polynuclear mixed-valence compounds display broad absorptions in the near-IR which are taken as evidence of electronic interaction between the metals.[3]

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(23) (a) Ammar, F.; Savéant, J. M. *J. Electroanal. Chem.* **1973**, *47*, 215. (b) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

(24) Poindexter, M. K. Ph.D. Thesis, Columbia University, 1988. The sample had been prepared by Dr. Poindexter.

(25) A sample of cobaltocenium salt **33** that was not completely pure was synthesized in 33% yield by combining [9]helicene **5** and 1 equiv of LiTMP in THF at 0 °C, adding 1 equiv of $CoBr_2$·DME, oxidizing with $FeCl_3·6H_2O$/HCl, and precipitating with NH_4PF_6.

(26) Calculated from measurements of ΔE_p vs scan rate by the method of Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

(27) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

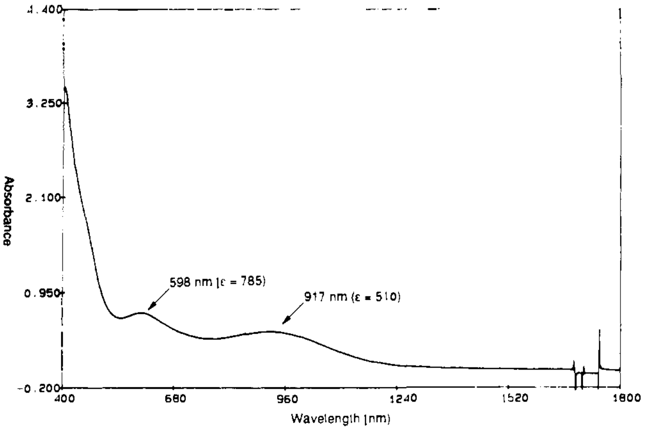

Figure 6. Visible–near-IR spectrum of **31**, formed by reducing **6** in THF with excess K(Hg).

Examples are the monocations of 1,1″-biferrocene (λ_{max} 1776–2000 nm, depending on the solvent, ϵ = 650–919),[3e] 1,1″-bicobaltocene (λ_{max} 1520–1700 nm, depending on the solvent, ϵ = 3100–4500),[28] bis(ferrocenyl)acetylene (1560 nm, in CH_2Cl_2, ϵ = 670),[1c] and bis(fulvalenyl)diiron (1,1″:1′,1‴-biferrocene, 1550 nm, in CH_3CN, essentially independent of solvent,[3e] ϵ = 2100).[1b] Accordingly, similar absorptions were sought in mixed-valence derivatives of **6**. Millimolar THF solutions were reduced at room temperature under argon with excess K(Hg) (eq 5). They gave dark green solutions that, like bis(indenyl)cobalt and unlike **6** (whose absorption maximum at longest wavelength is at 419 nm), absorbed in the visible at 598 nm (ϵ = 785). They also absorbed in the near-IR at 917 nm (ϵ = 510, Figure 6).[29–31] Removing the solvent in vacuo, extracting with hexanes and benzene, and evaporating gave a very air-sensitive green solid, presumed to be **31** because its visible spectrum showed the peaks at 598 nm described above and its mass spectrum showed the required parent peak. When this solid was combined at room temperature in THF with 1 equiv of **6**, the resulting green solution showed absorption maxima at 604 (ϵ = 413) and 913 nm (296). The spectrum appears to be an average of the spectra of **6** and **31**.

How the extent of reduction changes the absorption spectrum was studied by reducing **6** in a cell with an optically transparent thin-layer electrode (OTTLE). The spectra were analyzed from the near-visible to the near-IR, 400–2000 nm, while the number of coulombs passed through the cell was monitored. The solvent was CH_3CN, and the concentration was typically 1.5 mM. The major absorption maxima observed were at 600 and 920 nm, essentially the same as when **6** was reduced in THF by K(Hg). No band ascribable to an intervalence transition was seen between 1000 and 2000 nm, although we estimate that one with a molar absorptivity (extinction coefficient) above 350 cm^{-1} M^{-1} would have been detected.[32]

The possibility that the absorption at 920 nm is an intervalence transition [Co(III)Co(II) to Co(II)Co(III)] was eliminated by two observations. First, the absorption energy is essentially the same when the solvent is changed from THF to CH_3CN, in spite of the very different dielectric properties of the two solvents. In mixed-valent structures like the monocation of 1,1″-biferrocene, light excites an electron from one metal to another, and the wavelengths of maximum absorption in the near-IR vary significantly with the solvent.[3d,e,28] Although in other mixed-valent structures, those like the monocation of bis(fulvalenyl)-diiron that are fully delocalized in the ground states, there is no such dependence on solvent,[3e,28] it is unlikely that the monocation of **6** belongs among them, for **6** does not exhibit other characteristics of the delocalized species (like large separations between redox potentials, see the Discussion section below). The second observation implying that the absorption at 920 nm is not an intervalence transition is the steady increase in its intensity as electrons are added in the OTTLE cell to a total of two electrons per molecule. Figure 7 shows this for the 920- and 600-nm peaks if allowance is made for the unreliability with which the Cary 14 spectrometer measures absorbances below 0.02. The molar absorptivities measured for the 920- and 600-nm bands of **31** (the double reduction product of **6**) were 1500 and 2500 cm^{-1} M^{-1}.[31] If either of these were the intervalence transition of a mixed-valent product, its intensity would have peaked at 1 F/mol. We conclude that the near-IR band is a characteristic of *both* the one- and the two-electron reduction products, that is, that it arises from an optical transition associated with an *isolated Co(II) center*.

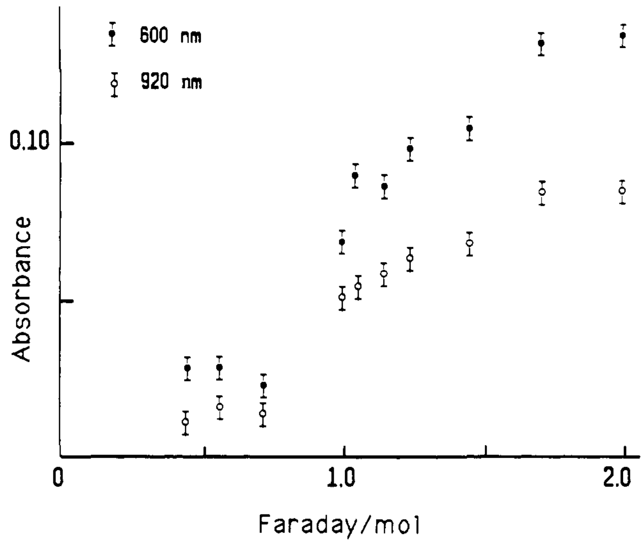

Figure 7. Absorbances at 600 and 920 nm as a function of number of Faraday/mol passed during electrolysis of ca. 1.5 mM **6** in an OTTLE cell. The bars indicate the estimated errors.

Proof is the observation that the reduction product of **29**, even though it cannot give a mixed-valent structure because it has only one cobalt, nevertheless shows the near-IR absorption. The spectrum observed after **29** had been electrolyzed under conditions identical to those used to reduce **6**, λ_{max} 598 (ϵ = 2100) and 957 nm (1400), was very similar to that described above for the reduction product of **6**.

Smart et al., who much earlier observed similar absorptions in bis(fulvalenyl)dicobalt (λ_{max} 980 nm, ϵ = 1150, solvent unspecified)[1d] and its monocation (λ_{max} 937 nm, ϵ = 7300, in CH_3CN),[33] as well as in related bis(fulvalenyl)dimetal derivatives,[34] attributed them at first to d–d transitions resulting from the interaction of metals forced to be close, and later, in part because the distance between the metals is too large, to a metal-ligand charge transfer.[33] In **6**, the separation of the metals by the hydrocarbon and the large distance between the metals excludes the former explanation. Accordingly, in the absence of a better understanding of cobaltocene's electronic spectrum,[35] we speculate that the absorption is indeed a metal-to-helicene charge-transfer band.

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(28) McManis, G. E.; Nielson, R. M.; Weaver, M. J. *Inorg. Chem.* **1988**, *27*, 1827.

(29) Fischer, E. O.; Seus, D. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1953**, *8*, 694.

(30) Bis(indenyl)cobalt does not absorb in the near-IR.

(31) Extinction coefficients in the near-IR spectra of **31**, produced by reducing 2–3-mg samples of **6** with K(Hg), were one-third as large as those measured in the spectroelectrochemical experiments (see below). The latter are likely to be more accurate.

(32) This figure is determined by the small length of the cell, the detection limits of the spectrometer, and the worsened response of the electrochemical cell when concentrations are small.

(33) Clark, S. F.; Watts, R. J.; Dubois, D. L.; Connolly, J. S.; Smart, J. C. *Coord. Chem. Rev.* **1985**, *64*, 273.

(34) Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 1009.

(35) Warren, K. D. In *Structure and Bonding*; Dunitz, J. D., Ed.; Springer-Verlag: Berlin, 1976; Vol. 27, pp 86–88. Cp_2Co has a broad absorption in the 500–650-nm region.[19]

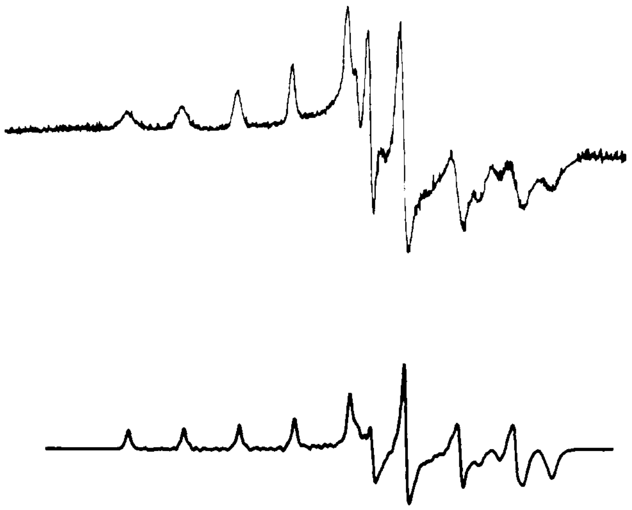

Figure 8. Experimental (top) and simulated (bottom) ESR spectra of monoreduced 6. The simulation is based on the parameters in Table IV. Experimental conditions: 1 mM CH_3CN solution of 6 after passage of 1 F/mol, $T = 77$ K.

