Helical Hydrocarbons Capped by Five-Membered Rings as Precursors of Polymeric Metallocenes

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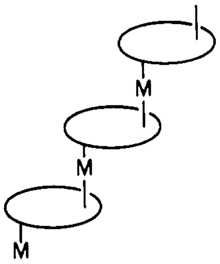
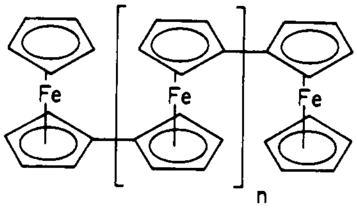
Abstract: The hypothesis is put forward that conjugated helical hydrocarbon dianions capped by a pair of five-membered rings will react with transition-metal halides to give metallocene polymers rather than hydrocarbon sandwiches containing two metal atoms. Syntheses are developed for two of the first members, VII and VIII, of a hypothetical series of such dianions, which, however, are too small to give polymers. With iron chloride they seem to form the sandwiches with two iron atoms; with $[Co(NH_3)_6]Cl_3$ and $NaPF_6$ VII gives a cobalticinium analogue. The syntheses of the conjugate acids of the hydrocarbon dianions, summarized in Schemes II–IV, fuse two five-membered rings to naphthalene and phenanthrene nuclei. An attempt, outlined in Scheme VI, to prepare a [6]helicene analogue by similarly fusing two five-membered rings to a benzo[*c*]phenanthrene gives instead two related ring systems.

Introduction

A few attempts have been made to synthesize polymers like I, in which conjugated arrays and metal atoms alternate, because unlike most organic substances they might be good conductors of electricity[1,2,9] and have other novel properties as well.[9,10] In one set of experiments the bonds created in the polymerization process were between carbon atoms, and when applied to preparations of polyferrocenylenes (structure II) gave small oligomers that were well characterized[11] and larger polymers that were sometimes impure.[9,12] In another set, with which the experiments below are concerned, the carbon–metal bonds were created in the polymerization process, and when applied to reactions of transition metal salts with dilithium *as*-indacenide (III) gave $(C_{12}H_8M)_n$, where M is Fe,[10a,b] Co, and Ni,[13] with dilithium pentalenide (IV) $(C_8H_6M)_n$—here M = Co[10c] or Ni[10d]—and with dilithium fulvenide (V) $(C_{10}H_8M)_n$, where M = Fe,[3a,16] Co,[14] Ni,[15] or Mo.[17] Unfortunately, the value of *n* in all these experiments was 2. The products were only dimers!



I



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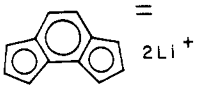
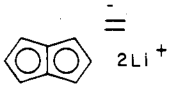
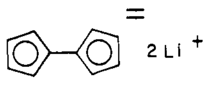


III



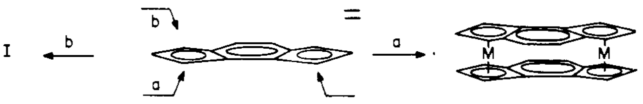
IV



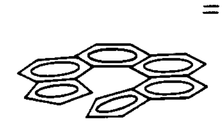
V

The hypothesis considered here is that the annoying tendency to dimerize would be withstood if the metal atoms could be constrained to opposite faces (Scheme I). If polymerization were then the alternative, a simple and general synthesis for the desired and unknown polymers of structure I would be at hand. While at first this proposition seems difficult to implement, a possible way to do it is proposed below.

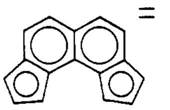
Scheme I



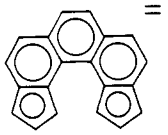
The idea is to incorporate the sandwich structure within helicenes[18,19] by constructing aromatic dianions resembling VI, for in such structures access to the bottom of the ring on the left should be blocked by rings on the right, and access to the top of the ring on the right should be blocked by rings on the left. This objective has not yet been realized, but in this paper one approach is studied, and preparations for anions VII and VIII are developed. The reactions of these anions with iron and cobalt chlorides are also described, as are two attempts to make anion VI using procedures similar to those that successfully give VII and VIII.



VI

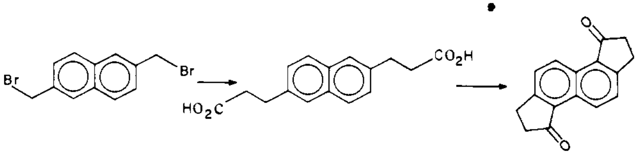


VII



VIII

The syntheses of the ring systems, related to ones used previously to make XI (eq 1),[20] involve double alkylations of benzyl halides and double cyclizations of dicarboxylic acids. Of these two steps the latter has previously been effective in giving polycyclic diketones,[20,21] and it works well for the syntheses required here, but the alkylation, although a classical transformation, required research to achieve acceptable yields.



IX X XI (1)

Results and Discussion

Alkylation Procedure. The transformation of IX to X, by alkylation of malonic ester, saponification, and decarboxylation, had been done before,[20] but the yields for us were poor (3%). Accordingly, the procedure of Rathke and Lindert, in which *tert*-butyl lithioacetate is alkylated,[22] was tried instead,

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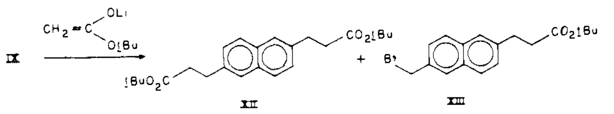
Table I. Yields on Alkylating 2,6-Di(bromomethyl)naphthalene (IX)[a] with $[CH_2CO_2\text{-}t\text{-}Bu]^-Li^+$

expt	mol of $LiCH_2CO_2$-*t*-Bu per mol of dibromide	mol of HMPA per mol of dibromide	temp, °C	time, min	yield, % XII	yield, % XIII
1	3	0[b]	RT[c]	10	38	
2	3	0	−5	225	32	
3	3	3	−5	80	40	
4	3	3	−15	30	50	
5	2	2	−15	30	62	19
6	2.5	2.5	−23	20	64	1
7	2	2	−23	60	64	13
8	2.5	2.5	−75	45	70	2

[a] All experiments were performed using 3 mmol of IX in ca. 30 mL of THF. [b] Me_2SO was added to the dibromide solution. The dibromide-Me_2SO molar ratio was 1:7. [c] Room temperature.

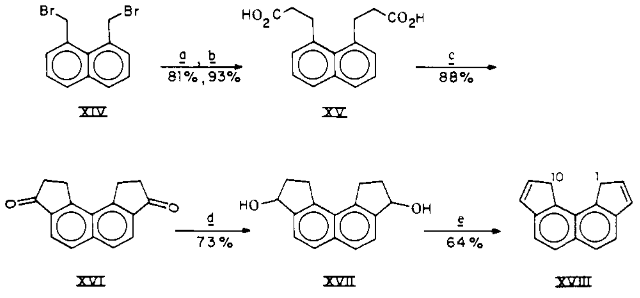
and, following steps analogous to those used to alkylate 1,2-dibromoethylbenzene,[23] the yield of XII (eq 2) was 23%.



Further experiments showed that this yield can be increased by adding the lithium enolate to the dihalide, rather than the halide to the enolate, by adding hexamethylphosphoric triamide (HMPA) to the tetrahydrofuran (THF) solutions of IX,[24] and by keeping the temperature low. The experiments are summarized in Table I. On a 40-mmol scale, the best conditions displayed (those of experiment 8) consistently give yields of 61-68%.

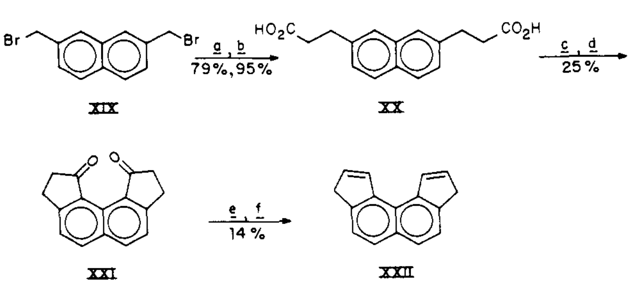
Synthesis and Reactions of VII. When applied to 1,8-di(bromomethyl)naphthalene[25] (XIV), this procedure gives an 81% yield of the diester, and the steps summarized[26] in Scheme II then lead to hydrocarbon XVIII. The ^1H and ^{13}C NMR spectra, described in the Experimental Section, show this hydrocarbon to be homogeneous and are in accord with the structure pictured.

Scheme II



(a) $LiCH_2CO_2$-*t*-Bu/THF-HMPA; (b) $NaOH/CH_3OH\text{-}H_2O$; (c) PPA; (d) Dibal/$C_6H_5CH_3$; (e) *p*-TsOH/C_6H_6.

