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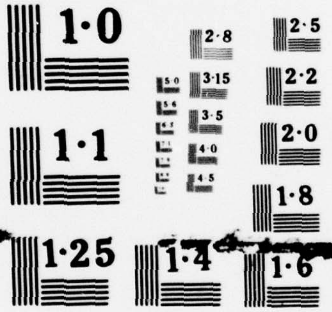

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Organometallic Compounds

Final Report

by

Thomas J. Katz

May 14, 1979

U.S. Army Research Office
Grant Numbers DA-ARO-D-31-124-G119
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Metallocene, Ferrocene, Polymer, Dimer, Dianion, Trianion, Hydrocarbon

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Studies are described aimed at testing whether novel polymeric chemical structures can be synthesized in which hydrocarbon rings and metal atoms alternate. A number of appropriate hydrocarbon dianions have been synthesized for the first time, as have a number of molecules containing two metal atoms sandwiched between a pair of planar hydrocarbons. Structures like this were not known before the start of the work. Some properties of these novel materials have been measured. [over please]

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The first attempts have been made to implement two schemes designed to prevent the combination of a hydrocarbon dianion and a metal halide from giving a dimeric structure rather than a polymer. One scheme involves the preparation of helical hydrocarbons capped by five-membered rings, and ways to make such materials are developed. The other involves the preparation of a hydrocarbon trianion with a three-fold axis of symmetry and three terminal five-membered rings. The first example, the trindene trianion, is prepared.

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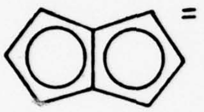
1. Statement of the Problem Studied

The reaction of a transition metal halide with a hydrocarbon dianion made up of two linked cyclopentadienyl anions is anticipated to give a polymeric metallocene in which hydrocarbon rings and metal atoms alternate. For example 1 might give 2 and the general analogue of 1 should similarly give 3. Structures like this are not known, but unlike most organic substances they might be good conductors of electricity and have other novel properties. We have therefore been devising ways to make such substances and studying the properties of the materials we make.



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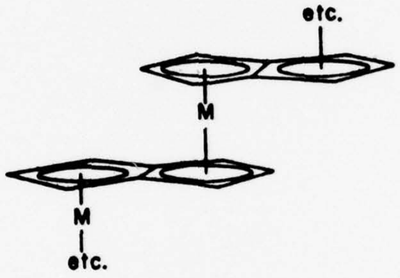

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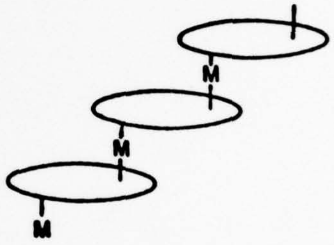

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2. Results and Conclusions

The reaction of the *as*-indacenyl dianion, 4, with ferrous chloride was found to give ferrocenes $(C_{12}H_8Fe)_n$, which although not high polymers, proved to be two dimers of structure 5 and 6. These bis(*as*-indacenyliron)s were the first substances to be prepared in which two metal atoms were sandwiched between a pair of planar hydrocarbon rings. Their structure has been proven by NMR spectroscopy and by X-ray crystallography.

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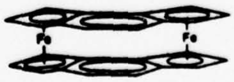

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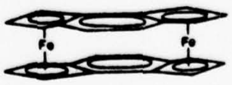

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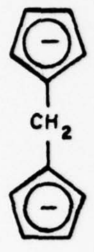
The nickel and cobalt analogues, bis(*as*-indacenylnickel) and bis(*as*-indacenylcobalt), have also been made and characterized.

The biscyclopentadienylmethane dianion, 7, was synthesized and with ferrous chloride was shown to give a series of cyclic oligomers that we call the $[1^n]$ ferrocenophanes, 8, of which the lower members, the dimer 9 and the trimer 10, as well as the tetramer and pentamer (8, n=4, 5) have been isolated and individually characterized. With titanium tetrachloride, 7 gives 1,1'-methylenetitanocene dichloride, a material that with lithium naphthalenide in tetrahydrofuran fixes nitrogen and with diethylaluminum chloride polymerizes ethylene.



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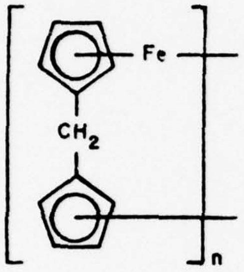

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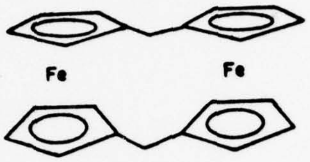

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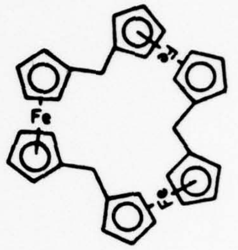

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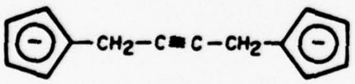
The dianions 11 and 12 were synthesized, and the cyclic dimers 13 and 14 formed upon reaction with ferrous chloride were isolated and characterized.



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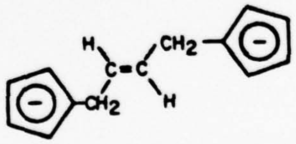

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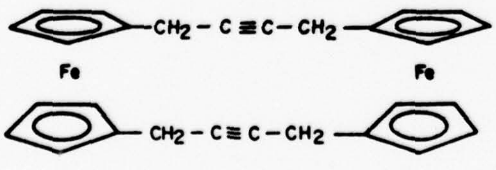

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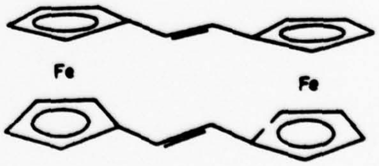

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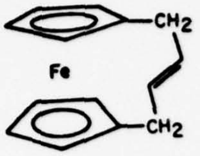

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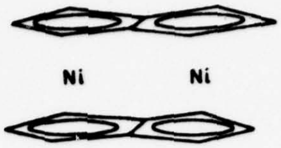

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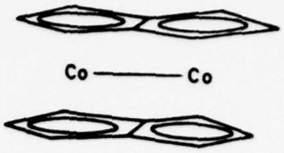

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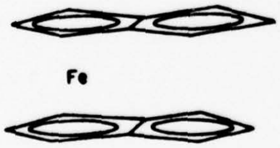
Dianion 12 gives besides 14 also the bridged monomer 15. The simplest substances in which transition metals are sandwiched between the rings of a pair of non-benzenoid aromatic molecules are bis(pentalenylnickel), 16, and bis(pentalenylcobalt), 17. The former is prepared by combining dilithium pentalenide, I, with nickel chloride or with nickelocene, and the latter analogously by combining I with cobaltous chloride. Ferrous chloride, however, does not give an analogous material. Instead it gives a molecule, bis(pentalenyl)iron, consisting of two pentalene moieties and only one iron atom, whose structure according to X-ray diffraction analysis is not 18, but 19. Oxidizing bis(pentalenylcobalt), 17, with hydrogen peroxide removes a cobalt atom and gives a cobalticinium salt isoelectronic and isostructural with bis(pentalenyl)iron (19).



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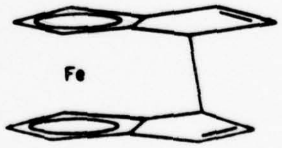

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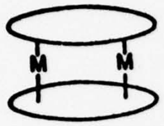
Bis(pentalenylcobalt), 17, is diamagnetic, but bis(*as*-indacenylcobalt) (5 or 6 with Fe replaced by Co) is paramagnetic. The magnetic susceptibility of bis(*as*-indacenylcobalt) has been measured between 81 and 286 K and indicates there to be one unpaired electron per cobalt atom, a large temperature-independent paramagnetism, and no antiferromagnetic interaction. Electronic spectra measured at lower temperatures (down to 10 K) reveal another form of this material in which possibly all the electrons are paired.

The experiments described above show that to achieve the syntheses of the new polymeric materials envisioned in the proposal the major obstacle to be circumvented is the tendency of ions like 1 and 4 in combining with transition metal salts to give dimers, like 20 rather than polymers like 2. We imagine two ways this might be accomplished. One is to cause the hydrocarbon to react with metals on opposite faces, at b rather than at a in



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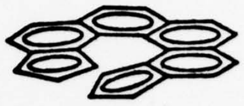

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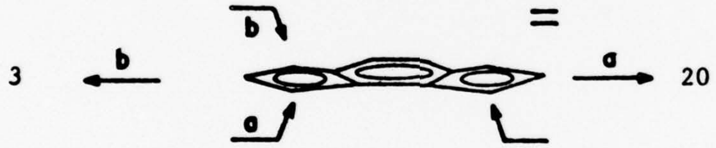
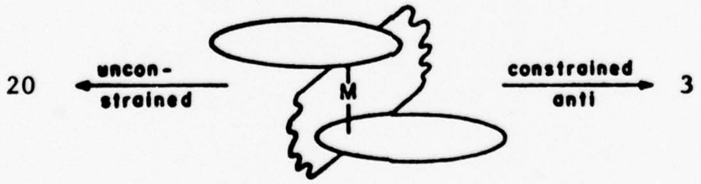
Scheme 1. The other is to constrain the hydrocarbons bonded by the metals to anti conformations, in which dimerization is impossible whether the metals attach to the same or to opposite faces of one ring (Scheme 2). Although at first it seems impossible to implement either scheme, we see paths toward

Scheme 1

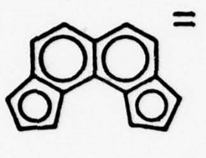


Scheme 2



the solutions and have made progress toward both.