ESR Spectra. Spectra were recorded of the reduction products of dinuclear **6** and mononuclear **29**. In summary, the results imply that the one-electron reduction product of **6** has a singly occupied MO that is *localized* on one Co(II) and that the two-electron reduction product of **6** at 77 K, the temperature of the analysis, is a *diradical*. The data follow.

The reduction of **6** at $E_{\text{appl}} = -2.0$ V was stopped when coulometry and rotating platinum electrode voltammetry showed that one electron had been added. A fluid sample removed to the ESR spectrometer showed no signal, but after the sample had been frozen to 77 K, it showed the spectrum in Figure 8. When electrolysis was allowed to proceed to the two-electron stage, the samples showed the same spectrum, but with greater intensity. Unfortunately, our facilities did not allow us to determine whether the more highly reduced samples had more spins. However, coulometry and rotating platinum electrode voltammetry imply that the solute present in the exhaustively reduced solution was the Co(II)Co(II) derivative **31**. No $g = 4$ transition, indicative of a triplet species, was observed. Accordingly, we assign diradical character to twice-reduced **6**, implying that magnetic coupling between the two d^7 centers is very weak.[36]

The ESR spectra of reduced **6** and reduced **29** are essentially superimposable. The parameters that simulate the spectra (Figure 8) show that the g-tensors have rhombic symmetry and that $g_1 = 2.09$, $g_2 = 2.02$, $g_3 = 1.89$, A_1(splitting by one Co, $I_{\text{Co}} = {}^7/_2$) $= 115 \times 10^{-4}$ cm^{-1}, $A_2(\text{Co}) > 10 \times 10^{-4}$ cm^{-1}, and $A_3(\text{Co}) = 35 \times 10^{-4}$ cm^{-1}. Because it is so small, the Co hyperfine splitting is uncertain for the g_2 component.

These values are compared in Table IV to those of other Co(II) π-complexes. Cobaltocene itself has a $^2E_{1g}$ ground state, owing to the orbital degeneracy of the d_{xz},d_{yz} pair,[37] which is split by Jahn–Teller distortion into two Kramers doublets. This distortion allows a spectrum to be observed that otherwise would not be because $g_\perp$ would equal 0.[38] The consequence is that the ESR parameters of cobaltocene, like those of other systems that are nearly orbitally degenerate, are markedly anisotropic and dramatically affected by the matrix. For cobaltocene in methyl-THF, the g tensor is axially symmetric, with both components less than the free-electron value (2.0023). The largest Co splitting (A_y) is 128×10^{-4} cm^{-1}. For the permethylated analogue Cp^*_2Co the data are similar: all g values under 2.0 and $A_y(\text{Co}) = 111 \times 10^{-4}$ cm^{-1}.

Table IV. ESR Data for Selected Cobalt(II) Complexes

complex	matrix	g values	A(Co) (10^{-4} cm^{-1})	ref
6, **29**^{a}	CH_3CN/ 77 °K	2.09	115	this work
		2.02	<10	
		1.89	35	
Cp_2Co	MeTHF	1.81		b
		1.69		
Cp^*_2Co	Cp^*_2Fe	1.75	65	c
		1.73	111	
		1.69	<6	
$(\text{indenyl})_2Co$	$(\text{indenyl})_2Fe$	2.082		b
		1.916		
$(C_5Ph_4H)_2Co$	$PhCH_3$/77 K	2.095	133	d
		1.999	33	
		1.884	82	
$CpCo(C_2Et_2B_2(CH_3)_2S)$		2.14	ca. 110^e	g
		2.04	f	
		1.98	f	
$(C_5H_4{-}C_5H_4)_2Co_2^+PF_6$	$DMF/CHCl_3$/ 77 K	2.21	72^h	i
		2.03		
		1.94		

^{a} Data for the $1e^-$ reduction product of each complex. ^{b} Ammeter, J. H. *J. Magn. Reson.* **1978**, *30*, 299. ^{c} Reference 40. ^{d} Reference 40. ^{e} Approximated from Figure 3 in the reference. ^{f} Too small to measure from the figure in the reference. ^{g} Reference 42. ^{h} 15 lines, due to splitting by two ($I = {}^7/_2$) Co. ^{i} Reference 1e.

Lowering the ligand field symmetry below D_5 increases the splitting of the d_{xz},d_{yz} pair, the relaxation times, and the g values. Thus for bis(tetraphenylcyclopentadienyl)cobalt, ($(C_5Ph_4H)_2Co$) $g_y = 2.095$ and $A_y(\text{Co}) = 133 \times 10^{-4}$ cm^{-1} (Table IV). These values and those for $CpCo[C_2Et_2B_2(CH_3)_2S]^-$ and for bis(fulvalenyl)dicobalt hexafluorophosphate (also listed in the table) are similar to the ones we observe for the reduction products of both **6** and **29**.

However, bis(fulvalenyl)dicobalt hexafluoroborate differs from the other molecules inasmuch as the unpaired electron is distributed over two cobalts. This is demonstrated by its lowest field resonance being split by both cobalts, each with spin $^7/_2$, into 15 lines.[1e] It is presumably because of this distribution that the resonance is split only half as much (72×10^{-4} cm^{-1}) as in the other molecules. Because the spectrum of the monocation of **6** does not show the reduced splitting, because it superimposes on that of the reduction product of **29**, and because it can be simulated if hyperfine splitting is by one cobalt, but not if by two, we conclude that the odd electron in the **6** monocation is not distributed between both cobalts but is localized on only one. That this localization is not a consequence of anisotropy in the solid matrix (an effect observed for some diiron cations[1g–j]) is suggested by the spectrum of the bis(fulvalenyl)dicobalt analogue, which when determined under similar conditions exhibits characteristics of delocalization.[1e]

The similarity of the resonance parameters for reduced **6** and **29** to those of other cobaltocenes suggests that in the former two, as in the others, the unpaired electron occupies an orbital in which cobalt's e_1 pair (d_{xz},d_{yz}) participates about 60–80%.[39,43]

Circular Dichroism Spectra. Since electron mobility in a mixed-valence species is likely to be high, experiments were tried to see whether partially reducing **6** would increase its circular dichroism. In one experiment, a THF solution of **6** was reduced in a CD cell with a slight excess of cobaltocene (2.1 mol), and the CD was observed as air bled through a septum,[44] reoxidizing the reduced

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(36) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88.

(37) Reference 35, pp 46–51. See also Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, F.; Stone, F. G. A., Eds.; Pergamon: Oxford, 1982; Vol. 3, p 28 for MO diagram.

(38) Reference 35, p 118.

(39) Ammeter, J. H. *J. Magn. Reson.* **1972**, *30*, 299.

(40) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882.

(41) Castellani, M. P.; Geib, S. J.; Rheingold, A. L.; Trogler, W. C. *Organometallics* **1987**, *6*, 1703.

(42) Siebert, W.; El-Essawi, M. E.-D. M.; Full, R.; Heck, J. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1985**, *40*, 458.

(43) Ammeter, J. H.; Swalen, J. D. *J. Chem. Phys.* **1972**, *57*, 678.

(44) Oxygen is known to oxidize cobaltocene to cobaltocenium cations. Kojima, H.; Takahashi, S.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1973**, 230.

Table V. Carbon–Carbon–Carbon Dihedral Angles in the Interior of Helicenes

helicene	angles, deg[a]	ref
[6]helicene	11.2, 15.2, 15.2, 11.2	*b*
[7]helicene[b]	16.8, 26.1, 23.4, 26.0, 21.9	*c*
34	4.8, 20.2, 40.8, 20.2, 4.8	*d*
35	15.8, 19.1, 27.8, 17.1, 15.1	*e*
6	1.8, 27.8, 26.1, 19.5, 28.4, 22.1, 11.9	this work
[10]helicene	21.3, 23.9, 24.4, 26.8, 25.1, 26.5, 24.0, 17.8	*f*
[11]helicene	13.9, 26.0, 21.9, 25.0, 28.8, 25.6, 23.9, 24.3, 18.3	*g*

[a] Angles are listed consecutively starting from one end of each molecule. [b] Reference 45a. [c] Reference 45b. [d] Reference 45c. [e] Reference 45d. [f] Reference 45e. [g] Reference 45f.

compound. Although this technique regenerates **1** from its reduced form,[2a] it destroys **6**. Circular dichroism was largely lost. In other experiments, a THF solution of **31**, prepared by reducing **6** with K(Hg), was briefly exposed in THF solution to air. All that was observed was the replacement of the CD spectrum of **31**, one positive Cotton effect at 386 nm ($\Delta\epsilon = 250$) and one negative Cotton effect at 273 nm (–210), by the CD spectrum of **6**, two positive Cotton effects at 482 ($\Delta\epsilon = 140$) and 382 nm (200) and one negative Cotton effect at 270 nm (–210). No intermediate could be detected.