Scheme III

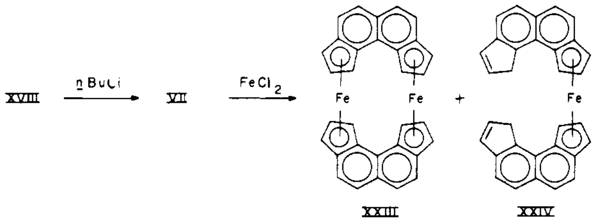


(a) $LiCH_2CO_2$-*t*-Bu/THF-HMPA; (b) $NaOH/CH_3OH\text{-}H_2O$; (c) $(COCl)_2/C_6H_6$; (d) $AlCl_3/CH_3NO_2$; (c) Dibal/$C_6H_5CH_3$; (f) *p*-TsOH/C_6H_6.

A double-bond isomer of XVIII, XXII, was similarly synthesized as summarized[26] in Scheme III, and, although we examined this synthesis only briefly, because the yields in two of the steps were low, we did note an interesting feature of the product, that the ^1H NMR of the olefinic protons pointing toward one another is at very low field like the analogous resonance of the 4 proton in phenanthrene.[27] While the positions of the other resonances in XXII and those in XVIII resemble those in indene,[28] this one resonance is at δ 7.74, at lower field even than the resonances of XXII's aromatic protons, and 0.64 ppm to lower fields than the resonance of the analogous olefinic proton in XVIII.

With *n*-butyllithium in THF at −78 °C, hydrocarbon XVIII reacts to form dianion VII, identified by its reaction with $D_2O + CF_3CO_2D$ giving dicyclopenta[*a*,*h*]naphthalenes (XVIII) deuterated at positions 1 and 10. The intensities of the methylene proton resonances in this deuterated material correspond to 1.94 protons, whereas in the precursor XVIII they were measured as 3.92. The mass spectrum shows the distribution[29,31] of deuterium atoms: 3 (XVIII-d_0), 13 (XVIII-d_1), 77 (XVIII-d_2), and 7% (XVIII-d_3). The absence of double-bond isomers is notable and might indicate less crowding of opposed hydrogens on carbons in peri positions when the carbons are tetrahedrally hybridized rather than trigonally.[32]

With $FeCl_2$, VII gives bis(dicyclopenta[*a*,*h*]naphthalenylene)diiron (XXIII) in about 60% yield, along with small amounts of a material containing only one iron atom, probably XXIV, which was isolated by column chromatography (eq 3).



These iron compounds are very difficult to characterize. Although XXIII is soluble in CH_2Cl_2, CS_2, THF, and benzene, attempts to crystallize it from benzene, CH_2Cl_2, and CS_2 failed. Sublimation at 220 °C and 10^{-5} Torr decomposed it, and it was therefore purified by precipitation from THF solution with *n*-hexane. The product obtained in this way exhibits a mass spectrum upon electron impact (24 eV) in which the most intense peaks are those attributable to the monocation of XXIII, and the ratio of the intensities of the parent peaks at *m/e* 517 and 516 are those expected: calcd, 41%; found, 45%. No peaks in the range $520 \leq m/e \leq 1000$ are observed in this spectrum nor in the range $1000 \leq m/e \leq 2000$ in a similar spectrum determined using an ionizing voltage of 30 eV. Attempts to record ^1H NMR spectra in CD_2Cl_2, CS_2, and toluene-d_8 were unsuccessful. The only NMR spectra observed were very broad, just like the resonances of bis(fulvalene)diiron

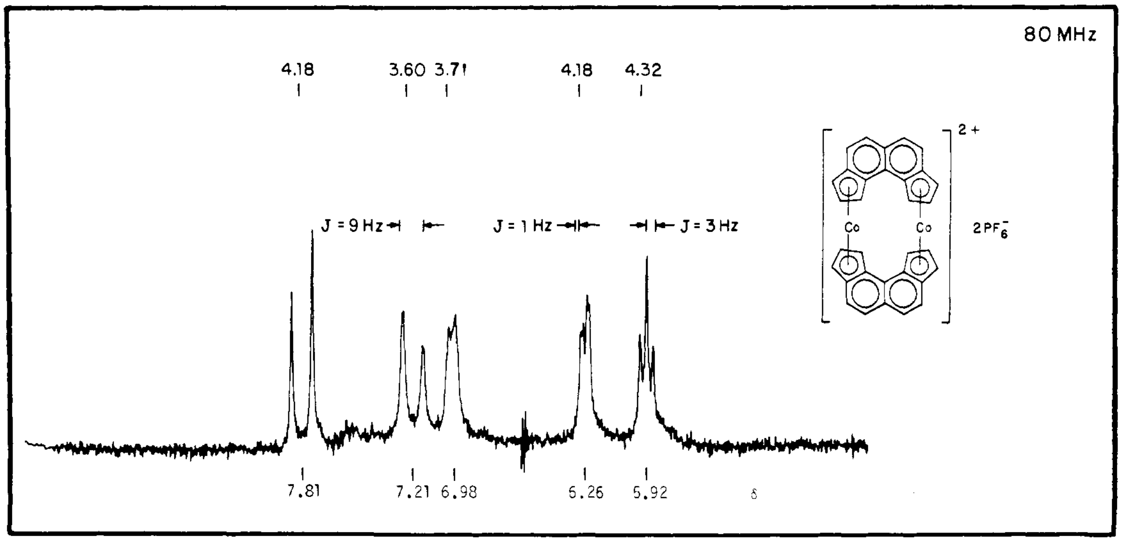


Figure 1. ^{1}H NMR spectrum of XXV (Fourier transform spectroscopy, 135 scans) in CD_3CN at room temperature. Chemical shifts are below the peaks and intensities above.

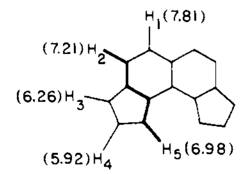
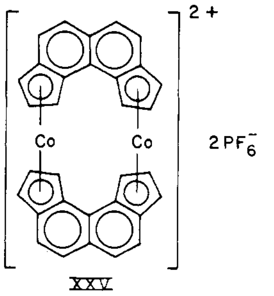


Figure 2. Assignment of ^{1}H NMR chemical shifts (δ) for XXV.

dication in CD_3CN,[33] attributable to electron exchange with small amounts of the ferricenium monocation (that might be present as an impurity) broadening the resonances beyond recognition. Attempts to avoid the broadening by reducing any ferricenium ion in samples in THF-d_8 using sodium, zinc, and ascorbic acid were ineffective. Because of these difficulties, the experiments to determine the sandwich's NMR spectrum were repeated with another metal derivative of dianion VII that was synthesized so as to resist oxidation more.

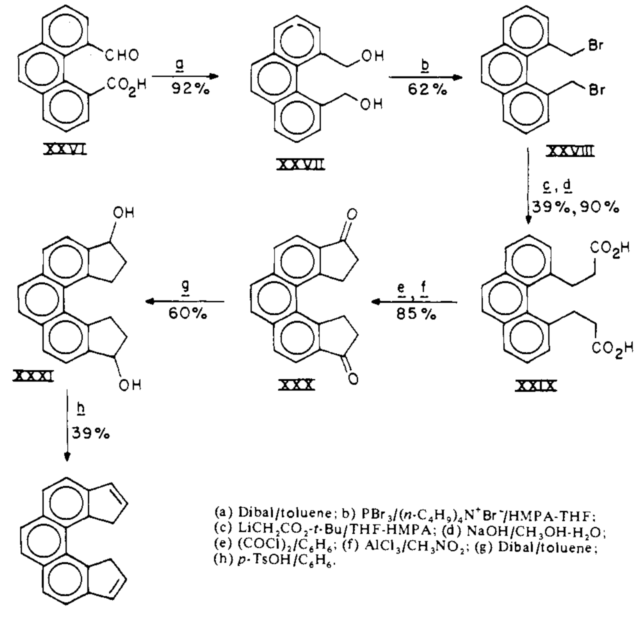
This was the biscobalticinium ion XXV, which can be made



XXV

from VII, prepared as above, and hexaamminecobalt(III) trichloride. Although the yield is only 4%, other procedures for preparing cobalticinium salts, by oxidizing the dicobalt(II) analogue of XXIII (prepared from VII and $CoBr_2$) with air[13] or by combining VII and $Co(acac)_3$,[34] give none. The ^{1}H NMR spectrum, displayed as Figure 1, is in accord with the structure, and it shows that, of the two possible stereoisomers, one in which the rings are eclipsed and one in which they are apart, only a single one is present. (The spectrum is too simple for both isomers to be there.) The peak assignments summarized in Figure 2 are based in part on the spectrum of bis(indenyl)cobalt(III) nitrate,[35] in which the metallocene resonances appear at δ 6.20 (a doublet) and 5.80 (a triplet, $J = 2.6$ Hz), and in part on the expectation that the resonance of H_5, like that of the "inside" protons of phenanthrene[27] and hydrocarbon XXII, would appear at particularly low field.