The way we imagine blocking the approach of metal atoms to one face of the hydrocarbon ring (Scheme 1) is to incorporate the hydrocarbon structure within a helicene by constructing aromatic dianions resembling 21, for in such a structure access to the bottom of the ring on the left would be blocked by the ring on the right and access to the top of the ring on the right is blocked by the ring on the left. We have developed syntheses for the two lower homologues of 21, ions 22 and 23. These are too small to give polymers, and with iron chloride they give sandwiches, 24 and 25, with two iron atoms. Similarly with $Co(NH_3)_6Cl_3$ and $NaPF_6$ 22 gives a cobalticinium analogue, 26. The syntheses summarized in Schemes 3 and 4 fuse five-membered



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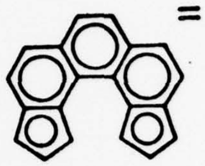

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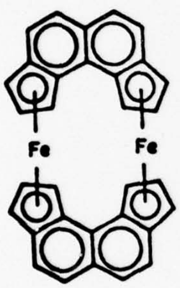

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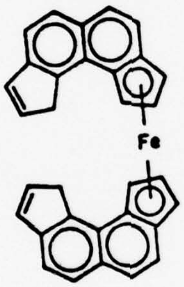

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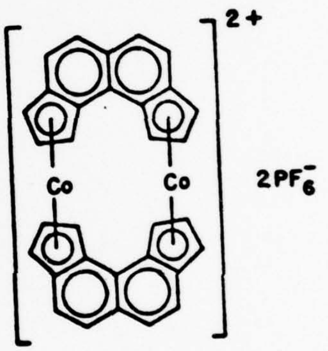

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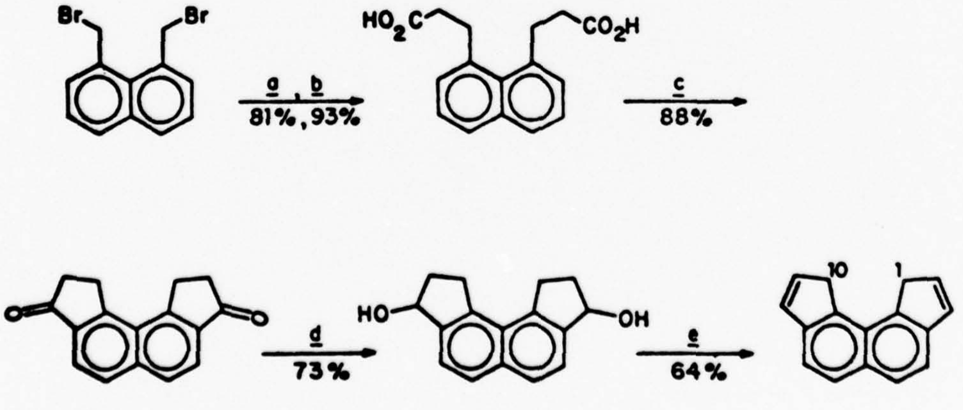
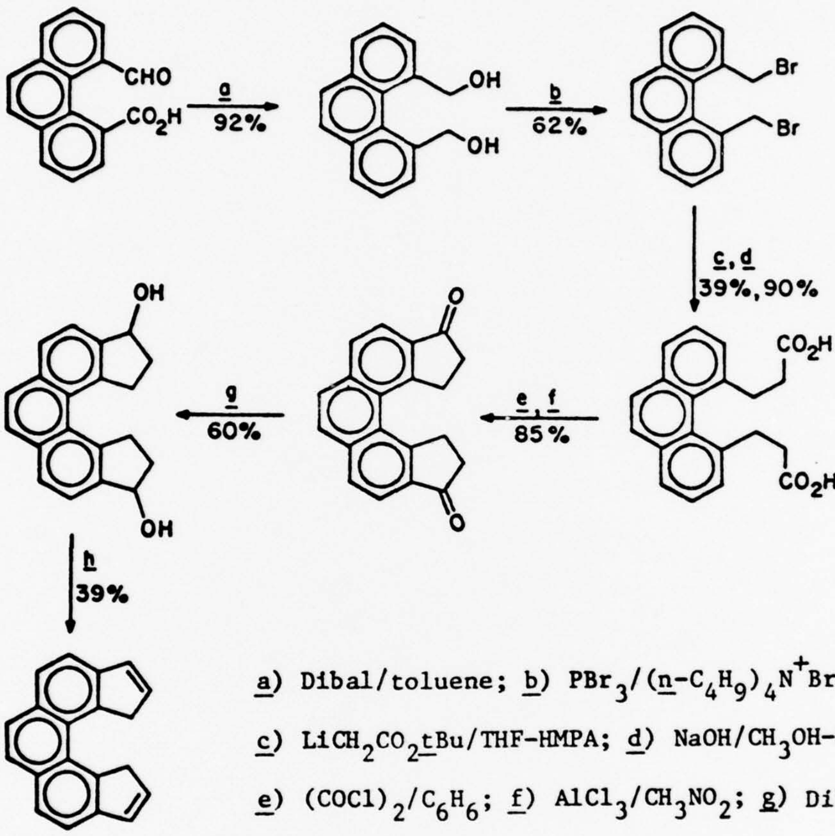
Scheme 3



(a) $LiCH_2CO_2$tBu/THF-HMPA; (b) $NaOH/CH_3OH-H_2O$; (c) PPA;
(d) Dibal/$C_6H_5CH_3$; (e) p-TsOH/C_6H_6.

rings to naphthalene and phenanthrene nuclei. An attempt, summarized in

<u>Scheme 4</u>



a) Dibal/toluene; b) $PBr_3/(\underline{n}\text{-}C_4H_9)_4N^+Br^-$/HMPA-THF;

c) $LiCH_2CO_2\underline{t}Bu$/THF-HMPA; d) $NaOH/CH_3OH\text{-}H_2O$;

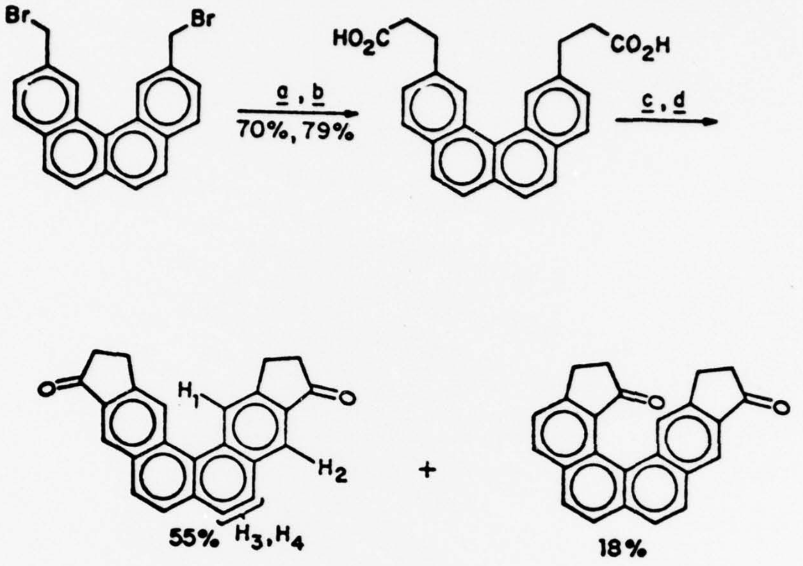
e) $(COCl)_2/C_6H_6$; f) $AlCl_3/CH_3NO_2$; g) Dibal/toluene;

h) $\underline{p}$-TsOH/C_6H_6.

Scheme 5, to prepare a [6]helicene analogue by similarly fusing two five-membered rings to benzo[c]phenanthrene gives instead two related ring systems. Other preparations of the [6]helicene must therefore be found.

The way we imagine strapping the hydrocarbons together to constrain rotation as in Scheme 2 is to make use of the trindene trianion, 27. The idea is that if this ion combined with two transition metal atoms in the way that 4 does, the remaining centers of reactivity on adjacent ring systems are likely to be kept apart by steric and coulombic repulsive forces and thus give 28 rather than 29. Since the bonds between the metals and

Scheme 5



(a) $LiCH_2CO_2$tBu/THF-HMPA; (b) $NaOH/H_2O$-CH_3OH;
(c) $COCl_2/C_6H_6$; (d) $AlCl_3/CH_2Cl_2$

the five-membered rings will then lock the positions of the rings, the resulting structure would be an example of the constrained intermediate symbolized in Scheme 2. For this reason, and also to see how difficult it is to synthesize a conjugated polyanion, we carried out a successful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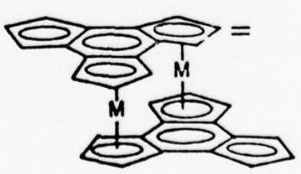

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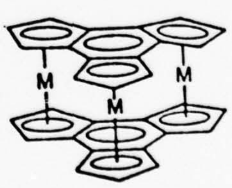

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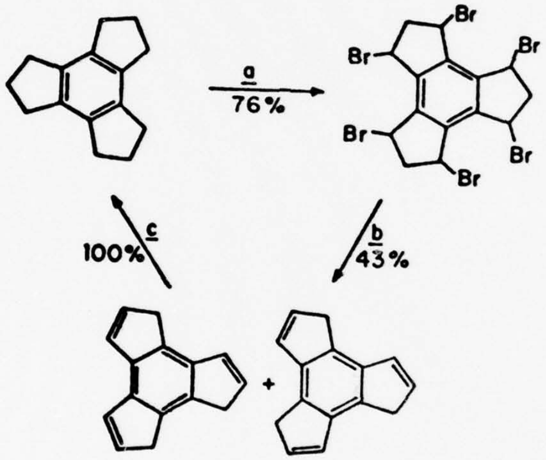
four-step synthesis of the trindene trianion (27) from cyclopentanone. Bromination and debromination, as summarized in Scheme 6, convert octahydro-1H-trindene ("trindane") into the dihydro-1H-trindenes, and these with *n*-butyllithium in tetrahydrofuran give 27. The trindene trianion, although it contains multiple charges in one π-electron system, is a favorable species because its rings are all five- and six-membered, because its highest occupied molecular orbital is low in energy, and because its lowest unoccupied molecular orbital is high in energy.