Discussion

X-ray Analysis. The dihedral angles between the carbon atoms along the interior of the helix are similar to those in other helicenes (Table V).[45] They show that much of the strain in splaying the helix is absorbed by the middle of the molecule. The angles between the Cp* centroids, the cobalts, and the centroids of the helix's cyclopentadienyl ring are 178.9 and 177.6°, nearly linear, as in other cobaltocenium salts.[46] The Co–Co intramolecular distance is 8.49 Å, and the closest nonbonding C–C distance, which causes the helix to splay, is between C_{11} and C_{19} (Figure 3, 2.964 Å). This distance is very similar to the smallest C–C nonbonding distance in [6]helicene (3.03 Å)[45a] and in [7]helicene (2.90 Å).[45b] The closest nonbonding C–H distance was not measured, as the hydrogen atom coordinates were not refined. The dihedral angle between the terminal cyclopentadienyl rings, 10.2°, is typical of large helicenes.[45e,f] The structure confirms the conclusion, previously reached through other data,[2] that the dextrorotatory helicene **5** has (*P*)-helicity.

34

35 (M = Fe)

Interaction between the Metals. In structures comprised of two linked electroactive groups, the difference between the first and second reduction potentials measures the stability of the mixed-valent species relative to those that are fully reduced and fully oxidized.[47] The significance of the difference measured here for **6** (130 mV) is indicated in Table VI by comparisons with known conjugatively linked bis-metallocenes. The table shows the role distance between the metals plays in determining the potential difference. In the absence of theories explaining the parts played by bonding, we note that the value of $\Delta E°$ for **6** seems appropriate, or possibly slightly large, for a material with metals so far apart.

Table VI. Distance Between the Metals (*r*) and the Difference (ΔE) Between the First and Second Electrochemical Potentials of Dinuclear Metallocenes

structure	*r*, Å	ΔE, mV (solvent, electrolyte)[a]
36a	3.98[b]	1011 (M, TBAC)[b]
36b		890 (M, TBAC)[c]
36c		830 (M, TBAC)[b]
37b	3.91[c]	930 (A, TBAH),[d,e] 880 (A, ?)[f]
37a	3.98[g]	590 (A, TEAC),[h] 590 (M,TBAF)[i]
2a	ca. 5.1[j]	410 (A, TBAC)[k]
2c		360 (A, ?)[l]
38a		395 (A, TBAH),[d] 350 (A, ?)[f]
38b		400 (D, TBAF),[m] 430 (P, TBAH)[n]
38c	4.68[o]	350 (M,TBAF),[i] 349 (A, TEAC)[p]
		330 (A, TEAC),[h] 315 (A, TBAF)[q]
38d		375 (P, TBAH)[n]
38e		385 (P, TBAH)[n]
39a	ca. 6.5[r]	355 (M,TBAF)[i] 340 (M, TBAC)[s]
40	6.59[t]	208 (M, TBAC)[u]
4b	5.831[v]	215 (P, TBAH)[v]
4a		210 (P, TBAH)[w]
39b		130 (M,TBAF),[i] 0 (M, TBAC)[s]
6	8.49	130 (A, TBAH)
1		120 (D, TBAH)[x]
41a	ca. 8.3[y]	113 (M, TBAC)[z]
41b		0 (M, TBAC)[aa]
41c		210 (M, TBAC)[aa]
42a		60 (M, TBAC)[aa]
42b		0 (M, TBAC)[aa]
42c	8.24[aa]	0 (M, TBAC)[aa]
41d		70 (M, TBAC)[z]

[a] A = CH_3CN, D = DMF, M = CH_2Cl_2, P = C_2H_5CN, TBAC = Bu_4NClO_4, TEAC = Et_4NClO_4, TBAF = Bu_4NBF_4, TBAH = Bu_4NPF_6. [b] Reference 48. [c] Reference 49. [d] Reference 28. [e] Reference 50. [f] Reference 51. [g] Reference 52. [h] Reference 53. [i] Reference 1c. [j] Estimated from the structure of bis(*as*-indacene)diiron (ref 54) and that of 1,1″-biferrocenes (ref 55). [k] Reference 1k. [l] Reference 56. [m] Reference 57. [n] Reference 58. [o] Structure of 1,1′-dibenzylferrocene (ref 58). [p] Reference 59. [q] Reference 60. [r] Reference 1f. [s] Reference 61. [t] Reference 62. [u] Reference 63. [v] Reference 1n. [w] Reference 1m. [x] Reference 2a. [y] Estimated from the structure of a 1,1″-biferrocene (ref 55) and the lengths of bonds in benzenes and biphenyl (ref 64). [z] Reference 65. [aa] Reference 66.

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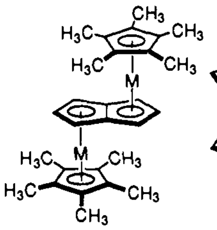
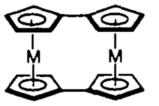
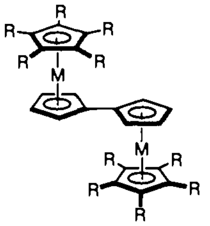
However, $\Delta E°$ seems too small for **6** to be among those dinuclear metallocenes (like **37a**[1a,b,67] and **39a**[1c,67]) whose mixed-valent derivatives are fully delocalized. As previously noted by others,[62] structures with $\Delta E°$ less than 350 mV do not have the characteristics of such delocalized molecules. Accordingly, it is reasonable that the two-electron reduction product of **6** has two unpaired electrons, just like decamethyl 1,1′-dicobaltocene (the reduction product of **38b**).[58] It is not diamagnetic like bis(fulvalenyl)dicobalt (the reduction product of **37b**).[1d] Note, incidentally, that the comparison has to be made with the decamethyl derivative, the reduction product of **38b**, not with the parent compound, the reduction product of **38a**, because the latter is unknown. Note also that electron transport is faster in the 1,1″-bicobaltocene monocation than in its iron analogue[28] and that the dication of 1,1″-biferrocene (**38c**$^{++}$) is also paramagnetic,[68] while that of bis(fulvalenyl)diiron (**37b**$^{++}$) is diamagnetic.[1b]



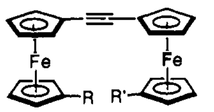
36 a: M = Fe
b: M = Co$^+$ PF$_6^-$
c: M = Ni



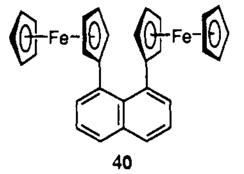
37 a: M = Fe
b: M = Co$^+$ PF$_6^-$



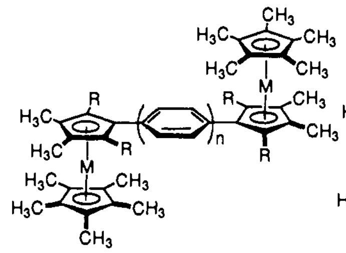
38 a: R = H, M = Co$^+$ PF$_6^-$
b: R = CH$_3$, M = Co$^+$ PF$_6^-$
c: R = H, M = Fe
d: R = CH$_3$, M = Fe
e: R = CH$_3$, M = Ni



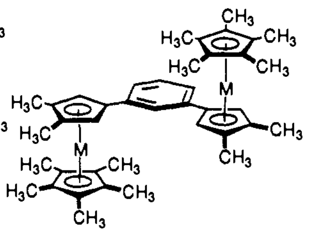
39 a: R, R′ = C≡C
b: R, R′ = H



40



41 a: n = 1, R = CH$_3$, M = Fe
b: n = 1, R = H, M = Co$^+$ BF$_4^-$
c: n = 1, R = H, M = Ni
d: n = 2, R = CH$_3$, M = Fe



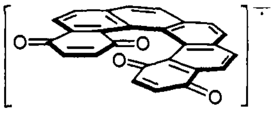
42 a: M = Fe
b: M = Co$^+$ BF$_4^-$
c: M = Ni

But in comparing the near-IR spectra of the monocation of **6** with those of **37b** and **38a**, one finds the analogy exactly reversed. The near-IR spectrum of the monocation derived from **6** does not show the absorptions displayed by the monocation of **38a** at wavelengths between 1520 and 1700 nm (depending on the solvent), which are attributed to the excitation of a valence trapped at one metal over to the other.[28] Instead, the spectrum (λ_{max} 913–920 nm) looks like those of the reduction products of **37b**, the monocation (λ_{max} 937 nm)[33] and the neutral molecule (λ_{max} 980 nm),[1d] species whose electrons appear to be highly delocalized, not trapped at one of the metal sites. While this suggests that the monocation of **6** might have its odd valence completely delocalized, as in **37b**, the alternative is that the valence is more firmly trapped than that in the monocation of **38a**.

That the valence is trapped at one of the metals is revealed by the ESR spectrum of the **6** monocation. Both the number and separation of the hyperfine lines show that the splitting is by only one cobalt. In the spectrum of the monocation of **37a**, in which the splitting is by two cobalts, the lines are almost twice as far apart.[1c]

It is possible that delocalization through curved ligands is inherently weak. This accords with the Mössbauer spectrum of the **2b** monocation displaying only one Fe doublet, even at 1.5 K, while the spectrum of the closely related monocation of **3** displays two, even at 273 K.[11] However, the parent of **2b**, structure **2a**, gives a monocation whose spectrum shows irons that are identical or different depending on the temperature,[1k] presumably because the Mössbauer spectrum is sensitive not just to the way the ligand mediates bonding between the metals but also to the environment in the solid.[1g-j] The Mössbauer spectrum may thus be an unreliable test of a ligand's abilities to delocalize electrons.

In mixed-valent molecules that are highly curved, like the anion radical of the helical quinone **43**, delocalization is much *more* efficient than in analogous linear species, an effect attributable to delocalization as on a Möbius strip, from one end of the helix to the other and then, through overlap of the helix's termini, back to the beginning again.[69] However, in the monocation of **6** this mode of delocalization appears ineffective in equalizing the electron distribution on the two metals, presumably because the odd electron resides too little on the helix.