Scheme IV



(a) Dibal/toluene; b) $PBr_3/(n\text{-}C_4H_9)_4N^+Br^-$/HMPA-THF; (c) $LiCH_2CO_2\text{-}t\text{-}Bu$/THF-HMPA; (d) $NaOH/CH_3OH\text{-}H_2O$; (e) $(COCl)_2/C_6H_6$; (f) $AlCl_3/CH_3NO_2$; (g) Dibal/toluene; (h) $p\text{-}TsOH/C_6H_6$.

Supporting the assignment of H_5 to the resonance at δ 6.98 is the complexity of this resonance compared to that at δ 6.26, attributable to a long-range zigzag coupling between H_2 and H_5.[28a,36] Consonant is the height of one portion of the aromatic AB pattern (that at δ 7.21) being smaller than the other (that at δ 7.81), from which it follows that the former is the resonance of H_2.

Synthesis and Reactions of VIII. Similar methodology, summarized in Scheme IV, converts 5-formyl-4-phenanthroic acid (XXVI) into hydrocarbon XXXII.

Step (a) had been carried out previously using $LiAlH_4$ and the ethyl[37] or methyl[38] esters, but $(i\text{-}C_4H_9)_2AlH$ does not require preparation of the esters and gives better yields. Step (b), when carried out as described before using PBr_3 in benzene-pyridine,[38] gives four times as much of the cyclic ether XXXIII as of the desired dibromide XXVIII, and adding small amounts of tetrabutylammonium bromide, which suppresses an analogous cyclization during the preparation of XIV,[25] is not an effective remedy. However, by changing the solvent from CH_2Cl_2 to HMPA-THF and adding large amounts of the tetrabutylammonium bromide, the yield of dibromide XXVIII

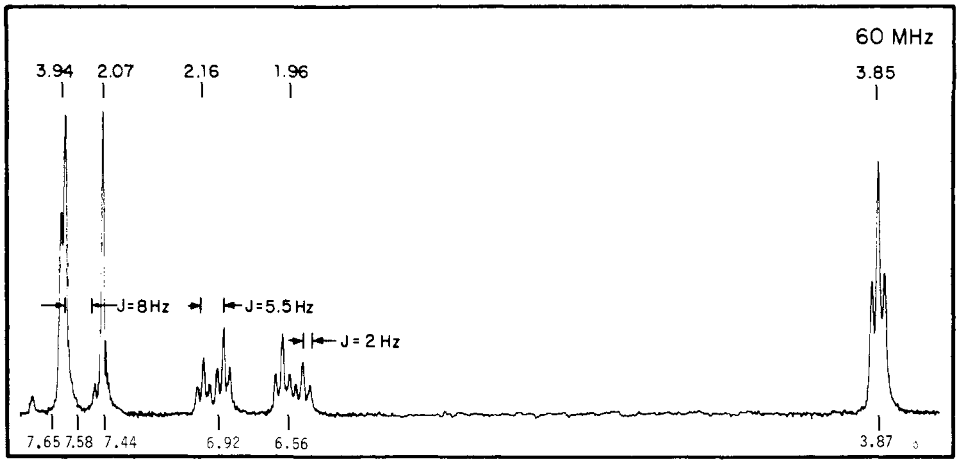
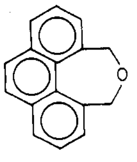


Figure 3. ^{1}H NMR spectrum of XXXII in CS$_2$ at 35 °C. The NMR frequency is 60 MHz and tetramethylsilane was the internal standard. Chemical shifts are below the peaks and intensities above.

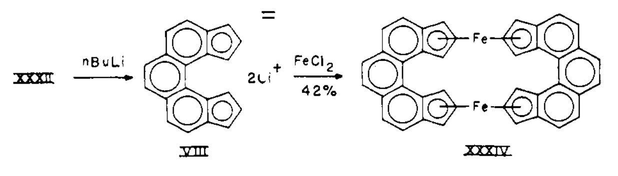


XXXIII

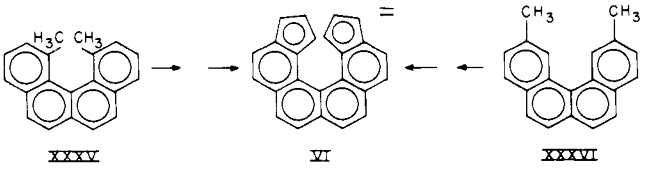
can be raised to 68% and the amount of ether XXXIII reduced to 17%. Step (c), the alkylation with *tert*-butyl lithioacetate, does not work well under the conditions effective for IX, XIV, and XIX (those in experiment 8 in Table I). A considerable amount (50% yield) of the monoalkylated product, the bromo ester, is obtained under these conditions and the yield of diester is low (11% yield). However, with a 100% excess of the enolate in THF in the presence of 20 mol of HMPA per mol of dibromide, the yield increases to 39%.

Hydrocarbon XXXII's ^{1}H NMR spectrum (Figure 3) proves its structure (the peak assignments are in the Experimental Section), shows it to be homogeneous, and reveals it to be either planar or to interconvert nonplanar conformers at least a few times per second at 35 °C. If the molecule had been nonplanar, the methylene hydrogens would have been nonequivalent and their resonances more complex. If double-bond isomers had been present, there would have been more peaks, and especially an unusual one like that observed (see above) in the spectrum of XXII. The substance's homogeneity is also indicated by its ^{13}C NMR spectrum (see Experimental Section) consisting of the expected ten peaks.

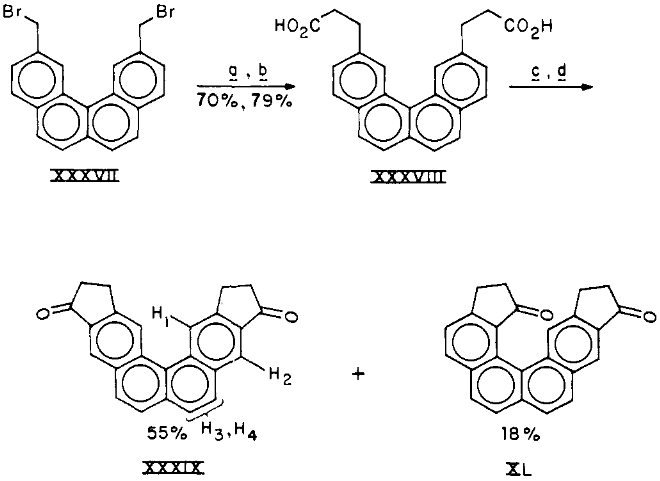
This hydrocarbon in THF reacts with *n*-butyllithium followed by ferrous chloride to give a reddish-brown substance whose mass spectrum appears appropriate for the dimer XXXIV (eq 4). There is a prominent parent peak at *m/e* 616, and the ratio of the intensities of the peaks at *m/e* 617 and 616 is appropriate (calcd, 50%; found, 44%). However, the peak at half this value of *m/e* is negligibly small, although the analogous peaks in the mass spectra of XXIII and bis(*as*-indacenylene)diiron[10b] are prominent. The material is soluble in THF, CH$_2$Cl$_2$, and CS$_2$, but attempts to measure its ^{1}H NMR spectra fail, just as they do for XXIII, and so do attempts to crystallize it. Experiments to make a cobalticinium analogue, by combining XXXII and *n*-butyllithium and then adding [Co(NH$_3$)$_6$]Cl$_3$ and NaPF$_6$, were also unsuccessful.



Scheme V



Scheme VI

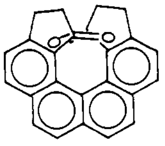


(a) LiCH$_2$CO$_2$-*t*-Bu/THF-HMPA; (b) NaOH/H$_2$O-CH$_3$OH; (c) COCl$_2$/C$_6$H$_6$; (d) AlCl$_3$/CH$_2$Cl$_2$

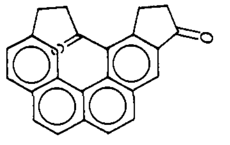
The iron compound seems to be easily destroyed, possibly by oxidation, and steps to purify it by dissolving it in THF and precipitating it with *n*-hexane do not give material with a satisfactory combustion analysis. Nevertheless, it does appear to be the ferrocene XXXIV, and it does not behave like a polymer.

Approaches to VI. Scheme V indicates two approaches, analogous to the routes that give the lower homologues VII and VIII, to the [6]helicene VI, one starting from 1,2-dimethylbenzo[*c*]phenanthrene (XXXV),[39] the other from its 2,11-dimethyl isomer (XXXVI).[40] The first approach remains unsuccessful because hydrocarbon XXXV resists the entry of bromine atoms into both its benzylic positions. Thus, combining it with NBS in the presence of light and peroxides gives only the monobromo derivative. The isomeric hydrocarbon, XXII, in contrast, is brominated easily,[40] and the transformations summarized in Scheme VI can then be effected. Unfortunately, the Friedel–Crafts reaction does not give any of the ketone having VI's ring system, but gives only XXXIX and XL. This is surprising in that polyacenes are usually substituted by electrophiles much more quickly at α positions than at β; witness, for example, the transformations of X and XX, both of which give the α-acylation products XI and XXI, even in nitromethane,[41] a solvent that favors β-acylation.[42] Presumably the cyclizations in Scheme VI give the β-acylation products because the α positions are crowded sterically.