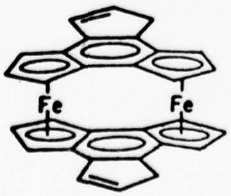
Sandwich molecules, assigned structures 30 and 31, containing two irons, are produced when the corresponding dianion is combined with ferrous chloride.

Scheme 6



(a) Br_2/CCl_4, hν; (b) Zn/DMF; (c) H_2/PtO_2

Related sandwich molecules containing two or many metal atoms might be



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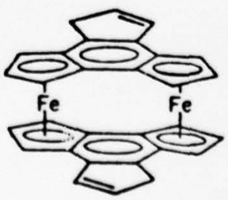

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prepared from these anions and other metal salts, but the study of these possibilities remains for future work.

3. Publications

1. Thomas J. Katz and Nancy Acton, "1,1'-Methylenetitanocene Dichloride," Tetrahedron Lett., 2497 (1970).
2. Ramsey Gitany, Iain C. Paul, Nancy Acton, and Thomas J. Katz, "The Structure of Bis(*as*-Indacenyliron)," Tetrahedron Lett., 2723 (1970).
3. Thomas J. Katz and Nancy Acton, "bis(pentalenylnickel)," J. Am. Chem. Soc., **94**, 3281 (1972).
4. Thomas J. Katz, Nancy Acton, and Geoffrey Martin, "Preparation of Metallocenes from Hydrocarbon Dianions," J. Am. Chem. Soc., **95**, 2934 (1973).
5. Thomas J. Katz and Wojciech Ślusarek, "Helical Hydrocarbons Capped by Five-Membered Rings as Precursors of Polymeric Metallocenes," J. Am. Chem. Soc., **101**, to be published ca. August (1979).
6. Thomas J. Katz and Wojciech Ślusarek, "The Trindene Trianion," submitted to J. Am. Chem. Soc. for publication.
7. Thomas J. Katz and Nancy Acton, "The Bis(*as*-indacenyl)metallocenes," *in preparation*.

4. Scientific Personnel and Degrees Earned

Nancy Acton
Valeria Balogh
Hiroshi Hayashi
N. Pisker Trifunac
James McGinnis, earned the Ph.D.
Ronald Roth, earned the Ph.D.
Wojciech Ślusarek, earned the Ph.D.

APPENDIX 1.

To be published in J. Am. Chem. Soc., ca. August 1979.

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

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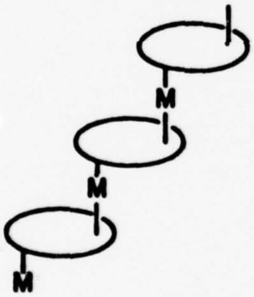
Abstract

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 2, 3, and 4, fuse two five-membered rings to naphthalene and phenanthrene nuclei. An attempt, outlined in Scheme 6, 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[10e] 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



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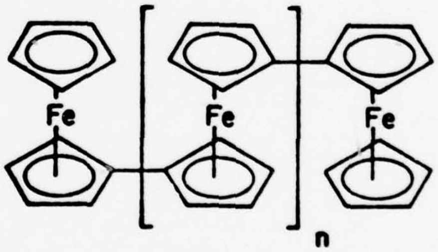

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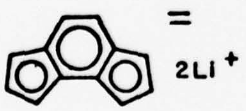
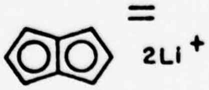
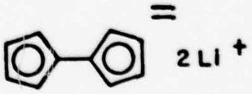


III



IV



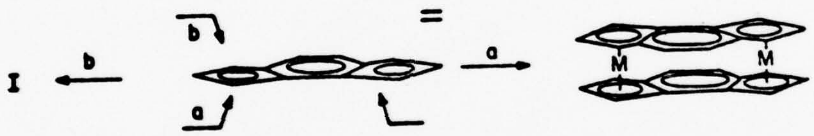
V

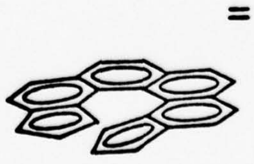
dimers!

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 1). 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.

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

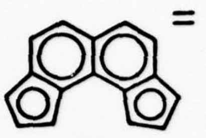
Scheme 1



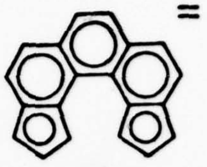


VI

procedures similar to those that successfully give VII and VIII.

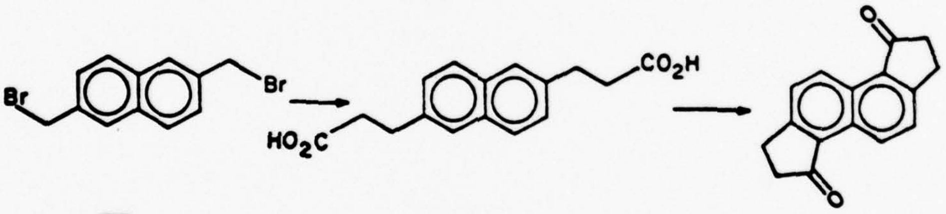


VII



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



IX X XI

works well for the syntheses required here, but the alkylation, although a classical transformation, required research to achieve acceptable yields.

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 t-butyl lithioacetate is alkylated,[22] was tried instead, and following steps analogous to those used to alkylate 1,2-dibromomethylbenzene,[23] the yield of XII (Eq. 2) was 23%.

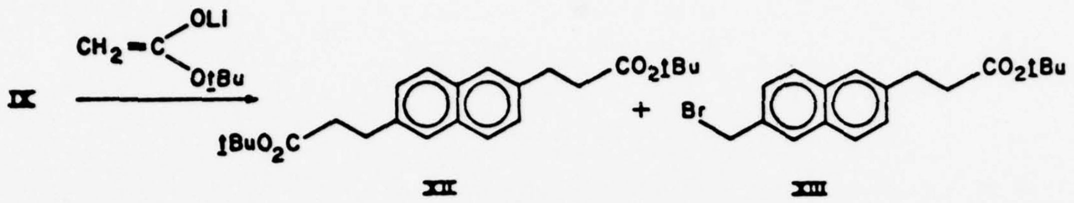
Table 1. Yields on Alkylating 2,6-di(bromomethyl)naphthalene (IX)[a] with $[CH_2CO_2tBu]^-Li^+$

Expt.	Moles of $LiCH_2CO_2tBu$ per mole of dibromide	Moles of HMPA per mole of dibromide	Temp. (°C)	Time (min)	Yield (%) XII	Yield (%) XIII
1	3	0[b]	r.t.[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 IX in ca. 30 mL THF. [b] DMSO was added to the dibromide solution. The dibromide-DMSO molar ratio was 1:7. [c] Room temperature.

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 1. On a 40 mmol scale, the best conditions displayed (those of experiment 8), consistently give yields of 61-68%.

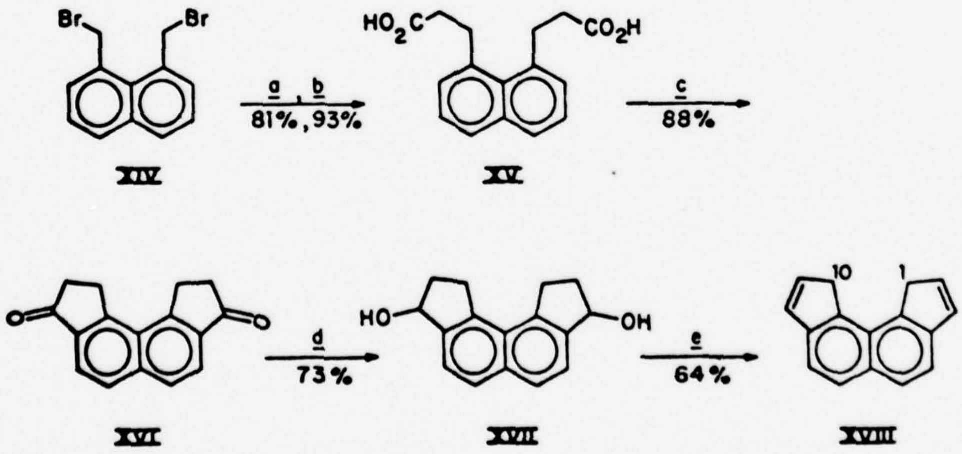
Synthesis and Reactions of VII. When applied to 1,8-dibromomethylnaphthalene[25] (XIV), this procedure gives an 81% yield of the diester, and the steps summarized[26] in Scheme 2 then lead to hydrocarbon XVIII. The ^1H and ^{13}C NMR spectra, described in the experimental section, show this hydrocarbon to be homogeneous and are in accord with the structure pictured.