43

Conclusions

The ESR parameters imply that the unpaired electron in singly reduced **6** and the unpaired electrons in doubly reduced **6** occupy molecular orbitals that are comprised largely of localized cobalt d_{xz},d_{yz} pairs. The absence of significant coupling between two added electrons, the difference between the first two reduction potentials (measured electrochemically to be 130 mV), the hyperfine splitting in the ESR spectrum characteristic of only one cobalt, and the absence of an intervalence transition in the electronic spectrum imply that the interaction between these orbitals on the two cobalts in **6** is small. That a near-infrared absorption maximum at 920 nm cannot be an intervalence transition is implied by the spectrum of reduced **29**, which has only one metal, showing a similar absorption. That spectrum also has the other prominent absorption exhibited by reduced **6** at 600 nm.

The reduction potentials of cobaltocenium ions in which the cyclopentadienyls are fused to arenes show that the more rings the arene has, the more the d^6 oxidation state is favored over the d^7.

The X-ray diffraction analysis shows that the cobalts in **6** are separated by 8.49 Å and that the (+)-isomer has the (*P*)-configuration.

Experimental Section

General Information. Reagents were combined under argon. Air-sensitive samples were handled using standard glovebox or Schlenk techniques.[70] Diethyl ether and tetrahydrofuran were distilled under argon from sodium or potassium benzophenone ketyl. Benzene (Fisher,

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Table VII. Crystallographic Data for $[C_{56}H_{50}Co_2][PF_6]_2\cdot 2THF$

(a) Crystal Parameters

formula	$C_{64}H_{66}P_2F_{12}Co_2O_2$	V, Å^3	5852.5
formula weight	1275.02	Z	4
crystal system	orthorhombic	cryst dimens, mm	0.62 × 0.60 × 0.48
space group	$P2_12_12_1$	cryst color	red
a, Å	11.560(4)	d(calc), g cm^{-3}	1.45
b, Å	12.244(3)	μ(Mo Kα), cm^{-1}	6.99
c, Å	41.349(17)	T, K	298

(b) Data Collection

diffractometer	Nicolet R3m	rflns collected	7377
monochromator	graphite	indpt rflns	5068
radiation	Mo Kα (λ = 0.710 73 Å)	indpt obsvd rflns $F_o \geq n\sigma(F_o)$ (n = 7.5)	4653
2θ scan range, deg	4–45	std rflns	3 std/197 rflns
data collected (h,k,l)	±13,+14,+45	var in stds	<1

(c) Refinement

$R(F)$, %	11.37	Δ/σ(max)	0.066	N_o/N_v	11.35
$R(wF)$, %	11.74	$\Delta(\rho)$, e Å^{-3}	1.40	GOF	1.755

spectranalyzed grade) for photocyclization reactions was used without purification. All other solvents were purified according to Perrin[71] and distilled under nitrogen or argon. n-Butyllithium/hexanes (Aldrich) and t-BuLi/pentane (Aldrich) were titrated according to Eastham.[72] Preparative silica gel (Woelm 32–62, 32–63 μm) column chromatography was conducted according to Still.[73] The plates used for thin-layer chromatography (TLC) were E. Merck 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 measured using a JASCO J-500A spectrometer with a DP-500N data processor. Elemental analyses were performed at Columbia University using a Perkin-Elmer 2400 CHN elemental analyzer.

Electrochemistry. Voltammetry and coulometry were conducted, as described elsewhere, under a nitrogen atmosphere in a Vacuum Atmospheres drybox.[2a] The supporting electrolyte was 0.1 M n-Bu_4NPF_6, and all potentials are referenced to the ferrocene/ferrocenium couple. To correct these figures to the SCE reference standard, add +0.40 V when the solvent is CH_3CN, +0.45 V when DMF, and +0.56 V when THF. The construction and properties of the gold minigrid OTTLE cell are described in ref 74. ESR spectra were measured using a modified Varian E-4 spectrometer. UV–Vis–NIR spectra were recorded using a Cary 14 or Perkin-Elmer Lambda-9 spectrophotometer. The CVs were simulated by the explicit finite difference method, assuming an EE mechanism.[75]

Crystal Structure Determination. Crystal data are collected in Table VII. A dark red crystal of 6·2THF was mounted on a glass fiber with epoxy cement. Unit-cell parameters were determined through least-squares refinements of the angular settings for 20 reflections (20° ≤ 2θ ≤ 25°). Systematic absences in the diffractometer data uniquely established the space group. No correction for absorption was required (low μ, well-shaped crystal). Because the crystal diffracted only weakly, two forms of the data were collected, but to increase the total data available, they were not averaged.

The structure was solved by direct methods (SOLV), which located the Co atoms. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses and least-squares refinements. Considerable disorder in the PF_6^- counterions could not be fully modeled. As a compromise, the geometries of the two counterions were fixed as rigid octahedrons [d(P–F) = 1.53 Å]. All non-hydrogen atoms except carbon were refined anisotropically. The solvent molecules (THF) were also disordered such that the carbon and oxygen atoms in the five-membered rings could not be distinguished. They were all treated as carbon atoms in the refinement. All hydrogen atoms were calculated and fixed to ideal isotropic positions (d_{CH} = 0.96 Å, U = 1.2U for attached C except in the THF molecules where they were ignored). Refinement of a multiplicative term 0.98(11) for $\Delta f''$ indicated that the correct enantiomer is pictured. The somewhat elevated R factor can be attributed to weak and diffuse diffraction, even at low angles, due to the disordered solvent molecules and counterions. All software and the sources of the scattering factors are contained in the SHELXTL (Sheldrick,[76] 1984, V5.1) program library. Table II lists selected bond lengths and angles. Additional crystallographic data, including atomic coordinates, are available as supplementary material.

((*P*)-(+)-[9]Helical Bis(indenyl))bis((pentamethylcyclopentadienyl)-cobalt) Bis(hexafluorophosphate) (6). $tert$-Butyllithium in pentane (0.55 mL, 1.67 M, 0.92 mmol) was added to a solution of 200 mg (0.44 mmol) of (P)-(+)-[9]helical bis(indene) **5**[2] in 30 mL of THF at −78 °C. After the mixture was stirred at −78 °C for 2 h and at 0 °C for 4 h, a solution of 202 mg (0.44 mmol) of $[Cp^*CoCl]_2$[4] in 10 mL of THF was added at −78 °C, and the stirred reaction mixture was warmed to room temperature for 10 h. The resulting black solution was treated with 262 mg (0.97 mmol) of $FeCl_3\cdot 6H_2O$ in 20 mL of 0.2 M HCl at room temperature, giving a bright orange solution. This was stirred for 30 min and then treated with 950 mg of solid NH_4PF_6. Organic solvents were evaporated, the aqueous slurry was filtered, and the orange precipitate was washed with 5 × 25 mL of H_2O and 5 × 25 mL of Et_2O. Precipitating twice from acetone/Et_2O gave 440 mg (0.39 mmol, 88% yield) of **6**, an orange solid. ^1H NMR (400 MHz, acetone-d_6): δ 0.91 (s, 30 H), 3.66 (d, 2 H), 4.72 (t, 2 H), 5.32 (m, 2 H), 7.59, 7.75 (dd, J = 8.3 Hz, 4 H), 7.23, 7.79 (dd, J = 9.1 Hz, 4 H), 8.07, 8.39 (dd, J = 8.3 Hz, 4 H), 8.48 (s, 2 H). ^{13}C NMR (75 MHz, acetone-d_6): δ 77.7, 79.4, 86.3, 95.8, 96.1, 96.7, 120.8, 123.6, 125.2, 126.1, 127.0, 128.9, 129.1, 129.5, 132.9, 133.1, 133.2, 134.5. $[\alpha]_D$ 8205° (c 0.0024, acetone). UV (CH_3CN) λ_{max} (log ϵ): 419 (4.23), 339 (4.61), 303 (sh, 4.60), 259 nm (4.84). CD (CH_3CN) λ_{max} ($\Delta\epsilon$): 430 (138), 382 (198), 335 (sh, 46), 307 (sh, −86), 270 (−214), 236 nm (51). MS (FAB, m-nitrobenzyl alcohol): m/z 985 (M − PF_6, 100), 840 (M − 2PF_6, 70), 647 (M − 2PF_6 − Cp*Co, 70). Anal. Calcd for $C_{56}H_{50}Co_2P_2F_{12}$: C, 59.48; H, 4.46. Found: C, 59.55; H, 4.63.

Pentamethylcyclopentadienyl Indenylcobalt Hexafluorophosphate (7). n-Butyllithium in hexanes (0.33 mL, 2.67 M, 0.87 mmol) was added to a solution of 0.1 mL (0.87 mmol) of indene in 10 mL of hexanes, giving a white slurry. After the mixture was stirred at room temperature for 3 h, the solid indenyllithium was isolated under argon by "observation tube" filtration,[70a] washed with 10 mL of hexanes, filtered, and dried in vacuo for 1 h. After the solid was dissolved in 15 mL of THF and cooled to −78 °C, a solution of 200 mg (0.44 mmol) of $[Cp^*CoCl]_2$[4] in 20 mL of THF at −78 °C was added in drops via cannula. After the solution was stirred at room temperature for 3.5 h, 280 mg (1.04 mmol) of $FeCl_3\cdot 6H_2O$ in 20 mL of 0.2 M HCl was added to give an orange solution which was stirred at room temperature for 30 min. Ammonium hexafluorophosphate (460 mg, 2.82 mmol) and 10 mL of acetone were added, and the organic solvents were evaporated, leaving an orange slurry. Filtration using a medium frit and washing with 3 × 50 mL of H_2O and 3 × 50 mL of Et_2O left a bright orange solid which was washed from the frit with ca. 50 mL of acetone. Evaporation left 230 mg (0.51 mmol, 58% yield) of 7, an orange solid. ^1H NMR (200 MHz, acetone-d_6): δ 1.78 (s, 15 H), 5.44 (t, J = 2.8 Hz, 1 H), 5.97 (d, J = 2.8 Hz, 2 H), 7.67 (m, 4 H). ^{13}C NMR (75 MHz, acetone-d_6): δ 8.92, 79.77, 89.12, 96.24, 99.39, 124.58, 131.65. IR (KBr, cm^{-1}): 3106 s, 3044 w, 2924 m, 1682 w, 1613 w, 1598 w, 1522 w, 1470 m, 1459 m, 1452 m, 1387 s, 1339 m, 1253 w, 1210 w, 1075 w, 1050 m, 1028 m, 828 s, 773 s. MS (FAB, m-nitrobenzyl alcohol): m/z 309 (M − PF_6, 100). UV (c = 6.65 × 10^{-5},

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CH_3CN) λ_{max} (log ϵ): 426 (3.20), 316 (4.44), 252 (3.83), 213 nm (4.28). Anal. Calcd for $C_{19}H_{22}CoPF_6$: C, 50.23; H, 4.88. Found: C, 50.01; H, 4.93.