The structures are assigned to the ketones XXXIX and XL on the basis of their ^{1}H NMR, IR, and mass spectra. In particular, the ^{1}H NMR spectrum of the ketone assigned structure XXXIX is extraordinarily simple. In the aromatic region there is a singlet at δ 9.12 assigned to the resonance of H_1, a singlet at δ 8.45 assigned to H_2, and an AB quartet at δ 8.04 and 7.82 (7-Hz splitting) assigned to H_3 and H_4. The position of the resonance assigned H_1 is characteristic of benzo[*c*]phenanthrenes[43] and implies that the structure cannot be XLI. The ^{1}H NMR spectrum of the ketone assigned structure XL is much more complex, and the only immediately recognizable feature is the equality of the intensities of the aromatic and methylene protons' resonances. The carbonyl stretching frequency in its infrared spectrum (1700 cm^{-1}, in KBr) is similar to that in XXXIX (1710 cm^{-1}, in KBr) and in the other indanones described above, and different from that in benzocyclooctanone (1675 cm^{-1}),[44] implying that the unsymmetrical ketone is not XLII, although the tensions in this ring system might displace the absorption.



XLI

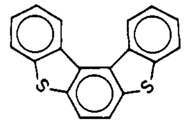


XLII

Discussion

The procedures developed here are effective for preparing hydrocarbons XVIII, XXII, and XXXII, in which two cyclopentene rings are fused to an aromatic system. However, these [4]- and [5]helicenes are not large enough to block access by two metal atoms to one face.

This is not surprising, for, although the benzenoid [5]helicene can be resolved at room temperature into optical antipodes,[18a,45] an analogue, XLIII, which like VIII has two five-membered rings, seemingly cannot be,[18a,46] and the extent to which helicenes overlap should depend primarily on the number and sizes of the rings that are fused and only secondarily on their arrangement.[18b] This means that, if helical dianions are to give polymeric metallocenes, they have to be larger than VIII. The synthesis of such materials remains for future research.



XLIII

Experimental Section

General. Infrared spectra were determined using Perkin-Elmer 137, 421, and 621 spectrophotometers and a JASCO IRA-1, ^{1}H NMR spectra using Varian A-60, T-60, and HA 100, Bruker WP-80, and Perkin-Elmer R 32 spectrometers, ^{13}C NMR spectra using a JEOL PS-100 spectrometer, and mass spectra using JEOL MS-07 and Finnigan 3300 mass spectrometers. (CI stands for chemical ionization, EI for electron impact.) Melting points, determined on a Thomas-Hoover melting point apparatus, are not corrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

In the experiments below, the tube for solid addition is a ₸ 14/20 male joint to which is attached a glass tube with a 105° bend. The Normag funnel for adding solids was purchased from Otto Fritz G.m.b.H., 6238 Hofheim am Jaunus, P.O. Box 1269, Federal Republic of Germany, and features a Teflon screw between the funnel and the reaction flask.

Alkylation of 2,6-Di(bromomethyl)naphthalene. In a 1000-mL round-bottomed, three-necked flask, equipped with a low-temperature thermometer, a mechanical stirrer, and an addition funnel, were placed 2,6-di(bromomethyl)naphthalene[47] (9.42 g, 30 mmol) and HMPA (13.4 g, 75 mmol), and THF (350 mL) was then distilled in from $LiAlH_4$. The dibromide was dissolved with sitrring and the flask was immersed in a dry ice-acetone bath. (Some dibromide precipitated.) To the vigorously stirred mixture, lithium enolate solution (ca. 75 mmol)[23] was added in drops at a rate that maintained the temperature below −70 °C. The addition took 20 min, and, as the mixture was stirred at −78 °C for an additional 60 min, it slowly cleared. The yellow solution was warmed to −5 °C, quenched with 100 mL of dilute hydrochloric acid (1:9), and poured into 100 mL of saturated aqueous NaCl, and the layers were separated. The aqueous layer was extracted with ether (3 × 200 mL), and the combined organic solutions were washed four times with 1 N HCl (ca. 800 mL total) and dried over $MgSO_4$. Evaporation gave 12.58 g of yellow semisolid, which after chromatography on silica (400 g), eluting with CH_2Cl_2, gave 7.92 g of white crystals (20.3 mmol, 68%), mp 77-78 °C. A sample was sublimed (115 °C, 0.1 mmHg): mp 78-79 °C; ^{1}H NMR ($CDCl_3$) δ 7.50 (m, 5.73 H), 3.07 (t, 3.88 H), 2.62 (t, 3.70 H), 1.39 (s, 18.68 H). In a similar experiment on a 40-mmol scale, the yield was 61%, and in three experiments on a smaller scale (3 mmol), 69, 70, and 79%.

Di-*tert*-butyl Naphthalene-1,8-dipropionate. 1,8-Di(hydroxymethyl)naphthalene was prepared from naphthalic anhydride in 74% yield:[48] mp 155.5-157 °C (lit. 154.5-155, 158 °C);[48,49] ^{1}H NMR (Me_2SO-d_6) δ 8.01-7.36 (m, 5.99 H), 5.18 (m, 6.01 H); (Me_2SO-d_6 + D_2O) δ 8.04-7.38 (m, 6.07 H), 5.16 (s, 3.93 H). It was converted on a 0.2-mol scale into 1,8-di(bromomethyl)naphthalene (IV), using the method of Hunter and Stothers,[25] mp 129-130 °C (lit. 130,[50a] 129-130 °C[50b]), yield 80%.

A solution of 1,8-di(bromomethyl)naphthalene (940 mg, 3 mmol) in 30 mL of THF and 1.3 mL (1.34 g, 7.5 mmol) of HMPA was placed in a 100-mL round-bottomed flask fitted with an argon inlet and a stirring bar. The solution was stirred at −78 °C and freshly prepared *tert*-butyl lithioacetate (7.5 mmol) in 10 mL of THF was added in drops over a period of 10 min, stirred at −78 °C for 45 min, warmed to 0 °C, and quenched with 10 mL of 1 N HCl. Pouring onto 20 mL of saturated brine, extracting with ether, washing with 1 N HCl (three times), and drying ($MgSO_4$) gave crude product, which was chromatographed on 50 g of silica gel with *n*-pentane-ether (9:1 v/v). Obtained was 950 mg (2.44 mmol, 81%) of colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.23-7.77 (m, 6.01 H), 3.48 (m, 3.74 H), 2.53 (m, 4.00 H), 1.40 (s, 18.25 H).

Naphthalene-1,8-bispropionic Acid (XV). The diester (950 mg, 2.45 mmol) was refluxed (20 h) with NaOH (400 mg, 10 mmol) in 20 mL of methanol-water (1:1 v/v). After extraction with ether, concentrated HCl precipitated the product, which was washed and dried, yield 630 mg (2.32 mmol, 95%), mp 186-188 °C. In two preparations on a larger scale (40 mmol) the combined yields of the acid from the dibromide without purification of the intermediate ester were 92 and 93%. ^{1}H NMR (Me_2SO-d_6): δ 7.78 q, 7.37 d, 3.45 broad t, 2.52 broad t. Absorption due to Me_2SO-d_5 partially obscure a peak at δ 2.52, making integration impossible. IR (KBr, cm^{-1}): 3065 m, 3020 m, 1710 vs, 1690 vs.

1,2,9,10-Tetrahydrodicyclopenta[*a*,*h*]naphthalene-3,8-dione (XVI). In a 1-L, three-necked, round-bottomed flask, fitted with a mechanical stirrer, a nitrogen inlet, and a thermometer, were placed 258 g of polyphosphoric acid and 10 g (36.76 mmol) of powdered XV. The flask was immersed in oil preheated to 85 °C and stirred for 1.5 h. Crushed ice (500 g) and water (2 L) precipitated crude product, which was washed and dried in vacuo over P_2O_5 for 11 h. Obtained was 8.6 g of yellow powder. One gram of this product was deposited on silica gel (10 g) by refluxing in $CHCl_3$ (100 mL) and the solvent evaporated. Chromatography on silica gel (50 g, ether-methylene chloride, 3:7 v/v) eluted 890 mg (3.77 mmol, 88%) of purified product (yellow powder). It crystallized from *o*-dichlorobenzene as fine, shiny plates that decomposed without melting at 320-330 °C: ^{1}H NMR ($CDCl_3$) δ 7.90 (s, 4.26 H), 3.77 (t, J = 5.5 Hz, 4.06 H), 2.87 (t, J = 5.5 Hz, 3.68 H); IR (KBr, cm^{-1}) 1710 vs; MS (CI, CH_4, peaks >15% except parent group) *m/e* (rel intensity) 236 (M, 5), 237 (M + 1, 100), 238 (M + 2, 17), 239 (M + 3, 2). The cyclization could also be effected using the acid chloride of XV (32 mmol) and $AlCl_3$ in CH_3NO_2 (19 h, room temperature), but the yield was lower (60%).