(2)

A double-bond isomer of XVIII, XXII, was similarly synthesized as summarized[26] in Scheme 3, 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 ^{1}H 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

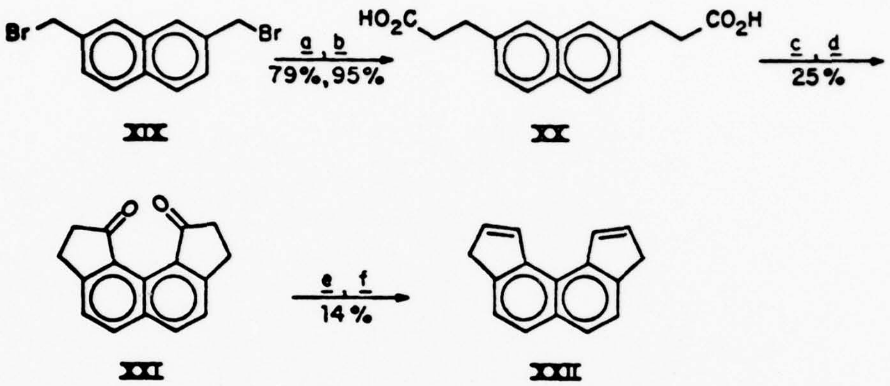
Scheme 2



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

positions of the other resonances in XXII and those in XVIII resemble those in indene,[28] this one resonance is at δ7.74, 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.

Scheme 3

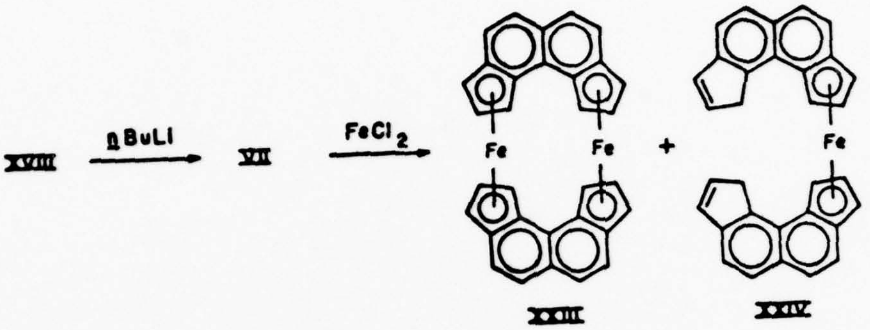


(a) $LiCH_2CO_2$tBu/THF-HMPA; (b) $NaOH/CH_3OH-H_2O$;
(c) $(COCl)_2/C_6H_6$; (d) $AlCl_3/CH_3NO_2$; (e) Dibal/$C_6H_5CH_3$;
(f) p-TsOH/C_6H_6.

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

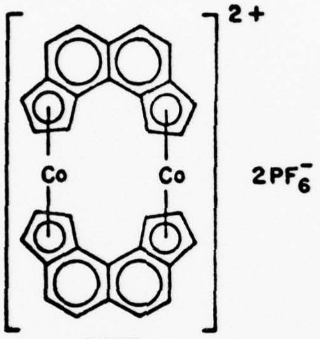
(XXIII) in about 60% yield, along with small amounts of a material containing only one iron atom, probably XXIV, which was isolated by column chromatography (Eq. 3). These iron compounds are very difficult to



(3)

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 mono cation 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 in toluene-d_8 were unsuccessful. The only NMR's observed were very broad, just like the resonances of bisfulvalenediiron 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 bis cobalticinium ion XXV, which can be made from VII,



XXV

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(acetylacetonate)$_3$,[34] give none. The ^1H NMR spectrum, displayed as Fig. 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 Fig. 2 are based in part on the spectrum of bis(indenyl)cobalt(III) nitrate,[35] in which the metallocene resonances appear at δ6.20 (a doublet) and δ5.80 (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. Supporting the

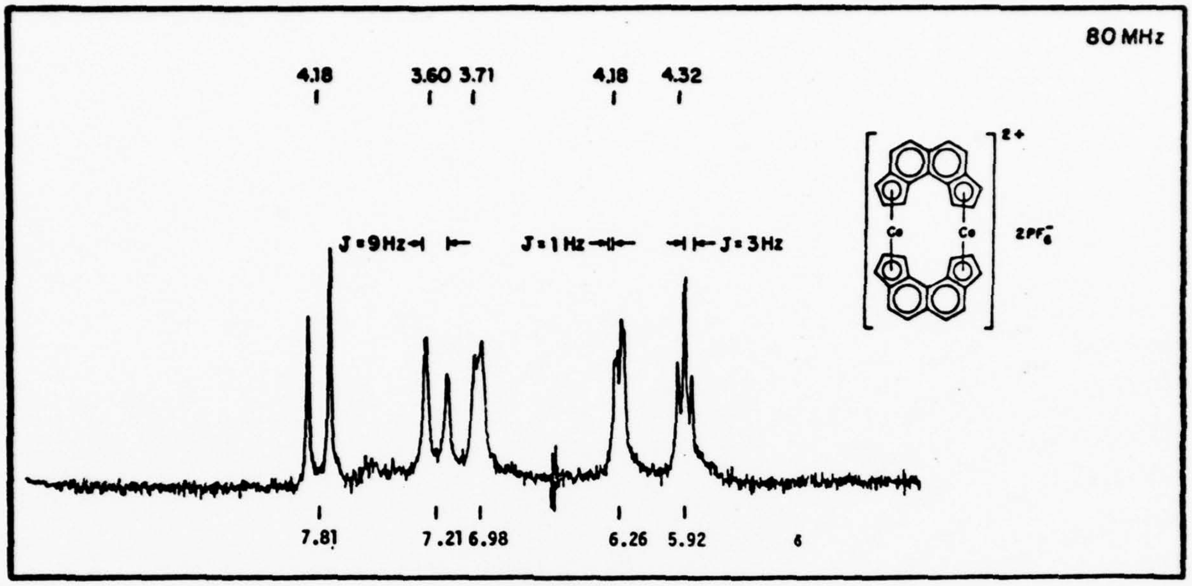


Figure 1 ^1H NMR Spectrum of XXV (Fourier Transform Spectroscopy, 135 scans) in CD_3CN at room temperature. Chemical shifts are below the peaks and intensities above.

assignment of H_5 to the resonance at δ6.98 is the complexity of this resonance compared to that at δ6.26, attributable to a long-range zig-zag

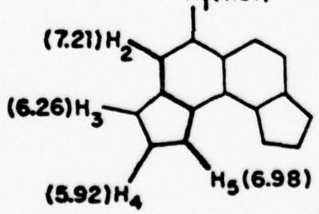
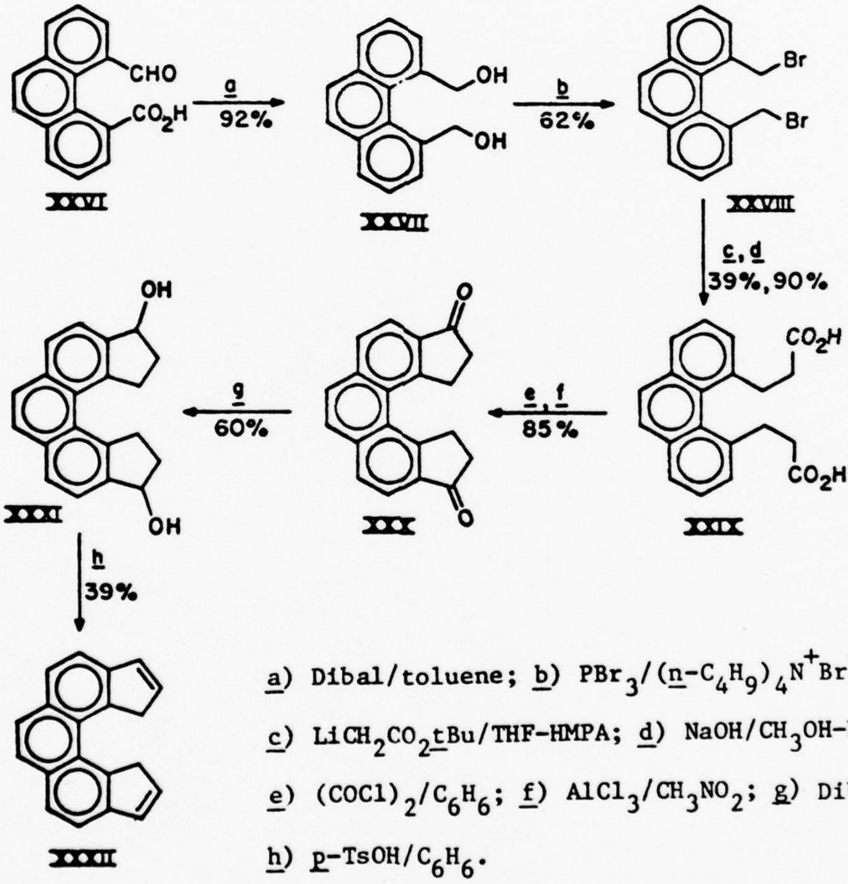


Figure 2 Assignment of ^1H NMR Chemical Shifts (δ) for XXV.

coupling between H_2 and H_5.[28a,36] Consonant is the height of one portion of the aromatic AB pattern (that at δ7.21) being smaller than the other (that at δ7.81), from which it follows that the former is the resonance of H_2.