Ethyl 4-Methyl-3-nitrobenzoate (11).[6] A modification of Kermack's procedure[6] was used. A solution of 100 g (0.55 mol) of 4-methyl-3-nitrobenzoic acid in 130 mL (2.2 mol) of ethanol, 1 mL of concentrated HCl, and 1 L of benzene was refluxed for 48 h using a Dean–Stark trap to remove water. After the mixture cooled to room temperature, extraction with 1 × 100 mL of water, 2 × 200 mL of 5% $NaHCO_3$ solution, and 1 × 100 mL of water, drying over $MgSO_4$, and evaporation gave a yellow liquid. Distillation under reduced pressure (105 °C, 0.3 mmHg; lit.[6] bp 163–170 °C, 10 mmHg) gave 91.04 g (0.47 mol, 86% yield) of **11**, a clear liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.40 (t, J = 7.2 Hz, 3 H), 2.63 (s, 3 H), 4.39 (q, J = 7.2 Hz, 2 H), 7.41 (d, J = 7.8 Hz, 1 H), 8.12 (dd, J = 2.3, 7.9 Hz, 1 H), 8.58 (d, J = 2.4 Hz, 1 H). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 14.02, 20.27, 61.44, 125.40, 129.55, 132.79, 133.13, 138.02, 164.24. IR (CCl_4, cm^{-1}); 3080 m, 2984 s, 2937 m, 2907 m, 2873 m, 1731 s, 1622 s, 1531 s, 1495 s, 1488 s, 1383 s, 1351 s, 1286 s, 1262 s, 1204 s, 1174 m, 1157 s, 1125 s, 1021 s, 839 m, 769 s, 758 m, 507 m. MS (EI): m/z 209 (M^+, 30), 192 (M + 1 – O, 75), (M – OEt, 100), 89 (M – CO_2Et – NO_2, 85).

Ethyl 3-Amino-4-methylbenzoate (12).[5] A modification of Bellamy's procedure[8] was used. A mixture of 500 mg of **11** (2.6 mmol), 2.92 g of $SnCl_2{\cdot}2H_2O$ (12.94 mmol), and 10 mL of ethanol was heated at 70 °C for 30 min. After the mixture cooled to room temperature, 10% NaOH was added until the mixture became strongly alkaline (pH > 11). Extraction with 2 × 25 mL of EtOAc, extraction of the combined organic layers with 50 mL of brine, drying over $MgSO_4$, and evaporation gave 425 mg (2.6 mmol, 100% yield) of **12**, a clear oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.39 (t, J = 7.1 Hz, 3 H), 2.22 (s, 3 H), 3.70 (br s, 2 H), 4.33 (q, J = 7.2 Hz, 2 H), 7.09 (d, J = 7.8 Hz, 1 H), 7.27 (s, 1 H), 7.39 (d, J = 7.2 Hz, 2 H). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 14.32, 17.51, 60.63, 115.51, 119.77, 127.45, 129.26, 130.28, 144.52, 166.87. IR (CCl_4, cm^{-1}): 3477 m, 3383 s, 2981 s, 2936 m, 2903 m, 2861 m, 1714 s, 1625 s, 1580 s, 1509 m, 1459 s, 1426 s, 1392 m, 1367 s, 1290 s, 1105 s, 1024 s, 998 m, 888 m, 788 m, 777 m, 768 m, 764 m, 691 m, 523 m, 511 m. MS (EI): m/z 179 (M^+, 100), 151 (M + 1 – Et, 25), 134 (M – OEt, 55), 106 (M – OEt – CO, 55). Another experiment using 42 g (0.22 mol) of **11**, 245 g (1.09 mol) of $SnCl_2{\cdot}$DME, and 800 mL of EtOH produced 22.81 g (0.14 mmol, a 65% yield) of **12** (bp 105 °C, 0.2 mmHg).

Ethyl 3-Bromo-4-methylbenzoate (13).[9] The procedure is that of Rinehart.[77] Sodium nitrite (1.54 g, 22.3 mmol) in 4 mL of H_2O was added in drops to 3.5 g (21.4 mmol) of **12** in 33 mL of 48% HBr and 66 mL of H_2O at –5 °C over 5 min. The resulting brown solution was stirred at –5 °C for 5 min and then suction filtered into 3.5 g (24.4 mmol) of CuBr, 10 mL of 48% HBr, and 35 mL of H_2O. After the mixture was heated at 70 °C for 1 h, the dark brown slurry was poured into a separatory funnel containing 200 mL of Et_2O. The aqueous layer was extracted with 100 mL of Et_2O and the organic layers were combined and then extracted with 1 × 100 mL of 1 M HCl, 1 × 100 mL of H_2O, and 1 × 100 mL of brine, dried over $MgSO_4$, filtered, and evaporated. The resulting brown oil was flash chromatographed on silica gel, eluting with hexanes/Et_2O (5/1 and 4/1), producing 4.04 g (17.8 mmol, 83% yield) of **13**, a clear oil (R_f = 0.56, 2/1 hexanes/Et_2O). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.40 (t, J = 7.1 Hz, 3 H), 2.46 (s, 3 H), 4.38 (q, J = 7.2 Hz, 2 H), 7.30 (d, J = 8.4 Hz, 1 H), 7.88 (dd, J = 2.4, 8.2 Hz, 1 H), 8.20 (d, J = 2.3 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 23.2, 61.2, 124.7, 128.3, 129.8, 130.7, 133.4, 143.2, 165.4. IR (neat, cm^{-1}): 3067 m, 2981 m, 2936 m, 2906 m, 1722 s, 1603 m, 1558 m, 1447 s, 1381 s, 1366 s, 1290 s, 1253 s, 1207 m, 1174 m, 1040 s, 1022 s, 893 m, 837 m, 757 s, 679 s, 520 s. MS (EI): m/z 379 (M^+, 50), 333 (M – OEt, 50), 299 (M – Br, 100), 271 (M – Br – CO, 20), 243 (M – Br – CO – Et, 100).

Ethyl 3-Bromo-4-(bromomethyl)benzoate (14). Ethyl 3-bromo-4-methylbenzoate (**13**) (8.24 g, 36.3 mmol), 6.46 g (36.3 mmol) of *N*-bromosuccinimide, 439 mg (1.81 mmol) of benzoyl peroxide, and 200 mL of CCl_4 were refluxed overnight (10 h). The product mixture was filtered while warm through a medium frit, and the filtrate was evaporated to leave a yellow oil. When pentane was added, a white solid precipitated, and precipitation was completed by cooling in a 5 °C refrigerator for 4 h. Filtration gave 6.75 g (29.7 mmol, 61% yield) of **14**, a white solid (R_f = 0.51, 2/1 hexanes/Et_2O). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.41 (t, J = 7.0 Hz, 3 H), 4.39 (q, J = 7.2 Hz, 2 H), 4.61 (s, 2 H), 7.52 (d, J = 8.0 Hz, 1 H), 7.97 (dd, J = 1.6, 8.0 Hz, 1 H), 8.24 (d, J = 1.6 Hz, 1 H). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 14.29, 32.29, 61.48, 124.21, 128.88, 131.04, 132.05, 134.23, 141.50, 164.61. IR (film, cm^{-1}): 3021 m, 2982 s, 1716 s, 1602 m, 1557 s, 1473 m, 1386 s, 1365 s, 1299 s, 1272 s, 1131 s, 1023 m, 907 m, 766. MS (EI): m/z 322 (M^+, 50), 277 (M – OEt, 30), 241 (M – Br, 100).

Diethyl (2-Bromo-4-carbethoxybenzenephosphonate (15). The procedure is that of Kosalapoff.[78] Triethyl phosphite (3.17 g, 3.27 mL, 19.1 mmol) and 5.83 g (19.1 mmol) of **14** were heated at 150 °C for 20 h. Evaporation gave a yellow oil which was chromatographed on silica gel, eluting with hexanes/EtOAc (2/1, 1/1, etc., through 1/6), giving 6.34 g (17.5 mmol, 92% yield) of **15**, a clear oil (R_f = 0.13, 1/3 hexanes/EtOAc). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.27 (t, J = 7.0 Hz, 6 H), 1.40 (t, J = 7.0 Hz, 3 H), 3.43 (d, J_{P-H} = 22.4 Hz, 2 H), 4.10 (m, 4 H), 4.38 (q, J = 7.2 Hz, 2 H), 7.53 (dd, J = 2.8, 8.0 Hz, 1 H), 7.94 (d, J = 8.2 Hz, 1 H), 8.26 (m, 1 H). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 14.20, 16.31, 32.64, 34.84, 61.82 (d, J_{P-C} = 69.1 Hz), 124.78, 128.25, 131.40, 133.86, 137.10, 164.97. IR (neat, cm^{-1}): 3476 br m, 3020 w, 2983 s, 2932 s, 2307 s, 1723 s, 1603 m, 1558 m, 1477 m, 1445 m, 1389 s, 1367 s, 1269 s, 1184 s, 1102 s, 1036 s, 966 s, 854 m, 762 s, 708 m, 676 m, 492 s. MS (EI): m/z 379 (M^+, 50), 335 (M – OEt, 50), 299 (M – Br, 100).