1,2,9,10-Tetrahydrodicyclopenta[*a,h*]naphthalene-3,8-diols (XVII). Diketone XVI (740 mg, 3.14 mmol) was added during 5 min from a funnel for adding solids to a solution of Dibal (9.41 mmol) in toluene (18 mL) in a 50-mL, round-bottomed, three-necked flask, equipped with a stirring bar, reflux condenser (argon inlet), and stopcock fitted with a septum. After the solution was stirred and heated until solid had dissolved, ethyl acetate (1 mL) was added, and the solution was poured onto ice. Concentrated aqueous HCl (10 mL) was added and the mixture extracted with ether (3 × 50 mL) and ethyl acetate (3 × 50 mL). The combined extracts on washing, drying ($MgSO_4$), and evaporation yielded 550 mg (2.29 mmol, 73%) of XVII. TLC (silica gel, methylene chloride-ethyl acetate, 4:1 v/v) suggested that two diols formed (R_f 0.15 and 0.27): ^{1}H NMR (Me_2SO-d_6) δ 7.72 and 7.45 (AB system, J = 9 Hz), 5.18 broad t, 4.49 broad s (removed by D_2O), 3.38 broad m, 2.32 broad m, 1.92 broad m; IR (KBr, cm^{-1}) 3300 s.

$LiBH_4$ in $(CH_3)_2CHOH$[51] gave XVII in 66% yield. $LiAlH_4$ in boiling ether (8 h) or THF (6 h) returned the starting diketone.

1,10-Dihydrodicyclopenta[*a,h*]naphthalene (XVIII). Diols XVII (480 mg, 2.00 mmol) were stirred (1 h) under argon with *p*-TsOH (7 mg) in benzene (100 mL) in a bath at 62 °C. Washing, drying ($CaCl_2$), concentration, and chromatography on silica gel (100 g) with *n*-pentane gave 260 mg (1.28 mmol, 64%) of white needles, mp 168–169 °C. A sample crystallized from CS_2–ether (1:1) at −78 °C formed long, frail needles, mp 175–177 °C. In another experiment on a larger scale (6.08 mmol), the crude product was purified by sublimation at 87–95 °C (10^{-4}–10^{-6} mmHg). The yield was only 27%. ^{1}H NMR ($CDCl_3$): δ 7.90 and 7.62 (an AB quartet, J = 9 Hz, 4.07 H), an AMX_2 system 7.10 (d of t, J_1 = 6, J_2 = 1.5 Hz, 2.08 H), 6.80 (d of t, J_1 = 6, J_2 = 1.5 Hz, 1.93 H), 3.77 (t, J = 1.5 Hz, 3.92 H). That the resonance at δ 7.90 is that of the proton nearer the five-membered ring is implied by decoupling at δ 3.77 sharpening this resonance and not the one at δ 7.62. ^{13}C NMR ($CDCl_3$, ppm): 41.1, 119.3 (2 peaks, revealed by off-resonance decoupling), 128.0, 130.6, 132.5, 134.2, 137.8, 142.5. IR (KBr, cm^{-1}): 3089 vw, 3055 w, 2925 w, 2889 w, 2857 vw, 1606 w, 1561 w, 1519 w, 1396 w, 1385 m, 1375 w, 1361 m, 1330 shoulder, 1323 m, 1314 m, 1248 w, 1222 w, 1122 w, 1102 w, 1019 w, 981 shoulder, 974 m, 918 m, 835 s, 781 m, 776 s, 724 w, 708 s, 618 w, 598 s. MS (CI, methane, peaks >5%) *m/e* (rel intensity): 204 (M, 17), 205 (M + 1, 100), 206 (M + 2, 16), 233 (M + 15, 15).

Anal. Calcd for $C_{16}H_{12}$: C, 94.07; H, 5.93. Found: C, 93.85; H, 6.15.

Dilithium Dicyclopenta[*a,h*]naphthalenide (VII). To a solution of 40 mg (0.20 mmol) of XVIII in 5 mL of THF, 0.20 mL of 2.2 M *n*-butyllithium in *n*-hexane (0.43 mmol) was added at −78 °C. A yellow precipitate formed which dissolved, forming a yellow solution of VII, when the mixture was stirred at −78 °C for 20 min and then warmed to room temperature.

1. Reaction with Deuterium Oxide. The solution prepared above was quickly poured under argon into a rapidly sitrred solution of 0.2 mL of $(CF_3CO)_2O$ in 10 mL of D_2O. Extracting with ether, washing, drying ($MgSO_4$), stripping the solvents, and chromatographing on silica gel (40 g) with 2% ether–98% petroleum ether yielded crystalline deuterated XVIII: ^{1}H NMR ($CDCl_3$) and AB quartet δ 7.82 (1.96 H) and 7.57 (2.22 H), 7.05 (d of d, J_1 = 6, J_2 = 1.5 Hz, 1.94 H), 6.73 (d of d, J_1 = 6, J_2 = 1.5 Hz, 1.94 H) 3.74 (m, 1.94 H); MS (CI, isobutane, average of 60 scans, M + 57 peaks) *m/e* (rel intensity) 260 (0.81), 261 (4.33), 262 (16.87), 263 (100), 264 (33.09), 265 (6.07); MS of undeuterated XVIII under the same instrument conditions (average of 45 scans) *m/e* (rel intensity) 259 (2.86), 260 (4.35), 261 (100), 262 (22.84), 263 (13.67). Accordingly,[29,31] the distribution of deuteriums is XVIII-d_0, 3%; XVIII-d_1, 13%; XVIII-d_2, 77%; XVIII-d_3, 7%.

2. Reaction with $FeCl_2$. Bis(dicyclopenta[*a,h*]naphthalenylene)diiron (XXIII). Each compartment of a flame-dried, argon-filled double Schlenk tube[52] was equipped with a stirring bar and stopcock fitted with a serum cap. In the left compartment were placed anhydrous ferrous chloride (95% from ROC/RIC, 187 mg, 1.47 mmol) and 4 mL of THF; in the right compartment was placed a solution of hydrocarbon XVIII (250 mg, 1.22 mmol) in 9 mL of THF, which was transformed into VII with 1.08 mL of 2.6 M *n*-butyllithium in *n*-hexane (2.82 mmol) as described above and then poured at room temperature onto the ferrous chloride slurry. The deep red-black mixture was then stirred at room temperature for 1.5 h, the solvents were removed by distillation at reduced pressure, and the residue was extracted under argon with two 30-mL portions of argon-purged CS_2. The extracts were filtered. The residue, insoluble in carbon disulfide (100 mg) after drying in vacuo for 2 h, did not show any IR peaks characteristic of ferrocenes, but only large bands, seemingly $-$OH vibrations. The carbon disulfide filtrate was evaporated, and the black residue obtained was dried in vacuo for 2 h, giving 225 mg (ca. 0.36 mmol, 60%). According to the TLC analysis (silica gel, hexanes CH_2Cl_2, 3:1 v/v) the crude product contained some starting material, XVIII, and the monoiron compound XXIV. Three unsuccessful attempts were made to purify it by crystallization from benzene, CH_2Cl_2, and CS_2. The product was, however, purified considerably by dissolving it in ca. 2 mL of THF and precipitating it with *n*-hexane. The precipitate was washed with *n*-hexane and dried in vacuo for 12 h, yielding 70 mg of a brown powder, soluble in CH_2Cl_2, THF, benzene, and CS_2: MS (EI, 76 V, peaks >15% reported) *m/e* (rel intensity) 200 (24), 201 (33), 202 (100, saturation), 203 (78), 204 (44), 258 (77), 259 (17), 462 (37), 463 (19), 514 (12), 515 (6), 516 (100), 517 (51), 518 (13), 519 (3.5); MS (EI, 24 V, peaks >15% reported) *m/e* (rel intensity) 204 (20), 462 (31), 463 (20), 514 (17), 515 (8), 516 (100, parent and base peak), 517 (45), 518 (12), 519 (3); IR (KBr, cm^{-1}) 3086 vw, 3037 w, 2921 w, 1518 w, 1495 w, 1453 m, 1317 w, 1335 m, 1277 w, 1232 w, 1172 w, 1134 vw, 1097 vw, 1030 m, 885 w, 836 s, 821 s, 723 w, 707 w, 612 broad m.