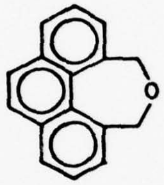
Synthesis and Reactions of VIII. Similar methodology, summarized in Scheme 4, converts 5-formyl-4-phenanthroic acid (XXVI) into hydrocarbon XXXII.

Scheme 4



a) Dibal/toluene; b) $PBr_3/(\underline{n}\text{-}C_4H_9)_4N^+Br^-$/HMPA-THF;
c) $LiCH_2CO_2\underline{t}Bu$/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) $\underline{p}$-TsOH/C_6H_6.

Step a had been carried out previously using $LiAlH_4$ and the ethyl[37] or methyl[38] esters, but $(\underline{i}\text{-}C_4H_9)_2AlH$ 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 can be raised to 68% and the amount of ether XXXIII reduced to 17%. Step c, the alkylation with t-butyl lithioacetate does not work well under the conditions effective for IX, XIV, and XIX (those in experiment 8 in Table 1).



XXXIII

A considerable amount (50% yield) of the monoalkylated product, the bromoester, 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 moles of HMPA per mole of dibromide, the yield increases to 39%.

Hydrocarbon XXXII's ^1H NMR spectrum (Fig. 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 non-planar conformers at least a few times per second at 35°C. If the molecule had been non-planar, the methylene hydrogens would have been non-equivalent 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 the experimental section)

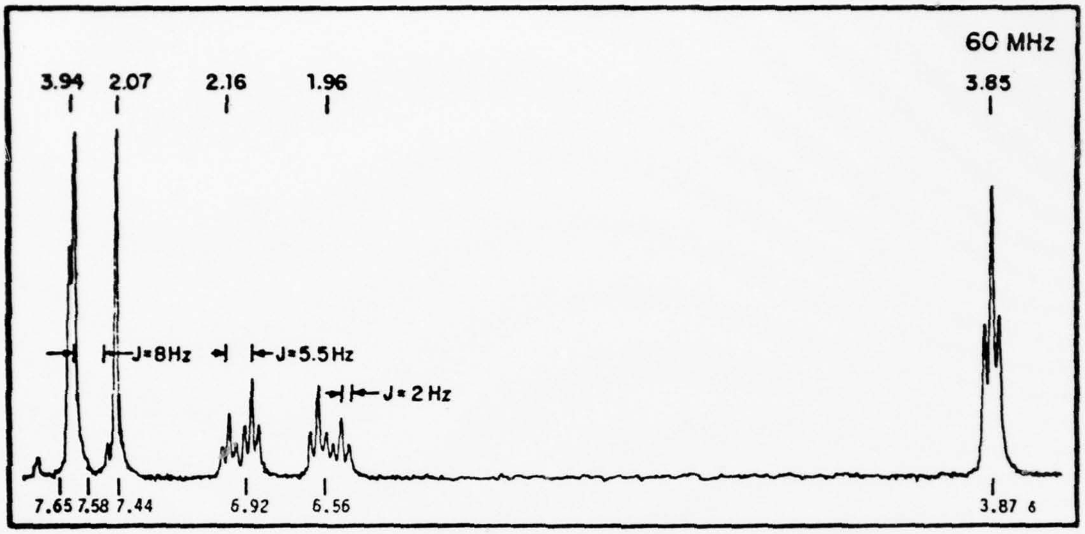
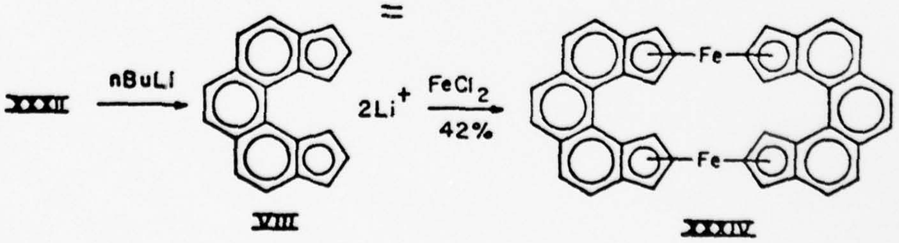


Figure 3. ^{1}H NMR Spectrum of XXXII in CS$_2$ at 35°C. The NMR frequency is 60 MHz and tetramethylsilane was the internal standard. Chemical shifts are below the peaks and intensities above.

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

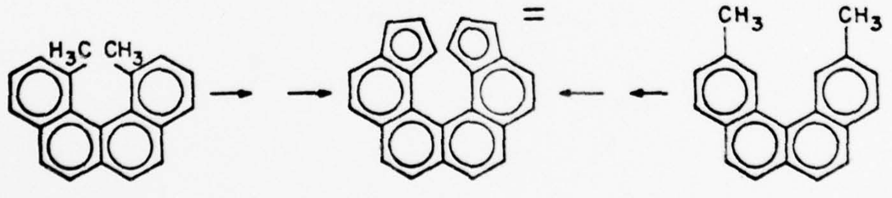


(4)

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_2Cl_2, and CS_2, but attempts to measure its ^1H 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. 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 5 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

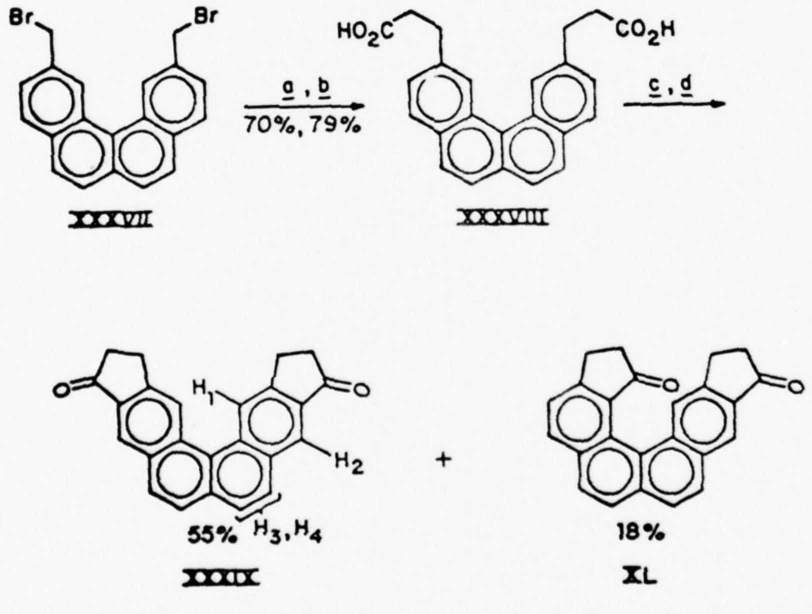
Scheme 5



XXXV VI XXXVI

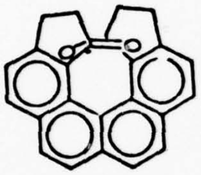
because hydrocarbon XXXV resists the entry of bromine atoms into both its benzylic positions. Thus, combining it with NBS in the presence of light and peroxides gives only the monobromo derivative. The isomeric hydrocarbon, XXII, *in contrast*, is brominated easily,[40] and the transformations summarized in Scheme 6 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 6 give the β-acylation products because the α-positions are crowded sterically.

Scheme 6

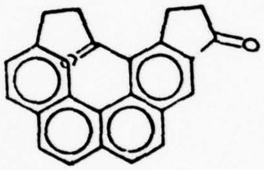


(a) $LiCH_2CO_2\underline{t}Bu$/THF-HMPA; (b) NaOH/$H_2O$-$CH_3OH$;
(c) $COCl_2/C_6H_6$; (d) $AlCl_3/CH_2Cl_2$

The structures are assigned to the ketones XXXIX and XL on the basis of their ^1H NMR, ir, and mass spectra. In particular, the ^1H NMR spectrum of the ketone assigned structure XXXIX is extraordinarily simple. In the aromatic region there is a singlet at $\delta 9.12$ assigned to the resonance of H_1, a singlet at 8.45 assigned to H_2, and an AB quartet at 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 ^1H 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

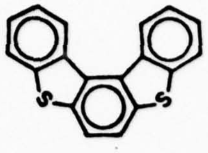


XLII

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

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.

Experimental

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, 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 Taunus, 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, 3-necked flask, equipped with a low temperature thermometer, a mechanical stirrer, and an addition funnel was 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 stirring 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 dilute hydrochloric acid (1:9), poured into 100 mL saturated aqueous NaCl, and the layers were separated. The aqueous layer was extracted with ether (3 x 200 mL), and the combined organic solutions were washed 4 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 white crystals (20.3 mmol, 68%), mp 77-78°C. A sample was sublimed (115°C, 0.1 mm Hg). Mp 78-79°C, ^1H NMR ($CDCl_3$) δ7.50 (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 3 experiments on a smaller scale (3 mmol), 69, 70%, and 79%.

Di-t-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°C, 158°C).[48,49] ^1H NMR (DMSO-d_6) δ8.01-7.36 (m, 5.99 H), 5.18 (m, 6.01 H); (DMSO-d_6 + D_2O) δ8.04-7.38 (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°C,[50a] 129-130°C[50b]); yield 80%.