Ethyl 3-Bromo-4-(*trans*-2-(2-naphthyl)ethenyl)benzoate (16). The procedure is that of Wadsworth and Emmons.[12] Sodium hydride (447 mg, 60% mineral oil dispersion, 11.2 mmol) was placed in a 250-mL round-bottomed flask and rinsed with 3 × 5 mL of hexanes. Tetrahydrofuran (20 mL) was added, and then 6.34 g (11.2 mmol) of **15** was added in drops via cannula, giving a bright yellow solution. After the mixture was stirred for 1.5 h at room temperature, 1.71 g (10.9 mmol) of 2-naphthaldehyde and 30 mL of THF were added in drops via cannula. This mixture was stirred for 18 h at room temperature and heated at 65 °C for 18 h. After the reaction was carefully quenched with H_2O, the product solution was extracted with 2 × 100 mL of Et_2O. The combined Et_2O layers were washed with 1 × 100 mL of H_2O and 1 × 100 mL of brine, dried over $MgSO_4$, filtered, and evaporated. Flash chromatography on silica gel, eluting with hexanes/EtOAc 15/1 to 7/1, produced 2.36 g of a 2.2/1 mixture (^{1}H NMR analysis) of **16** (R_f = 0.40, 3/1 hexanes/Et_2O) and 2-naphthaldehyde (R_f = 0.33, 3/1 hexanes/Et_2O).

This mixture was heated with 222 mg (1.33 mmol) of Girard's Reagent T in 25 mL of EtOH. After 1 h, TLC analysis showed that no 2-naphthaldehyde remained. Extracting with 50 mL of Et_2O, washing with 1 × 100 mL of H_2O and 1 × 100 mL of brine, drying over $MgSO_4$, filtering, and evaporating left 1.95 g (5.1 mmol, a 46% yield from **15**) of **16**, a white solid (R_f = 0.40, 3/1 hexanes/Et_2O). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.42 (t, J = 7.2 Hz, 3 H), 4.40 (q, J = 7.4 Hz, 2 H), 7.30 (d, J = 8.2 Hz, 1 H), 7.49 (m, 2 H), 7.61 (d, 1 H), 7.84 (m, 7 H), 8.00 (dd, J = 1.6, 8.7 Hz, 1 H), 8.29 (d, J = 1.6 Hz, 1 H). ^{13}C NMR (62.8 MHz, $CDCl_3$): δ 14.35, 61.23, 123.49, 123.82, 126.11, 126.43, 126.49, 126.61, 127.77, 127.82, 128.22, 128.50, 130.46, 133.56, 134.00, 134.26, 141.18, 165.08. IR ($CHCl_3$, cm^{-1}) 3060 w, 2986 w, 1722 s, 1710 s, 1627 m, 1597 s, 1465 w, 1390 m, 1368 m, 1291 s, 1112 m, 1038 m, 1018 m, 959 m. MS (EI): m/z 381 (M^+, 25), 228 (M – CO_2Et – Br, 100).

3-Bromo-4-(*trans*-2-(2-naphthyl)ethenyl)benzyl Alcohol (17). The procedure is that of Yoon.[15] A 1.0 M solution of diisobutylaluminum hydride in hexanes (10.5 mL, 10.5 mmol) was syringed in drops into 1.91 g (5.1 mmol) of **16** in 50 mL of $PhCH_3$ at 0 °C. After the solution was stirred for 1 h at room temperature, the reaction was quenched by carefully adding 5 mL of 1 M HCl. Extracting with 100 mL of Et_2O, washing with 1 × 200 mL of H_2O and 1 × 100 mL of brine, drying over Na_2SO_4, and evaporating left 1.74 g (5.1 mmol, 100% yield) of **17**, a white solid (R_f = 0.16, 1/1 hexanes/Et_2O). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.70 (t, 1 H), 4.71 (d, 2 H), 7.15–8.00 (complex m, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 69.29, 123.58, 124.24, 126.06, 126.13, 126.40, 126.66, 127.15, 127.32, 127.72, 128.08, 128.42, 131.42, 131.43, 133.22, 133.61, 134.46, 136.32, 141.79. IR ($CHCl_3$, cm^{-1}): 3604 s, 3422 m, 3062 m, 3007 m, 2928 m, 1628 m, 1598 s, 1510 m, 1486 m, 1402 s, 1392 s, 1272 m, 1176 m, 1126 m, 1038 s, 1017 s, 961 s, 894 s, 845 s, 822 s. MS (EI) m/z 338 (M^+, 100).

3-Bromo-4-(*trans*-2-(2-naphthyl)ethenyl)benzyl Bromide (18). The procedure is that of Smith.[16] Pyridine (0.1 mL, 1.23 mmol) was added to a 0 °C solution of 480 mg of PBr_3 (0.17 mL, 1.8 mmol) in 30 mL of benzene, followed by 1.67 g (4.92 mmol) of **17** in 150 mL of benzene added in drops via cannula. After being stirred for 1.5 h at room temperature, the reaction mixture was extracted with 2 × 200 mL of H_2O and 1 × 200 mL of brine, dried over $MgSO_4$, filtered, and evaporated, leaving a light yellow solid. Flash chromatography on silica gel, eluting with hexanes/Et_2O (3/1 to 1/1), gave 990 mg (2.46 mmol, a 50% yield)

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of **18**, a white solid (R_f = 0.58, 1/1 hexanes/Et$_2$O). ^{1}H NMR (200 MHz, CDCl$_3$): δ 4.60 (s, 2 H), 7.19 (s, 1 H), 7.37 (dd, 1 H), 7.49 (m, 3 H), 7.68 (m, 2 H), 7.85 (m, 5 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 31.97, 123.55, 124.04, 126.25, 126.45, 126.81, 126.97, 127.36, 127.73, 128.11, 128.30, 128.46, 132.15, 133.30, 133.54, 134.29, 137.22, 138.42. MS (EI): *m/z* 402 (M$^+$, 50), 321 (M − Br, 100), 241 (M − 2Br, 15).

Diethyl (3-Bromo-4-(*trans*-2-(2-naphthyl)ethenyl)benzenephosphonate (19). Triethyl phosphite (397 mg, 0.41 mL, 2.39 mmol), **18** (801 mg, 1.99 mmol), and 30 mL of DME were refluxed for 114 h. Evaporation left an oil, which was chromatographed on silica gel, eluting with 1/3 hexanes/EtOAc, giving 850 mg (1.85 mmol, 93% yield) of **19**, a white solid (R_f = 0.13, 1/3 hexanes/EtOAc). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.30 (m, 3 H), 3.12 (d, 2 H), 4.07 (m, 2 H), 7.23 (m, 2 H), 7.51 (m, 3 H), 7.69 (q, 2 H), 7.82 (m, 5 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 16.35, 16.43, 32.24, 34.08, 62.24, 62.34, 123.61, 124.00, 126.12, 126.40, 126.52, 126.57, 127.12, 127.26, 127.72, 128.08, 128.41, 129.03, 129.12, 131.38, 132.72, 132.84, 133.26, 133.65, 134.11, 134.21, 134.52, 135.68, 135.76. MS (EI) *m/z* 460 (M$^+$, 80).

Bis-Stilbene 21. The procedure is that of Wadsworth and Emmons.[12] Sodium hydride (80 mg, 60% mineral oil dispersion, 1.99 mmol) in a 200-mL round-bottomed flask was washed with 3 × 5 mL of hexanes, and DME (20 mL) was added, followed in drops by 830 mg (1.81 mmol) of **19** in 20 mL of DME. After the solution was stirred for 1 h, 590 mg (1.81 mmol) of (*R*)-3-[(*tert*-butyldimethylsilyl)oxy]-2,3-dihydro-1*H*-benz[*e*]indene-8-carboxaldehyde (**20**)[2] in 25 mL of DME was added via cannula, and the resulting solution was stirred overnight (10 h). Careful quenching of the reaction with 2 mL of a saturated NH$_4$Cl solution precipitated a yellow solid. The mixture was poured into a separatory funnel containing 100 mL of H$_2$O, extracted with 2 × 100 mL of CH$_2$Cl$_2$, dried over MgSO$_4$, filtered, and evaporated, leaving a yellow solid. Flash chromatography on silica gel, eluting with 3/1 hexanes/CH$_2$Cl$_2$ to 2/1 hexanes/CH$_2$Cl$_2$ produced 850 mg (1.34 mmol, 74%) of **21**, a yellow solid. ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.21 (s, 3 H), 0.23 (s, 3 H), 0.98 (s, 9 H), 2.11 (m, 1 H), 2.66 (m, 1 H), 3.08 (m, 1 H), 3.91 (m, 1 H), 5.47 (t, 1 H), 7.27 (m, 4 H), 7.48 (m, 6 H), 7.76 (m, 4 H), 7.83 (m, 6 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ −4.68, 4.40, 14.03, 18.29, 22.64, 25.96, 28.07, 31.58, 35.94, 122.71, 122.85, 123.63, 123.71, 124.65, 125.64, 126.13, 126.41, 126.56, 126.94, 127.12, 127.36, 127.73, 128.09, 128.43, 128.97, 130.32, 130.61, 130.94, 131.21, 133.26, 133.68, 134.43, 134.62, 135.96, 138.35, 138.84, 143.00. MS (CI, CH$_4$): *m/z* 661 (M + 29, 10), 632 (M$^+$, 100), 501 (M − OSi*t*-BuMe$_2$, 50).