A 40-mg sample of crude product obtained similarly, when chromatographed on 20 g of silica gel with argon-purged hexanes–CH_2Cl_2 (7:3 v/v), gave starting material (XVIII), identified by TLC (silica gel, hexanes–methylene chloride, 3:1 v/v) and a red, crystalline compound, probably bis(dicyclopenta[*a,h*]naphthalenyl)iron (XXIV): MS (EI, 24 V, peaks >10%) *m/e* (rel intensity) 202 (17), 203 (20), 460 (12), 461 (8), 462 (100, parent and base peak), 463 (39), 464 (11), 465 (2); IR (KBr, cm^{-1}) 3045 w, 3005 w, 2925 w, 2878 w, 2836 w, 1595 w, 1568 w, 1513 w, 1448 w, 1428 w, 1389 w, 1377 w, 1356 w, 1337 w, 1309 w, 1275 w, 1245 w, 1227 w, 1162 w, 1060 w, 1030 m, 1022 m, 973 w, 941 m, 913 w, 906 w, 892 w, 824 s, 812 w, shoulder 800 m, 780 w, 758 m, 709 m, 670 m.

3. Reaction with $[Co(NH_3)_6]Cl_3$. Bis(dicyclopenta[*a,h*]naphthalenylene)dicobalt(III) Hexafluorophosphate (XXV). In the left compartment of the Schlenk tube were placed THF (2 mL) and hexaamminecobalt(III) trichloride (143 mg, 0.55 mmol) that had been prepared according to Bjerrum and McReynolds[53] in 92% yield (lit. 85%). The solution in the right compartment, prepared as above from 102 mg (0.50 mmol) of XVIII, 1.10 mmol of *n*-butyllithium, and 16 mL of THF, was poured into the slurry of the cobalt salt in THF, which was at −78 °C. The deep green mixture was then stirred at room temperature for 33 h. The solvents were stripped and the residue was dried in vacuo for 1 h and then extracted with 2 × 10 mL of dilute (1:9) aqueous HCl and with 2 × 10 mL of acetone. The acetone extracts were evaporated to dryness, and the residue was dissolved in water and filtered. The combined aqueous filtrates were concentrated to 40 mL and treated with a solution of 0.7 g of $NaPF_6$ in 1 mL of water. The resulting reddish precipitate was collected, washed with water, and dried in vacuo for 19 h, yielding 7.5 mg (9.2 μmol, 4%). Crystallized from ca. 2 mL of acetone this gave 2.3 mg of small, dark prisms: ^{1}H NMR (CD_3CN) δ 7.81 and 7.21 (an AB quartet, J = 9 Hz, 7.78 H), 6.98 (m, 3.71 H), 6.26 (d of d, J_1 = 3, J_2 = 1 Hz, 4.18 H), 5.92 (t, J = 3 Hz, 4.32 H); IR (KBr, cm^{-1}) 3155 vw, 3120 w, 3025 w, 2927 w, 2851 vw, 1603 w, 1580 w, 1506 w, 1492 w, 1452 w, 1437 w, 1384 w, 1184 w, 899 shoulder, 887 shoulder, 835 s, 779 w, 751 w, 737 w, 695 m, 623 w, 593 w, 553 m, 489 w, 472 w, 418 w, 406 w.

Attempt to effect the synthesis using either $Co(acac)_3$ or $CoBr_2$ followed by oxidation were not successful. Thus combining XVIII (102 mg, 0.5 mmol) in 7 mL of THF with *n*-C_4H_9Li in hexane (1.05 mmol) at −78 °C and pouring onto $Co(acac)_3$ (196 mg, 0.55 mmol) in 3 mL of THF gave, after 1.5 h at room temperature and removal of solvents, a material that was insoluble in benzene, dilute aqueous HCl, and acetone.

Following the procedure used to make XXIII, the hydrocarbon XVIII (204 mg, 1 mmol) and $CoBr_2$ (241 mg, 1.1 mmol) gave 110 mg (42% yield) of the cobalt analogue of XXIII: MS (EI, 60 eV) *m/e* (rel intensity) 189 (16), 200 (10), 201 (12), 202 (37), 203 (31), 204 (30), 205 (16), 206 (13), 207 (35), 261 (34), 281 (12), 398 (14), 399 (11), 522 (M, 100), 523 (M + 1, 33), 524 (M + 2, 6). Suspended in water, this was oxidized with a stream of air, filtered, concentrated, and combined with aqueous $NaPF_6$. The precipitate, after washing, drying, and storing, decomposed.

2,7-Di(bromomethyl)naphthalene (XIX). 2,7-Dimethylnaphthalene was prepared on a 0.6-mol scale,[54] mp 96–97 °C (lit. 95,[54] 96–97

Table II, Ratios of Products Formed from XXVII[a] and PBr_3[b]

expt	solvent	molar ratio PBr_3/XXVII	molar ratio n-$Bu_4N^+Br^-$/XXVII	molar ratio XXVIII/XXXIII[c]	yield XXVIII, %
1	benzene (20 mL)	2.2	0	2:9	
2	CH_2Cl_2 (120 mL)	2.2	0.33	1:4	20
3	CH_2Cl_2 (15 mL)	3	2	3:7	
4	HMPA (10 mL)-THF (10 mL)	3	4	4:1	62
5	HMPA (0.6 mL)-THF (20 mL)	3	8	9:2	59

[a] 0.8 mmol in experiments 1 and 3, 22 mmol in experiment 2, and 0.4 mmol in experiments 4 and 5. [b] Reactions were effected at −5 °C, except that the experiment in benzene was run at 48 °C, conditions that have previously been said to give XXVIII (ref 38). [c] Listed are the ratios of intensities of ^1H NMR absorptions at δ 5.05 and 4.9, except in experiment 2, where it is the ratio of the moles of products isolated.

°C[55]), yield 92% (lit.[54] 87%). Brominating 10 g according to the procedure of Baker et al.[55] gave material that was purified by a simple procedure. Succinimide was washed out with 1.5 N NaOH (500 mL) and H_2O (500 mL), and the residue crystallized from benzene gave 9.21 g (29.3 mmol, 46% yield): mp 147–148 °C (reported 147 °C);[56] ^1H NMR ($CDCl_3$) δ 7.95–7.45 (m, 5.99 H), 4.65 (s, 4.01 H).

Naphthalene-2,7-bispropionic Acid (XX). Dibromide XIX (0.94 g, 3 mmol) was alkylated by the same procedure used for XIV, giving after chromatography 910 mg (2.37 mmol, 79%) of ester: ^1H NMR ($CDCl_3$) δ 7.73, 7.29 (an AB quartet, J = 8.5 Hz), 7.58 s (total integration 6.11 H), 3.05 (t, J = 7 Hz, 4.07 H), 2.58 (t, J = 7 Hz, 4.36 H), 1.42 (s, 17.45 H).

This was hydrolyzed by the procedure used to make XV, yield 95%.

2,3,8,9-Tetrahydrodicyclopenta[*a,h*]naphthalene-1,10-dione (XXI). Acid XX (300 mg, 1.10 mmol) was combined with aqueous NaOH and dried, giving the salt, which was converted to the acid chloride with oxalyl chloride in benzene–pyridine. Dissolved in 20 mL of nitromethane, it was cooled in ice–salt (−6 °C), and aluminum chloride (470 mg, 3.5 mmol) was added in portions during 5 min. After stirring at room temperature for 24 h and pouring onto ice–concentrated aqueous HCl, the mixture was extracted with chloroform, washed with water, dried ($CaCl_2$), and evaporated. Dissolved in CH_2Cl_2, it was chromatographed on neutral alumina (25 g, from Fisher Scientific, 80–200 mesh, Brockman activity I) eluting with chloroform, yield 60 mg (0.254 mmol, 25%) of crystalline XXI. It decomposed at 270–280 °C without melting. ^1H NMR ($CDCl_3$): δ 8.14, 7.64 (an AB quartet, J = 8 Hz, 4.05 H), 3.88 (m, 3.92 H), 2.87 (m, 4.02 H). IR (KBr, cm^{-1}): 1725 s, 1715 s, 1705 s, 1695 s. MS (CI, methane, peaks >2%): *m/e* (rel intensity) 235 (M − 1, 3), 236 (M, 27), 237 (M + 1, 100), 238 (M + 2, 20), 239 (3), 265 (12), 277 (4).

3,8-Dihydrodicyclopenta[*a,h*]naphthalene (XXII). Diketone XXI (120 mg, 0.508 mmol) was reduced by the procedure used to reduce XVI and dehydrated as XVII was previously, but at a lower temperature (52 °C): yield 13.5%; mp 106–109 °C; ^1H NMR (CCl_4) δ 7.65 and 7.51 (an AB quartet, J = 8 Hz), an AMX_2 system 7.74 (broad d), 6.67 (d of t, J_1 = 6, J_2 = 1.5 Hz, 2.05 H), 3.45 (t, J = 1.5 Hz, 3.93 H), total integration of resonances at δ 7.74, 7.65, and 7.51 was 6.01 H; IR (CCl_4, cm^{-1}) 3100 w, 3035 w, 2950 m, 2920 s, 2895 shoulder, 2845 m, 1460 m, 1385 m, 1370 w, 1330 m, 1265 m, 1195 w, 1170 w, 1095 broad, 1025 broad, 950 m, 910 w, 835 s, 795 s; MS (CI, isobutane) *m/e* (rel intensity) 202 (7), 203 (11), 204 (95), 205 (100), 206 (16), 207 (2), 247 (7), 261 (7).