A solution of 1,8-di(bromomethyl)naphthalene (940 mg, 3 mmol) in 30 mL THF and 1.3 mL (1.34 g, 7.5 mmol) 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 a freshly prepared *t*-butyl lithioacetate (7.5 mmol) in 10 mL 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 1 N HCl. Pouring onto 20 mL saturated brine, extracting with ether, washing with 1 N HCl (3 x) and drying ($MgSO_4$), gave crude product, which was chromatographed on 50 g silica gel with n-pentane-ether (9:1, v/v). Obtained was 950 mg (2.44 mmol, 81%) of colorless oil. ^1H NMR ($CDCl_3$) δ7.23-7.77 (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-bis-propionic acid (XV). The diester (950 mg, 2.45 mmol) was refluxed (20 h) with NaOH (400 mg, 10 mmol) in 20 mL methanol-water (1:1, v/v). After extraction with ether, conc. 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%. ^1H NMR (DMSO-d_6) δ7.78 q, 7.37 d, 3.45 broad t, 2.52 broad t. Absorption due to DMSO-d_5 partially obscure a peak at δ2.52, 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 3-necked, round-bottomed flask, fitted with a mechanical stirrer, a nitrogen inlet and a thermometer was placed 258 g polyphosphoric acid and 10 g (36.76 mmol) powdered XV. The flask was immersed in oil preheated to 85°C and stirred for 1½ 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 hrs. 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).

in 10 mL 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 1 N HCl. Pouring onto 20 mL saturated brine, extracting with ether, washing with 1 N HCl (3 x) and drying ($MgSO_4$), gave crude product, which was chromatographed on 50 g silica gel with *n*-pentane-ether (9:1, v/v). Obtained was 950 mg (2.44 mmol, 81%) of colorless oil. ^1H NMR ($CDCl_3$) δ7.23-7.77 (m, 6.01 H), 3.48 (m, 3.74 H), 2.53 (m, 4.00 H), 1.40 (s, 18.25 H).

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It crystallized from o-dichlorobenzene as fine, shiny plates that decomposed without melting at 320-330°C. ^{1}H NMR ($CDCl_3$) δ7.90 (s, 4.26 H), 3.77 (t, 5.5 Hz, 4.06 H), 2.87 (t, 5.5 Hz, 3.68 H). Ir (KBr, cm^{-1}) 1710 vs. Ms (CI, CH_4, peaks >15% except parent group) m/e (rel int): 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, 3-necked flask, equipped with a stirring bar, reflux condenser (argon inlet), and stopcock fitted with a septum. After stirring and heating until solid had dissolved, ethyl acetate (1 mL) was added, and the solution was poured onto ice. Conc. aq HCl (10 mL) was added and the mixture extracted with ether (3 x 50 mL) and ethyl acetate (3 x 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 (DMSO-d_6) δ7.72 and 7.45 (AB system, 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} mm Hg. The yield was only 27%. ^1H NMR ($CDCl_3$) δ7.90 and 7.62 (an AB quartet, 9 Hz, 4.07 H), an AMX_2 system: 7.10 (d of t, J_1 = 6 Hz, J_2 = 1.5 Hz, 2.08 H), 6.80 (d of t, J_1 = 6 Hz, J_2 = 1.5 Hz, 1.93 H), 3.77 (t, 1.5 Hz, 3.92 H). That the resonance at δ7.90 is that of the proton nearer the five-membered ring is implied by decoupling at δ3.77 sharpening this resonance and not the one at δ7.62. ^{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 int): 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) XVIII in 5 mL 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 stirred solution of 0.2 mL $(CF_3CO)_2O$ in 10 mL 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. ^1H

NMR ($CDCl_3$): an AB quartet δ7.82 (1.96 H) and δ7.57 (2.22 H), 7.05 (d of d, J_1 = 6 Hz, J_2 = 1.5 Hz, 1.94 H), 6.73 (d of d, J_1 = 6 Hz, 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 int): 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 int): 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 was placed anhydrous ferrous chloride (95% from ROC/RIC, 187 mg, 1.47 mmol) and 4 mL THF, in the right compartment a solution of hydrocarbon XVIII (250 mg, 1.22 mmol) in 9 mL 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 1½ h, the solvents 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 mono-iron 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

From 1816 to 1823, Fresnel explored the theory and the methods of production of circularly and elliptically polarized light [47]. While there are today more sophisticated instrumental methods than those developed by Fresnel, the accepted theoretical framework for the understanding of the phenomena is still exactly that which he presented. He envisioned two orthogonal wave trains of plane polarized light propagating along a common line, with a relative phase difference of 90° or one quarter of a wavelength (see Figure 7). The extremum of the vector sum of the two wave trains--that vector always orthogonal to the line of propagation--describes a helical movement through space. The distance traveled along the line of propagation by that vector in going through one complete turn is, then, one wavelength. If the amplitude of the wave trains are the same, the result is CPL; if not, elliptically polarized light results.

Fresnel produced CPL from plane polarized light by two means. The simpler of the two involved utilization of quarter-wave plate, a birefringent plate of such thickness d that for a given range of wavelength about some particular λ_0 the phase lag

$$\phi = 2\pi d(\eta_x-\eta_y)/\lambda \qquad (1\text{-}1)$$

is close to a value of $\pi/2$ radians (see above, the subsection on Birefringence and Figure 4, p. 23). Orientation of the plate such that the plane of polarization of incident and 16 mL 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 x 10 mL dilute (1:9) aq. HCl and with 2 x 10 mL 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 $NaPF_6$ in 1 mL 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 acetone this gave 2.3 mg of small dark prisms. ^1H NMR (CD_3CN) δ7.81 and 7.21 (an AB quartet, 9 Hz, 7.78 H) 6.98 (m, 3.71 H), 6.26 (d of d, J_1= 3 Hz, J_2= 1 Hz, 4.18 H) 5.92 (t, 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(acetylacetonate)$_3$ [Co(acac)$_3$] or $CoBr_2$ followed by oxidation were not successful. Thus combining XVIII (102 mg, 0.5 mmol) in 7 mL THF with $\underline{n}C_4H_9Li$ in hexane (1.05 mmol) at -78°C, and pouring onto Co(acac)$_3$ (196 mg, 0.55 mmol) in 3 mL THF gave, after 1.5 h at room temperature and removal of solvents, a material that was insoluble in benzene, dilute aq. 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 int): 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 aq. $NaPF_6$. The precipitate after washing, drying, and storing, decomposed.

2,7-Di(bromomethyl)naphthalene (XIX). 2,7-Dimethylnaphthalene was prepared on 0.6 mol scale,[54] mp 96-97°C (lit 95°C,[54] 96-97°C[55]) yield 92% (lit[54] 87%). Brominating 10g according to the procedure of Baker et al.[55] gave material that was purified by a simple procedure. Succinimid 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 ($CDCl_3$) δ7.95-7.45 (m, 5.99 H), 4.65 (s, 4.01 H).

Naphthalene-2,7-bis-propionic 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%) ester. ^1H NMR ($CDCl_3$) δ7.73, 7.29 (an AB quartet, 8.5 Hz), 7.58 s (total integration: 6.11 H), 3.05 (t, 7 Hz, 4.07 H), 2.58 (t, 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 aq. NaOH and dried, giving the salt, which was converted to the acid chloride with oxalyl chloride in benzene-pyridine. Dissolved in 20 mL 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-conc. aq. 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$_3$) δ8.14, 7.64 (an AB quartet, 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 int): 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. ^{1}H NMR (CCl$_4$) δ7.65 and 7.51 (an AB quartet, 8 Hz), an AMX$_2$ system 7.74 (broad d), 6.67 (d of t, J_1 = 6 Hz, J_2 = 1.5 Hz, 2.05 H), 3.45 (t, J = 1.5 Hz, 3.93 H). Total integration of resonances at δ7.74, 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 int): 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 toluene were placed in a 2 L round-bottomed, 3-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 2¼ 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 ice-water. After conc. aq. HCl (200 mL) had been slowly stirred in, filtration, washing and drying yielded 42.5 g diol (0.179 mol, 92%). ^{1}H NMR (DMSO-d$_6$) δ7.79 (m, 8.05 H), 4.83 (m, 5.95 H). ^{1}H NMR (DMSO-d$_6$, D$_2$O added) δ7.82 (m, 8.19 H), 4.72 (d, 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, 3-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 dried in vacuo over P_2O_5 for 5 h, yielding 42.5 g. Crystallized from 450 mL benzene, the yield of XXVIII was 40.69 g (0.112 mol, 62%), mp 195-196°C dec (lit[38] 194°C dec). ^{1}H NMR ($CDCl_3$) δ7.57-7.91 (m, 7.96 H), 5.03 (s, 4.04 H).

The ratio of the amount of the ether XXXIII [^{1}H NMR δ7.6-8.1 (m, 8.23 H), 4.9 (s, 3.77 H)][37,38] and dibromide XXVIII in other experiments is summarized in Table 2.

Phenanthrene-4,5-bis-propionic 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; t-butyl lithioacetate, 110 mmol in 120 mL THF. The product was chromatographed twice on 350 g 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. ^{1}H NMR ($CDCl_3$) δ7.50-7.73 (m, 8.73 H), 3.47 (t, 7 Hz, 3.93 H), 2.22 (m, 3.99 H), 1.13 (s, 17.35 H).