***exo*- and *endo*-3-[(*tert*-Butyldimethylsilyl)oxy]-11-bromo[8]helicene ((*P*)-(+)-24 and (*M*)-(−)-25).** A solution of bis-stilbene **21** (300 mg, 0.474 mmol), I$_2$ (265 mg, 1.04 mmol), and propylene oxide (7.6 mL, 109 mmol) in 1300 mL of benzene was degassed by bubbling Ar through for 30 min and irradiated through Pyrex for 11 h with a medium-pressure Hg lamp. The resulting yellow solution was extracted with 500 mL of dilute aqueous NaHCO$_3$ and Na$_2$S$_2$O$_3$, dried with MgSO$_4$, filtered, and concentrated to a small volume. The solution was filtered through a short column of neutral alumina and eluted further with benzene until the filtrate was colorless, and the solvent was evaporated. The whole procedure was repeated three times so that a total of 710 mg of **21** was transformed. Flash chromatography on silica gel, eluting with hexanes/CH$_2$Cl$_2$ (6/1 to 2/1), gave 115 mg (0.183 mmol, 28% yield) of *endo*-3-[(*tert*-butyldimethylsilyl)oxy]-11-bromo[8]helicene ((*M*)-(−)-**25**) (R_f = 0.48, 3/1 hexanes/CH$_2$Cl$_2$) and 176 mg (0.280 mmol, 43% yield) of *exo*-3-[(*tert*-butyldimethylsilyl)oxy]-11-bromo[8]helicene ((*P*)-(+)-**24**) (R_f = 0.23, 3/1 hexanes/CH$_2$Cl$_2$) as yellow solids.

(*P*)-(+)-24. ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.05 (s, 3 H), 0.15 (s, 3 H), 0.41 (m, 1 H), 0.90 (s, 9 H), 0.97 (m, 1 H), 1.29 (m, 1 H), 1.73 (m, 1 H), 4.80 (t, 1 H), 6.40 (t, 1 H), 6.74 (d, 1 H), 6.93 (m, 2 H), 7.14 (d, 1 H), 7.39 (dd, 2 H), 7.58 (d, 2 H), 7.91 (s and d, 3 H), 8.35 (s, 1 H), 8.41 (d, 1 H). $[\alpha]_D$ = 3100° (*c* = 0.079, CH$_2$Cl$_2$).

(*M*)-(−)-25. ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.00 (s, 3 H), 0.13 (s, 3 H), 0.89 (m, 2 H), 1.07 (s, 9 H), 1.10 (m, 1 H), 1.58 (m, 1 H), 4.59 (t, 1 H), 6.38 (t, 1 H), 6.78 (d, 1 H), 6.92 (m, 2 H), 7.13 (d, 1 H), 7.35 (m, 3 H), 7.59 (dd, 2 H), 7.89 (s and d, 3 H), 8.32 (s, 1 H), 8.41 (d, 1 H). $[\alpha]_D$ = −2800° (*c* = 0.079, CH$_2$Cl$_2$).

***exo*-3-[(*tert*-Butyldimethylsilyl)oxy][8]helicene ((*P*)-(+)-26).** A solution of *n*-BuLi in hexanes (0.74 mL, 2.43 M, 1.80 mmol) was added in drops to a −78 °C solution of 283 mg (0.68 mmol) of (*P*)-(+)-**24** and 15 mL of THF. The resulting orange solution was stirred at −78 °C for 30 min, and the reaction was quenched with 5 mL of NH$_4$Cl solution. After being warmed to room temperature, the reaction mixture was extracted with 100 mL of Et$_2$O. The extracts were washed with 2 × 50 mL of H$_2$O and 1 × 50 mL of brine, dried over MgSO$_4$, filtered, and evaporated, leaving a yellow solid. Flash chromatography on silica gel, eluting with hexanes/CH$_2$Cl$_2$ (3/1 to 2/1), produced 220 mg (0.40 mmol, 89% yield) of (*P*)-(+)-**27**, a yellow solid (R_f = 0.25, 3/1 hexanes/CH$_2$Cl$_2$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.06 (s, 3 H), 0.13 (s, 3 H), 0.49 (m, 1 H), 0.90 (s, 9 H), 0.98 (m, 1 H), 1.28 (m, 1 H), 1.71 (m, 1 H), 4.79 (t, 1 H), 6.39 (t, 1 H), 6.83 (d, 1 H), 6.94 (m, 2 H), 7.15 (d, 1 H), 7.29 (d, 1 H), 7.40 (t, 2 H), 7.60 (t, 2 H), 7.87 (t, 2 H), 8.00 (complex m, 4 H).

***endo*-3-[(*tert*-Butyldimethylsilyl)oxy][8]helicene ((*M*)-(−)-27).** The same procedure was applied to 180 mg (0.45 mmol) of (*M*)-(−)-**25** using 0.47 mL (2.43 M, 1.15 mmol) of *n*-BuLi in hexanes. Flash chromatography on silica gel, eluting with hexanes/CH$_2$Cl$_2$ (5/1 to 3/1), produced 120 mg (0.22 mmol, 76% yield) of (*M*)-(−)-**27**, a yellow solid (R_f = 0.42, 3/1 hexanes/CH$_2$Cl$_2$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.00 (s, 3 H), 0.11 (s, 3 H), 1.05 (m, 2 H), 1.06 (s, 9 H), 1.20 (m, 1 H), 1.55 (m, 1 H), 4.59 (t, 1 H), 6.38 (t, 1 H), 6.91 (d, 3 H), 7.16 (d, 1 H), 7.29 (d, 1 H), 7.40 (t, 2 H), 7.61 (m, 2 H), 7.83 (t, 2 H), 8.00 (complex m, 4 H).

(*P*)-(+)-[8]Helical Indene ((*P*)-(+)-28). *p*-Toluenesulfonic acid monohydrate (8 mg, 0.04 mmol), 220 mg (0.40 mmol) of (*P*)-(+)-**26**, and 25 mL of benzene were refluxed for 30 min. After extraction with Na$_2$CO$_3$ solution, drying over MgSO$_4$, filtration, and evaporation, a yellow solid was isolated. Flash chromatography on silica gel, eluting with benzene, produced 152 mg (0.37 mmol, 93% yield) of (*P*)-(+)-**28**, a yellow solid (R_f = 0.26, 3/1 hexanes/CH$_2$Cl$_2$). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.21 (dt, *J* = 23.7, 2.1 Hz, 1 H), 1.99 (dt, *J* = 23.8, 1.8 Hz, 1 H), 5.82 (dt, *J* = 5.5, 1.9 Hz, 1 H), 6.38 (dt, *J* = 5.5, 1.8 Hz, 1 H), 6.45 (dd, *J* = 7.7, 1.3 Hz, 1 H), 6.80 (m, 2 H), 7.19 (AB q, *J* = 8.0 Hz, 2 H), 7.28 (m, 2 H), 7.42 (AB q, *J* = 8.6 Hz, 2 H), 7.54 (d, *J* = 8.4 Hz, 1 H), 7.72 (d, *J* = 8.2 Hz, 1 H), 7.82 (m, 2 H), 8.02 (s, 1 H), 8.05 (m, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 40.23, 119.76, 123.10, 123.62, 123.85, 124.58, 124.69, 124.99, 125.46, 125.55, 126.03, 126.30, 126.45, 126.49, 126.49, 126.66, 126.79, 126.84, 127.02, 127.66, 128.37, 128.62, 129.31, 130.27, 130.78, 130.89, 130.94, 131.28, 131.73, 132.25, 132.63, 138.38, 142.80. MS (FAB, *m*-nitrobenzyl alcohol): *m/z* 416 (M$^+$, 30). $[\alpha]_D$ 6600° (*c* 0.083, CH$_2$Cl$_2$). UV (CH$_3$CN) λ_{max} (log ε) 342 (4.02), 315 (4.25), 269 (4.70), 247 nm (4.67). CD (CH$_3$CN) λ_{max} (Δε) 372 (+173), 314 (−95), 276 nm (−215). HRMS (FAB) calcd for C$_{33}$H$_{20}$ 416.1565, found 416.1561 (and the observed and calculated pattern of parent peak intensities match).

(*M*)-(−)-[8]Helical Indene ((*M*)-(−)-28). *p*-Toluenesulfonic acid monohydrate (4 mg, 0.02 mmol), 120 mg (0.22 mmol) of (*M*)-(−)-**27**, and 25 mL of benzene were refluxed for 30 min. After extraction with Na$_2$CO$_3$ solution, drying over MgSO$_4$, filtration, and evaporation, a yellow solid was isolated. Flash chromatography on silica gel, eluting with benzene, produced 93 mg (0.22 mmol, 100% yield) of (*M*)-(−)-**28**, a yellow solid (R_f = 0.26, 3/1 hexanes/CH$_2$Cl$_2$). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.21 (dt, *J* = 23.7, 2.1 Hz, 1 H), 1.99 (dt, *J* = 23.8, 1.8 Hz, 1 H), 5.82 (dt, *J* = 5.5, 1.9 Hz, 1 H), 6.38 (dt, *J* = 5.5, 1.8 Hz, 1 H), 6.45 (dd, *J* = 7.7, 1.3 Hz, 1 H), 6.80 (m, 2 H), 7.19 (AB q, *J* = 8.0 Hz, 2 H), 7.28 (m, 2 H), 7.42 (AB q, *J* = 8.6 Hz, 2 H), 7.54 (d, *J* = 8.4 Hz, 1 H), 7.72 (d, *J* = 8.2 Hz, 1 H), 7.82 (m, 2 H), 8.02 (s, 1 H), 8.05 (m, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 40.23, 119.75, 123.09, 123.61, 123.85, 124.58, 124.98, 125.44, 125.50, 126.02, 126.29, 126.43, 126.48, 126.51, 126.65, 126.78, 126.83, 127.01, 127.65, 128.35, 128.62, 129.29, 130.26, 130.77, 130.87, 130.92, 131.26, 131.72, 132.24, 132.61, 138.37, 142.78. $[\alpha]_D$ −6300° (*c* 0.05, CH$_2$Cl$_2$). UV (CH$_3$CN) λ_{max} (log ε) 342 (4.07), 315 (4.28), 269 (4.73), 247 nm (4.70). CD (CH$_3$CN) λ_{max} (Δε) 372 (−160), 314 (+88), 276 nm (+203).