4,5-Di(hydroxymethyl)phenanthrene (XXVII). Dibal (270 mL, 2.9 M in toluene, 0.782 mol) and 150 mL of toluene were placed in a 2-L, round-bottomed, three-necked flask, equipped with a stopcock fitted with a serum cap, a reflux condenser connected to nitrogen, a mechanical stirrer, and a Normag funnel for adding solids. 5-Formyl-4-phenanthrenecarboxylic acid (48.9 g, 0.195 mol), prepared according to a published procedure,[57] was added during 2.25 h (heat evolved), and the solution was refluxed for 6 h and cooled to room temperature. Ethyl acetate (30 mL) was syringed in slowly, and the mixture was then poured onto 2 L of ice–water. After concentrated aqueous HCl (200 mL) had been slowly stirred in, filtration, washing, and drying yielded 42.5 g of diol (0.179 mol, 92%): ^1H NMR (Me_2SO-d_6) δ 7.79 (m, 8.05 H), 4.83 (m, 5.95 H); ^1H NMR (Me_2SO-d_6, D_2O added) δ 7.82 (m, 8.19 H), 4.72 (d, J = 9 Hz, 3.81 H).

4,5-Di(bromomethyl)phenanthrene (XXVIII). To tetra-*n*-butylammonium bromide (220 g, 0.682 mol), HMPA (300 mL), and THF (1.3 L) in a 4-L, three-necked, round-bottomed flask, equipped with a mechanical stirrer, a Normag funnel, a thermometer, and an addition funnel connected to nitrogen, first stirred for 5 min at room temperature and then at −10 °C, phosphorus tribromide (145.5 g, 0.537 mol) was added in drops during 15 min, and then XXVII (42.50 g, 0.179 mol) at −5 to 0 °C during 20 min. The extracts obtained after stirring at room temperature for 15 h, pouring into water (1 L), extracting with ether (2 L, in portions), and repeated washing with water (3–4 L) were set aside at room temperature, whereupon crystals appeared (!) and were collected by filtration. The evaporated filtrate washed with *n*-pentane was filtered and the combined solids were dried in vacuo over P_2O_5 for 5 h, yielding 42.5 g. Crystallized from 450 mL of benzene, the yield of XXVIII was 40.69 g (0.112 mol, 62%): mp 195–196 °C dec (lit.[38] 194 °C dec); ^1H NMR ($CDCl_3$) δ 7.57–7.91 (m, 7.96 H), 5.03 (s, 4.04 H).

The ratio of the amount of the ether XXXIII [^1H NMR δ 7.6–8.1 (m, 8.23 H), 4.9 (s, 3.77 H)][37,38] and dibromide XXVIII in other experiments is summarized in Table II.

Phenanthrene-4,5-bispropionic Acid (XXIX). XXVIII was alkylated the way XIV was, except that the amounts of the reagents were different: XXVIII (10 g, 27.5 mmol), HMPA (78.8 g, 440 mmol), THF (600 mL), and *tert*-butyl lithioacetate (110 mmol) in 120 mL of THF. The product was chromatographed twice on 350 g of silica, using CH_2Cl_2 to elute the product the first time and to elute impurities the second. Then ether–CH_2Cl_2 (2:98 v/v) eluted the diester (4.57 g, 10.53 mmol, 38%), a greenish oil: ^1H NMR ($CDCl_3$) δ 7.50–7.73 (m, 8.73 H), 3.47 (t, J = 7 Hz, 3.93 H), 2.22 (m, 3.99 H), 1.13 (s, 17.35 H).

This was saponified with 5 g of KOH in 150 mL of H_2O and 100 mL of CH_3OH for 40 h. Ether extraction (waste) and acidification yielded 2.6 g of the acid (77% yield): IR (KBr, cm^{-1}) 3200 m, 1707 s; ^1H NMR (Me_2SO-d_6) δ 7.53–7.80 (m), 3.33 (m), 2.17 (m). Absorption due to the carboxylic proton could not be detected. Integration was not possible because of a partial overlap between the Me_2SO-d_5 peak and the absorption at δ 2.17.

1,2,11,12-Tetrahydrodicyclopenta[*c,g*]phenanthrene-3,10-dione (XXX). To solid diacid chloride, prepared by refluxing 2.09 g of XXIX (6.5 mmol) and 10.4 g of oxalyl chloride (81.5 mmol) in 70 mL of benzene, in 110 mL of CH_3NO_2 cooled in a salt–ice bath (−6 °C), $AlCl_3$ (3.47 g, 26 mmol) was added in portions through a Gooch tube. After stirring for 17 h at room temperature, the mixture was poured into ice and concentrated aqueous HCl, extracted with 3 × 200 mL of CH_2Cl_2, washed with water, aqueous $NaHCO_3$, and brine, and dried ($CaCl_2$). The dried solution was filtered through Celite and evaporated almost to dryness. The off-white crystalline product XXX was filtered, washed with ether, and dried in vacuo for 1 h, yield 1.57 g (5.49 mmol, 85%). The compound does not melt below 280 °C. ^1H NMR ($CDCl_3$): δ 8.06, 7.95 (an AB quartet, J = 8 Hz, 4.14 H), 7.90 (s, 1.98 H), 3.60 (t, J = 6 Hz, 3.94 H), 2.82 (t, J = 6 Hz, 3.94 H). IR (KBr, cm^{-1}): 1702 vs. MS (CI, CH_4, parent group): *m/e* (relative intensity) 287 (M + 1, 76), 288 (M + 2, 17), 315 (M + 29, 13), 327 (M + 41, 6).

The ketone could be made in lower yield (43%) by heating XXIX (830 mg) and polyphosphoric acid (10 g) to 80 °C for 40 min, working up with water and chloroform, and chromatographing on 60 g of silica gel, eluting with 9:1 CH_2Cl_2–$CH_3CO_2C_2H_5$.

1,2,11,12-Tetrahydrodicyclopenta[*c,g*]phenanthrene-3,10-diols (XXXI). The procedure for making XVII when carried out with 920 mg of XXX gave XXXI in 60% yield. TLC (silica gel, ethyl acetate–methylene chloride, 1:4 v/v) showed two spots of equal intensity

(UV and iodine detection), R_f 0.25 and 0.12, presumably for epimeric diols. ^{1}H NMR (Me$_2$SO-d_6): δ 7.79, 7.71 (an AB system, J = 10 Hz), 7.66 (s), 5.28 (m), 4.03 (broad s, removed by added D$_2$O), 3.22 (broad m), 2.33 (broad m), 1.66 (broad m). Because Me$_2$SO-d_5 partially obscured the peak at δ 2.33, integration was not possible.

1,12-Dihydrodicyclopenta[*c,g*]phenanthrene (XXXII). The diols XXXI (560 mg) were dehydrated the way XVII was, using 10 mg of p-TsOH in 50 mL of benzene. Chromatography on silica (300 g) with n-pentane-ether (98:2 v/v) gave 198 mg of crystals (39% yield): mp 151-152 °C; ^{1}H NMR (CS$_2$) δ 7.65, 7.58 (an AB system, J = 8 Hz, 3.94 H), 7.44 (s, 2.07 H), and an AMX$_2$ system, 6.92 (d of t, J_1 = 5.5, J_2 = 2 Hz, 2.16 H), 6.56 (d of t, J_1 = 5.5, J_2 = 2 Hz, 1.96 H), 3.87 (t, J = 2 Hz, 3.86 H).

The A and B aromatic resonances have different shapes, but this difference disappears when the resonance at δ 3.87 is irradiated, implying there to be a long-range splitting in the resonance at δ 7.65. Accordingly, this resonance is assigned to the benzene proton nearest the five-membered ring. ^{13}C NMR (CDCl$_3$, ppm): 45.0, 121.2, 126.6, 128.1, 128.9, 131.8, 132.7, 133.6, 139.8, 144.8. IR (KBr, cm^{-1}): 3035 w, 2908 w, 2878 vw, 2827 w, 1615 w, 1584 w, 1555 w, 1429 w, 1403 w, 1385 m, 1319 w, 1308 w, 1280 w, 1237 w, 1210 w, 1194 w, 1156 m, 1150 m, 1129 w, 1115 w, 1090 w, 1069 w, 1021 w, 1007 w, 976 m, 954 w, 919 w, 905 w, 869 w, 848 s, 835 m, 820 m, 796 m, 759 w, 750 w, 738 s, 722 w, 710 s, 700 s, 666 m, 625 w, 617 w, 602 s. MS (EI, methane): m/e (rel intensity) 253 (M − 1, 2) 254 (M, 36), 255 (M + 1, 100), 256 (M + 2, 23), 257 (M + 3, 4), 283 (M + 29, 13), 284 (M + 30, 4), 295 (M + 41, 3).