This was saponified with 5 g KOH in 150 mL H_2O and 100 mL CH_3OH for

Table 2. Ratios of products formed from XXVII[a] and PBr_3.[b]

Expt.	Solvent	Molar Ratio PBr_3/XXVII	Molar Ratio $nBu_4N^+Br^-$/ 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 (reference 38). c) Listed are the ratios of intensities of ^1H NMR absorptions at δ5.05 and 4.9, except in experiment 2, where it is the ratio of the moles of products isolated.

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 (DMSO-d_6) δ7.53-7.80 (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 DMSO-d_5 peak and the absorption at δ2.17.

1,2,11,12-Tetrahydrodicyclopenta[c,g]phenanthrene-3,10-dione (XXX). To solid diacid chloride, prepared by refluxing 2.09 g XXIX (6.5 mmol) and 10.4 g oxalyl chloride (81.5 mmol) in 70 mL benzene, in 110 mL 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 17 h at room temperature, the mixture was poured into ice and conc. aq. HCl, extracted with 3 x 200 mL CH_2Cl_2, washed with water and aq. $NaHCO_3$, 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. ^{1}H NMR ($CDCl_3$) δ8.06, 7.95 (an AB quartet, 8 Hz, 4.14 H), 7.90 (s, 1.98 H), 3.60 (t, 6 Hz, 3.94 H), 2.82 (t, 6 Hz, 3.94 H). Ir (KBr, cm^{-1}): 1702 vs. Ms (EI, peaks >15%) m/e (rel int): 202 (17), 215 (39), 216 (26), 229 (19), 230 (50), 314 (1), 315 (M, 100), 316 (23), 317 (3).

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 and working up with water and chloroform, and chromatographing on 60 g 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 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 (DMSO-d_6) δ7.79, 7.71 (an AB system, 10 Hz), 7.66 (s), 5.28 (m), 4.03 (broad s, removed by added D_2O), 3.22 (broad m), 2.33 (broad m), 1.66 (broad m). Because DMSO-d_5 partially obscured the peak at δ2.33, 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 p-TsOH in 50 mL benzene. Chromatography on silica (300 g) with n-pentane-ether (98:2 v/v) gave 198 mg crystals (39% yield), mp 151-152°C. ^{1}H NMR (CS_2) δ7.65, 7.58 (an AB system, 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 Hz, J_2 = 2 Hz, 2.16 H), 6.56 (d of t, J_1 = 5.5 Hz, 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 3.87 is irradiated, implying there to be a long range splitting in the resonance at $\delta 7.65$. 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 int): 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) was placed ferrous chloride (95% from ROC/RIC, 80 mg, 0.630 mmol) and 3 mL THF, in the right, a solution of hydrocarbon XXXII (120 mg, 0.472 mmol) in 9 mL THF, which when cooled to -78°C was treated with 0.40 mL 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, and under argon the sticky residue was extracted with 65 mL 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 the *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_2Cl_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 int): 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 int): 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 ^1H NMR spectrum (CS_2, sealed tube). In both cases no sharp signals were observed. (The TMS signal, however, was sharp).

An attempt to make the cobalticinium analogue in the way XXV was prepared gave only a trace of solid when aq. $NaPF_6$ was added. Its ^1H NMR spectrum in $(CD_3)_2CO$ 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-bromosuccinimid (205 mg, 1.148 mg), and 1 mg dibenzoyl peroxide in 5 mL CCl_4 were refluxed and irradiated (300 W incandescent bulb) under nitrogen for 1 h. Filtration, evaporation, and chromatography (50 g silica, pentane) yielded 70 mg (0.21 mmol, 38%) of crystalline 1-bromomethyl-12-methylbenzo[c]phenanthrene

^1H NMR ($CDCl_3$) δ7.20-7.98 (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-bis-propionic acid (XXXVIII). 2,11-Di(bromomethyl)benzo[c]phenanthrene XXXVII[40] (300 mg, 0.725 mmol) in 4 mL THF and 0.32 mL (325 mg, 1.812 mmol) HMPA was alkylated with t-butyl lithioacetate as described in the preparation of acid XIX. Obtained after chromatography was 245 mg (0.506 mmol, 70%) of white solid. ^1H NMR ($CDCl_3$) δ8.94 (s, 1.90 H), 7.84 and 7.43 (an AB system, 8 Hz), 7.74 and 7.65 (an AB system, 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 H_2O-2 mL CH_3OH 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. ^1H NMR (DMSO-d_6) δ8.87 (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, 7 Hz), 7.26 (t, 7 Hz). Because of the presence of the DMSO-d_5 absorption at δ7.5, integration of the whole spectrum was not possible. The ratio of the intensities of the downfield aromatic singlet (δ8.87) and the upfield aromatic AB systems is 1.79/8.21.

Cyclization of benzo[c]phenanthrene-2,11-bis-propionic acid (XXXVIII). Aluminum chloride (86 mg, 0.645 mmol) was added in portions to a CH_2Cl_2 solution (20 mL) of diacid chloride prepared from 60 mg XXXVIII, as its sodium salt, and oxalyl chloride. After stirring at room temperature for 18 h, pouring onto a mixture of ice and conc. aq. HCl, and extracting with CH_2Cl_2 (3 x 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 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 ($CDCl_3$) δ9.12 (s, 2.11 H), 8.45 (s, 1.91 H), 8.04 and 7.82 (an AB system, 7 Hz, 3.97 H), 3.48 (t, 6 Hz, 3.82 H), 2.88 (t, 6 Hz, 4.18 H). Ir (KBr, cm^{-1}): 1710 vs. Ms (CI, methane) m/e (rel int): 336 (5), 337 (100, M+1), 338 (26), 339 (2).

Spectra of XL ^{1}H NMR ($CDCl_3$) δ8.40-7.66 (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 int): 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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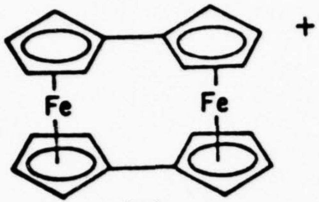
References and Notes

(1) For recent reviews of one-dimensional complexes see (a) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1; (b) Yoffe, A. D. *Chem. Soc. Rev.* **1976**, *5*, 51.

(2) Some reasons for thinking electrons might be transported easily through structure I are (a) that the iron atoms in the mono cation of bisfulvalenediiron (BFD, structure i) appear to be equivalent,[3] although



(i)

those in the mono cation of biferrocene do not,[3b,c,4] (b) that the corresponding dication is diamagnetic,[3a,5] (c) that the electrical conductivity of biferrocene monopicrate is a million times greater than that of either ferrocene or ferrocenium picrate,[4] (d) that partially oxidized ferrocene-containing polymers are semiconductors,[4,6] and (e) that the conductivity of $BFD^+ (TCNQ)_2^-$,[7] where BFD^+ is structure i and TCNQ is tetracyanoquinodimethane, is comparable to that of the most highly conducting TCNQ salts.[8]

(3) (a) 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; (b) Morrison, Jr., W. H.; Hendrickson, D. N. J. Chem. Phys. 1973, 59, 380; (c) Morrison, Jr., W. H.; Hendrickson, D. N. Inorg. Chem. 1975, 14, 2331.

(4) Cowan, D. O.; LeVanda, C.; Park, J.; Kaufman, F. Acc. Chem. Res. 1973, 6, 1 and references therein.

(5) Morrison, Jr., W. H.: Krogsrud, S.; Hendrickson, D. N. Inorg. Chem. 1973, 12, 1998.

(6) Pittman, Jr. C. U.; Sasaki, Y. Chem. Lett. 1975, 383.

(7) Mueller-Westerhoff, U. T.; Eilbracht, P. J. Am. Chem. Soc. 1972, 94, 9272.

(8) (a) Garito, A. F.; Heeger, A. J. *Acc. Chem. Res*. **1974**, *7*, 232; (b) Gemmer, R. V.; Cowan, D. O.; Poehler, T. O.; Bloch, A. N.; Pyle, R. E.; Banks, R. H. *J. Org. Chem*. **1975**, *40*, 3544; (c) Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc*. **1976**, *98*, 3916; (d) Engler, E. M.; Scott, B. A.; Etemad, S.; Penney, T.; Patel, V. V. *ibid*. **1977**, *99*, 5909.

(9) Metallocene polymers and their conductivities are discussed in (a) Neuse, E. W.; Rosenberg, H. "Metallocene Polymers," [*Rev. Macromol. Chem*. *5*, Part 1], Marcel Dekker, Inc.: New York, 1970; (b) Lorkowski, H.-J. *Fortschr. Chem. Forsch*. **1967**, *9/2*, 207.

(10) (a) Katz, T. J.; Schulman, J. *J. Am. Chem. Soc*. **1964**, *86*, 3169; (b) Katz, T. J.; Balogh, V.; Schulman, J. *ibid*. **1968**, *90*, 734; (c) Schneider, R. S. *J. Polym. Sci., C* **1970**, 27; (d) Katz, T. J.; Acton, N. *J. Am. Chem. Soc*. **1972**, 94, 3281; (e) Katz, T. J.; Acton, N.; McGinnis, J. *ibid*.**1972**, *94*, 6205.

(11) (a) Nesmeyanov, A. N.; *et al*. *Izv. Akad. Nauk SSSR, Ser. Khim*. **1963**, 667; (b) Watanabe, H.; Motoyama, I.; Hata, K. *Bull. Chem. Soc. Jpn*. **1966**, *39*, 790; (c) Roling, P. V.; Rausch, M. D. *J. Org. Chem*. **1972**, *37*, 729; (d) Izumi, T.; Kasahara, A. *Bull. Chem. Soc. Jpn*. **1975**, *48*, 1955; (e) Bednarik, L.; Gohdes, R. C.; Neuse, E. W. *Transition Met. Chem. (Weinheim Ger*.) **1977**, *2*, 212.