(*P*)-(+)-[8]Helical Indenyl(pentamethylcyclopentadienyl)cobalt Hexafluorophosphate ((*P*)-(+)-29). A solution of *t*-BuLi in pentane (0.11 mL, 1.70 M, 0.17 mmol) was added in drops to a −78 °C solution of 66 mg (0.158 mmol) of (*P*)-(+)-**28** and 30 mL of THF. The blood-red solution was warmed to 0 °C for 30 min. After the solution was cooled to −78 °C, 40 mg (0.09 mmol) of [Cp*CoCl]$_2$ in 10 mL was added via cannula. The resulting brown solution was stirred overnight (10 h) at room temperature. After the solution was cooled to 0 °C, 100 mg (0.37 mmol) of FeCl$_3$·H$_2$O in 20 mL of 0.2 M HCl was added via syringe, which precipitated a brown solid. After the mixture was stirred at room temperature for 30 min, 850 mg (5.22 mmol) of NH$_4$PF$_6$ was added, followed by 10 mL of acetone. The organic solvents were evaporated, and the remaining slurry was filtered through a coarse glass frit packed with Celite and washed with 2 × 50 mL of water. The product was washed from the frit with acetone, and 925 mg (5.68 mmol) of NH$_4$PF$_6$ was added to the resulting dark orange filtrate. This solution was concentrated to ca. 10 mL, and water was added, precipitating an orange solid. This was filtered through Celite, washed from the filter with acetone, mixed with additional NH$_4$PF$_6$, and precipitated by adding water. This last procedure was repeated three more times, until TLC analysis (1/1 hexanes/CH_2Cl_2) showed that the acetone solution contained no more starting hydrocarbon. The acetone solution was then concentrated to ca. 10 mL, and pentane was slowly added to precipitate an orange solid. Filtration through a medium frit produced 112 mg (0.148 mmol, a 94% yield) of (*P*)-(+)-**29**, an orange solid. ^{1}H NMR (400 MHz, acetone-d_6): δ 0.93 (s, 15 H), 3.66 (m, 1 H), 4.66 (t, $J = 2.1$ Hz, 1 H), 5.48 (dd, $J = 2.1, 1$ Hz, 1 H), 6.42 (td, $J = 5.8$ Hz, 2 H), 6.83 (d, $J = 6.8$ Hz, 1 H), 7.05 (dt, $J = 5.6, 0.9$ Hz, 2 H), 7.26 (dd, $J = 6.5, 0.9$ Hz, 1 H), 7.37 (m, 2 H), 7.45 (d, $J = 6.4$ Hz, 1 H), 7.64 (d, $J = 7.0$ Hz, 1 H), 7.87 (d, $J = 6.2$ Hz, 1 H), 8.21 (m, 2 H), 8.32 (d, $J = 6.2$ Hz, 2 H), 8.33 (s, 1 H). ^{13}C NMR (75 MHz, acetone-d_6): δ 8.03, 78.01, 79.06, 85.92, 95.51, 96.36, 96.69, 120.22, 124.06, 124.81, 125.12, 125.40, 125.92, 125.95, 126.31, 127.34, 127.79, 127.86, 128.08, 128.18, 128.22, 128.27, 128.87, 129.02, 129.10, 132.59, 132.71, 132.85, 133.14, 133.25, 133.54. MS (FAB, *m*-nitrobenzyl alcohol): *m/z* 609 (M – PF_6, 100), 474 (M – Cp* – PF_6, 10). $[\alpha]_D = 4500°$ ($c = 0.000\,63$, CH_3CN). UV ($c = 8.37 \times 10^{-6}$, CH_3CN): λ_{max} (log ϵ): 334 (4.34), 265 nm (4.72). CD ($c = 8.37 \times 10^{-6}$, CH_3CN) λ_{max} ($\Delta\epsilon$): 361 (+145), 267 nm (–242). HRMS calcd for $C_{43}H_{34}Co$ 609.1993, found 609.1989 (and the observed and calculated pattern of parent peak intensities match).

Bis((*M*)-(–)-[8]helical Indenyl)cobalt Hexafluorophosphate ((*M*)-(–)-30). A solution of *t*-BuLi in pentane (0.12 mL, 1.70 M, 0.20 mmol) was added in drops to solution at –78 °C of 75 mg (0.180 mmol) of (*M*)-(–)-**28** in 20 mL of THF. The blood-red solution was warmed to 0 °C for 45 min. After the solution was cooled to –78 °C, 28 mg (0.09 mmol) of $CoBr_2{\cdot}DME$[21] in 10 mL was added via cannula. After the resulting brown solution had stirred for 4 h, it was cooled to 0 °C and 32 mg (0.12 mmol) of $FeCl_3{\cdot}H_2O$ in 20 mL of 0.2 M HCl was added via syringe. A red solid precipitated. After the mixture was stirred at room temperature for 30 min, 147 mg (0.90 mmol) of NH_4PF_6 was added, followed by 10 mL of acetone. The organic solvents were evaporated, and the remaining slurry was filtered through a coarse glass frit packed with Celite and washed with 2 × 50 mL of water. The product was washed from the frit with acetone, and 200 mg (1.23 mmol) of NH_4PF_6 was added to the resulting red filtrate. After being stirred at room temperature for 12 h, this solution was concentrated to ca. 10 mL and water was added, precipitating a red solid. This was filtered through Celite, washed from the filter with acetone, mixed with additional NH_4PF_6, and precipitated by adding water. This last procedure was repeated three more times, until TLC analysis (1/1 hexanes/CH_2Cl_2) showed that the acetone solution contained no more starting hydrocarbon. The acetone solution was then concentrated to ca. 10 mL, and pentane was slowly added to precipitate a red solid. Filtration through a medium frit produced 53 mg (0.05 mmol, a 66% yield) of (*M*)-(–)-**30**, a red solid. ^{1}H NMR (200 MHz, acetone-d_6): δ 3.60 (s, 1 H), 4.41 (t, 1 H), 4.79 (m, 1 H), 5.12 (d, 1 H), 6.19 (t, 1 H), 6.52 (t, 2 H), 6.78 (t, 1 H), 6.97–7.18 (m, 4 H), 7.89 (d, 1 H), 7.63 and 8.02 (**AB** q, 2 H), 8.22 (m, 6 H). ^{13}C NMR (75 MHz, acetone-d_6): δ 74.46, 75.18, 80.08, 95.54, 98.03, 117.72, 123.73, 124.95, 125.69, 126.12, 127.55, 127.70, 127.77, 127.90, 127.90, 127.98, 128.11, 128.31, 128.57, 128.72, 128.99, 129.03, 129.13, 129.31, 129.35, 129.60, 129.78, 132.25, 132.29, 132.65, 133.07, 133.34, 133.78. Several small peaks are also seen, attributed to an impurity. MS (FAB, *m*-nitrobenzyl alcohol): *m/z* 889 (M – PF_6, 40), 474 (M – [8]helicene – PF_6, 15). $[\alpha]_D$ 13 600° (c 0.000 87, CH_3CN). UV ($c = 8.40 \times 10^{-6}$, CH_3CN) λ_{max} (log ϵ): 335 (4.52), 264 nm (4.98). CD ($c = 8.40 \times 10^{-6}$, CH_3CN) λ_{max} ($\Delta\epsilon$): 479 (–86), 360 (–262), 269 nm (640). HRMS (FAB) calcd for $C_{66}H_{38}Co$ 889.2306, found 889.2300 (and the observed and calculated pattern of parent peak intensities match).

(*P*)-(+)-[9]Helical Bis(indenyl) Bis(pentamethylcyclopentadienyl)cobalt (31). Potassium amalgam (25 mg, 1.6%, 0.63 mmol of potassium) was added to a THF (20 mL) solution of 150 mg (0.13 mmol) of **6**. The solution turned green and was stirred at room temperature for 4 h. The solvent was removed in vacuo, and the resulting green residue was extracted under argon with 3 × 10 mL of hexanes and 1 × 10 mL of benzene. Evaporation of solvent in vacuo gave 100 mg (0.12 mmol, 90% yield) of **31**, a dark green solid. MS (CI, CH_4): *m/z* 841 (M + 1, 90), 648 (M – Cp*Co, 70). UV/vis/near-IR (THF) λ_{max} (ΔE): 254 (5.28), 335 (4.66), 427 (4.29), 598 (2.90), 917 nm (2.71). CD (THF) λ_{max} ($\Delta\epsilon$): 386 (+250), 273 nm (–210).

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Supplementary Material Available: ^{1}H NMR spectrum of **6** and X-ray diffraction data for its crystals; ^{13}C NMR spectrum of **7**; ^{1}H and ^{13}C NMR spectra of **28–30**; UV and CD spectra of (*P*)-(+)-**28**; and UV–near-IR spectra of **6** while it is being reduced (18 pages); lists of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.