Anal. Calcd for C$_{20}$H$_{14}$: C, 94.45; H, 5.55. Found: C, 93.86; H, 5.73.

Bis(dicyclopenta[*c,g*]phenanthrenylene)diiron (XXXIV). In the left compartment of the double Schlenk tube (see the preparation of XXIII) were placed ferrous chloride (95% from ROC/RIC, 80 mg, 0.630 mmol) and 3 mL of THF; in the right was placed a solution of hydrocarbon XXXII (120 mg, 0.472 mmol) in 9 mL of THF, which when cooled to −78 °C was treated with 0.40 mL of 2.6 M solution of n-butyllithium in n-hexane (1.039 mmol), whereupon it turned red. After stirring at −78 °C for 20 min and then at room temperature, the solution, now a dirty orange, was slowly poured onto the ferrous chloride slurry, also at room temperature, and the resulting deep-red solution was stirred for 6 h. Solvents were stripped, under argon the sticky residue was extracted with 65 mL of CS$_2$, and the extracts were filtered. The IR spectrum of the insoluble residue (50 mg) exhibited only broad bands, attributable to -OH groups. The evaporated filtrate, 160 mg (quantitative yield), was washed under argon with three 1.5-mL portions of n-pentane and dried, first in a stream of argon and then in vacuo. Two unsuccessful attempts were made to crystallize the crude product, from benzene and from CS$_2$, and it was therefore purified by dissolving it in a small volume of THF, filtering, and adding n-hexane under argon. The precipitated product when filtered, washed with n-hexane, and dried in vacuo for 12 h is a red-brown solid, moderately soluble in THF, CH$_2$Cl$_2$, and CS$_2$: IR (KBr, cm^{-1}) 3080 vw, 3035 w, 2966 vw, 2922 w, 2904 vw, 2859 vw, 1709 m, 1597 w, 1516 w, 1487 w, 1437 w, 1420 w, 1380 w, 1347 w, 1324 m, 1280 w, 1256 w, 1230 w, 1200 w, 1163 w, 1030 m, 945 w, 905 w, 830 s, 810 s, 766 m, 753 w, 727 w, 703 w, 665 w, 626 w, 595 m; MS (EI, 75 V, peaks >10% reported except for a group of peaks at 499-505)[10b] m/e (rel intensity) 225 (24), 240 (11), 250 (100), 251 (84), 252 (57), 253 (31), 254 (17), 499 (2), 500 (3), 501 (3), 502 (4), 503 (3), 504 (7), 505 (4), 610 (2), 611 (1), 612 (19), 613 (9), 614 (9), 615 (12), 616 (48.5), 617 (21.5), 618 (5); MS (EI, 24 V. peaks >10%) m/e (rel intensity) 226 (26), 250 (96), 251 (100), 252 (77), 253 (26), 254 (20), 612 (11), 613 (5), 614 (5), 615 (7), 616 (32), 617 (15), 618 (4). Two attempts were made to measure the ^{1}H NMR spectrum (CS$_2$, sealed tube). In both cases no sharp signals were observed. (The Me$_4$Si signal, however, was sharp.)

An attempt to make the cobalticinium analogue in the way XXV was prepared gave only a trace of solid when aqueous NaPF$_6$ was added. Its ^{1}H NMR spectrum in (CD$_3$)$_2$CO showed only ill-defined bands.

Bromination of 1,12-Dimethylbenzo[*c*]phenanthrene (XXXV). 1,12-Dimethylbenzo[c]phenanthrene[39] (140 mg, 0.547 mmol), N-bromosuccinimide (205 mg, 1.148 mg), and 1 mg of dibenzoyl peroxide in 5 mL of CCl$_4$ were refluxed and irradiated (300-W incandescent bulb) under nitrogen for 1 h. Filtration, evaporation, and chromatography (50 g of silica, pentane) yielded 70 mg (0.21 mmol, 38%) of crystalline 1-bromomethyl-12-methylbenzo[c]phenanthrene: ^{1}H NMR (CDCl$_3$) δ 7.20-7.98 (m, 10.31 H), 4.55 (s, 1.74 H), 1.97 (s, 2.95 H). No dibromide was found. Without light there was no reaction.

Benzo[*c*]phenanthrene-2,11-bispropionic Acid (XXXVIII). 2,11-Di(bromomethyl)benzo[c]phenanthrene (XXXVII,[40] 300 mg, 0.725 mmol) in 4 mL of THF and 0.32 mL (325 mg, 1.812 mmol) of HMPA was alkylated with $tert$-butyl lithioacetate as described in the preparation of acid XIX. Obtained after chromatography was 245 mg (0.506 mmol, 70%) of white solid: ^{1}H NMR (CDCl$_3$) δ 8.94 (s, 1.90 H), 7.84 and 7.43 (an AB system, J = 8 Hz), 7.74 and 7.65 (an AB system, J = 8.5 Hz, integration for both AB systems 7.92 H), 3.22 (m, 3.98 H), 2.70 (m, 4.08 H), 1.32 (s, 18.12 H).

The diester was refluxed with NaOH (160 mg, 4 mmol) in 4 mL of H$_2$O-2 mL of CH$_3$OH for 31 h and worked up as XIX was, yielding 149 mg (0.401 mmol, 79%): IR (KBr, cm^{-1}) 3030 w, 2960 s (broad), 1700 vs; ^{1}H NMR (Me$_2$SO-d_6) δ 8.87 (s), 7.88 and 7.80 (an AB system, J = 8 Hz), 7.96 and 7.52 (an AB system, J = 8 Hz), 6.83 (t, J = 7 Hz), 7.26 (t, J = 7 Hz). Because of the presence of the Me$_2$SO-d_5 absorption at δ 7.5, integration of the whole spectrum was not possible. The ratio of the intensities of the downfield aromatic singlet (δ 8.87) and the upfield aromatic AB systems is 1.79/8.21.

Cyclization of Benzo[*c*]phenanthrene-2,11-bispropionic Acid (XXXVIII). Aluminum chloride (86 mg, 0.645 mmol) was added in portions to a CH$_2$Cl$_2$ solution (20 mL) of diacid chloride prepared from 60 mg of XXXVIII, as its sodium salt, and oxalyl chloride. After stirring at room temperature for 18 h, pouring onto a mixture of ice and concentrated aqueous HCl, and extracting with CH$_2$Cl$_2$ (3 × 25 mL), the combined organic solutions were washed twice with 5% NaOH, dried over CaCl$_2$, and evaporated, yielding 50 mg of yellow powder. It was chromatographed on 40 g of silica gel, first with ether-methylene chloride (3:97 v/v) to elute product XXXIX (30 mg, 0.09 mmol, 55%, R_f 0.27, silica gel plate, chloroform) and then with ether-methylene chloride (1:9 v/v) to elute product XL (10 mg, 0.03 mmol, 18%, R_f 0.14).

Spectra of XXXIX. ^{1}H NMR (CDCl$_3$): δ 9.12 (s, 2.11 H), 8.45 (s, 1.91 H), 8.04 and 7.82 (an AB system, J = 7 Hz, 3.97 H), 3.48 (t, J = 6 Hz, 3.82 H), 2.88 (t, J = 6 Hz, 4.18 H). IR (KBr, cm^{-1}): 1710 vs. MS (CI, methane): m/e (rel intensity) 336 (5), 337 (100, M + 1), 338 (26), 339 (2).

Spectra of XL. ^{1}H NMR (CDCl$_3$): δ 8.40-7.66 (m, 8.06 H), ca. 3.5-ca. 2.7 (m, 7.93 H). IR (KBr, cm^{-1}): 3040 w, 2920 m, 2840 w, 1700 vs, 1620 m, 1610 s, 1595 m, 1485 m, 1440 m, 1430 shoulder, 1410 w, 1385 w, 1360 m, 1295 w, 1280 m, 1260 w, 1245 m, 1210 w, 1190 w, 1160 w, 1145 s, 1095 m, 1040 m, 975 w, 905 s, 860 s, 840 s, 700 w. MS (CI, methane): peaks >15% except parent group m/e (rel intensity) 61 (72), 63 (54), 67 (21), 71 (34), 73 (41), 75 (23), 83 (30), 84 (19), 85 (38), 91 (21), 97 (30), 99 (17), 111 (19), 336 (4), 337 (100, M + 1), 338 (21), 365 (15, M + 29).

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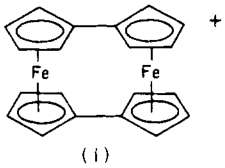

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