(12) (a) Bilow, N.; Landis, A. L.; Rosenberg, H. *J. Polym. Sci., Part A-1* **1969**, *7*, 2719; (b) Neuse, E. W.; Crossland, R. K. *J. Organometal. Chem*. **1967**, *7*, 344.

(13) Katz, T. J.; Acton, N. Unpublished experiments in this laboratory.

(14) Davison, A.; Smart, J. C. *J. Organometal. Chem*. **1973**, *49*, C43.

(15) Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc*. **1977**, *99*, 956.

(16) Bisfulvalenediiron, the reaction product ov V and $FeCl_2$, has also been

made from ferrocene: (a) Hedberg, F. L.; Rosenberg, H. J. Am. Chem. Soc. 1969, 91, 1258; (b) Rausch, M. D.; Kovar, R. F.; Kraihanzel, C. S. ibid. 1969, 91, 1259; (c) Reference 3a. It's structure has also been verified by X-ray crystallography [Churchill, M. R.; Wormald, J. Inorg. Chem. 1969, 8, 1970]. So has that of bis(as-indacenylene)diiron: Gitany, R.; Paul, I. C.; Acton, N.; Katz, T. J. Tetrahedron Lett. 1970, 2723.

(17) Smart, J. C.; Curtis, C. J. Inorg. Chem. 1977, 16, 1788.

(18) Reviews on benzenoid and hetero helicenes are in (a) Martin, R. H. Angew. Chem. Int. Ed. Engl. 1974, 13, 649 and (b) Wynberg, H. Acc. Chem. Res. 1971, 4, 65.

(19) Benzenoid helicenes as large as [14]helicene have been prepared: Martin, R. H.; Baes, M. Tetrahedron 1975, 31, 2135.

(20) Schneider, R. S.; Ullman, E. F. Tetrahedron Lett. 1969, 3249.

(21) (a) Rahman, A.; Vuano, B. M.; Rodriguez, N. M. Chem. Ind. (London), 1970, 1173; (b) Rahman, A.; Vuano, B. M. Chem. Ber. 1970, 103, 2320; (c) Rahman, A.; Tombesi, O. L. Chem. Ind. (London) 1968, 1840; (d) UrRahman, A.; Perl, C. Justus Liebigs Ann. Chem. 1968, 718, 127; (e) UrRahman, A.; del Carmen Torre, M. ibid. 1968, 718, 136; (f) UrRahman, A.; Tombesi, O. L. Chem. Ber. 1966, 99, 1805; (g) UrRahman, A.; Khan, A. A. ibid. 1962, 95, 1786.

(22) Rathke, M. W.; Lindert, A. J. Am. Chem. Soc. 1971, 93, 2318.

(23) Ewing, G. D.; Paquette, L. A. J. Org. Chem. 1975, 40, 2965.

(24) HMPA has been useful before as a co-solvent in alkylations of lithiated esters of α,β-unsaturated carboxylic acids in THF, but in the metalation step, not the alkylation: (a) Rathke, M. W.; Sullivan, D. Tetrahedron Lett. 1972, 4249; (b) Hermann, J. L.; Kieczykowski, G. R.; Schlessinger, R. H. Tetrahedron Lett. 1973, 2433.

(25) Hunter, D. M.; Stothers, J. B. *Can. J. Chem.* **1973**, *51*, 2884.

(26) PPA = polyphosphoric acid; Dibal = diisobutylaluminum hydride; *p*TsOH = *p*-toluenesulfonic acid.

(27) (a) Figeys, H. P. *Tetrahedron Lett.* **1966**, 4625; (b) Martin, R. H.; Defay, N.; Figeys, H. P.; Flammang-Barbieux, M.; Cosyn, J. P.; Gelbeke, M.; Shurter, J. J. *Tetrahedron* **1969**, *25*, 4985; (c) Reid, C. *J. Mol. Spectroscopy* **1957**, *1*, 18.

(28) (a) Douris, J.; Mathieu, A. *Bull. Soc. Chim. Fr.* **1971**, 3365; (b) Elleman, D. D.; Manatt, S. L. *J. Chem. Phys.* **1962**, *36*, 2346.

(29) The M + 57 peak, corresponding to addition of $C_4H_9^+$, rather than the M + 1 peak in the isobutane chemical ionization mass spectrum was used to determine the deuterium distribution,[30,41] because in the spectrum of the undeuterated material the ratio of the intensities was larger (*ca.* 0.3) for the peaks at M and M + 1 than for the peaks at M + 56 and M + 57 (0.04). The contribution from M + 56 was neglected in the calculations.[31]

(30) Katz, T. J.; Rothchild, R. *J. Am. Chem. Soc.* **1976**, *98*, 2519.

(31) Biemann, K. "Mass Spectrometry", McGraw-Hill: New York, 1962; 61.

(32) Hückel molecular orbital calculations do not reveal any appreciable difference in charge density at the two likely places where protonation might occur.

(33) Mueller-Westerhoff, U. T.; Eilbracht, P. *Tetrahedron Lett.* **1973**, 1855.

(34) (a) Pauson, P. L., Wilkinson, G. *J. Am. Chem. Soc.* **1954**, *76*, 2024; (b) Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 6148.

(35) Fritz, H. P.; Kreiter, C. G. *J. Organometal. Chem.* **1965**, *4*, 198.

(36) (a) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press:

Oxford, England, 1969; 333ff; (b) Elvidge, J. A.; Foster, R. G. J. Chem. Soc. 1963, 590; (c) Defay, N. Org. Magn. Resonance 1974, 6, 221.

(37) Newmann, M. S.; Whitehouse, H. S. J. Am. Chem. Soc. 1949, 71, 3664.

(38) Badger, G. M.; Campbell, J. E.; Cook, J. W.; Raphael, R. A.; Scott, A. I. J. Chem. Soc. 1950, 2326.

(39) (a) Newman, M. S.; Wolf, M. J. Am. Chem. Soc. 1952, 74, 3225; (b) Newman, M. S.; Wise, R. M. J. Am. Chem. Soc. 1956, 78, 450.

(40) DeStefano, N. J.; Johnson, D. K.; Lane, R. M.; Venanzi, L. M. Helv. Chim. Acta, 1976, 59, 2674.

(41) Ślusarek, W. Dissertation, Columbia University 1978.

(42) Gore, P. H.: Siddiquei, A. S. J. Chem. Soc., Perkin I 1972, 1442.

(43) Martin, R. H.; Defay, N.; Geerts-Evrard, F.; Delavarenne, S. Tetrahedron 1964, 20, 1073.

(44) Schubert, W. M.; Sweeney, W. A.; Latourette, H. K. J. Am. Chem. Soc. 1954, 76, 5462.

(45) Goedicke, Ch.; Stegemeyer, H. Tetrahedron Lett. 1970, 937.

(46) Groen, M. B.; Schadenberg, H.; Wynberg, H. J. Org. Chem. 1971, 36, 2797.

(47) Golden, J. H. J. Chem. Soc. 1961, 3741.

(48) Burnham, J. W.; Eisenbraun, E. J.; Hamming, M.C.; Keen, G. W. Org. Prep. Proc. Int. 1972, 4, 35.

(49) Beyler, R. E.; Sarett, L. H. J. Am. Chem. Soc. 1952, 74, 1406.

(50) (a) Reid, W.; Boden, H. Chem. Ber. 1958, 91, 1981; (b) Ghilardi, G.; Kalopissis, G. Bull. Soc. Chim. Fr. 1952, 19, 217.

(51) Kollonitsch, J.; Fuchs, O.; Gábor, V. Nature 1954, 173, 125.

(52) Shriver, D. F. "The Manipulation of Air-sensitive Compounds", McGraw-Hill: New York, 1969; 251.

(53) Bjerrum, J.; McReynolds, J. P. Inorg. Synth. 1946, 2, 217.

(54) Wolinska-Mocydlarz, J.; Cannone, P.; Leitch, L. C. Synthesis 1974, 566.

(55) Baker, W.; McOmie, J. F. W.; Warburton, W. K. J. Chem. Soc. 1963, 3295.

(56) Laarhoven, W. H.; Cuppen, Th. J. H. M. Tetrahedron 1974, 30, 1101.

(57) Dessy, R. E.; Newman, M. S. Org. Synth. 1963, Coll. Vol. IV, 484.

APPENDIX 2.

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The Trindene Trianion

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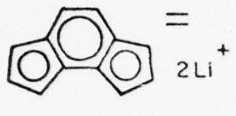
Abstract

The lithium salt of the trindene trianion (6) is synthesized in four steps from cyclopentanone. Bromination and debromination, as summarized in Scheme 3, convert trindane (octahydro-1H-trindene, 14) into the dihydro-1H-trindenes, 16a and 16b, and these with *n*-butyllithium in tetrahydrofuran give 6. The formation of the trianion is evidenced by quenching with deuterated water yielding the required trideuterio derivatives of 16a and b. When only two moles of *n*-butyllithium are used, the dianion 18 forms instead, as evidenced by reaction with deuterated water yielding molecules of 16a and b containing two allylic deuterium atoms. Sandwich molecules, assigned structures 19a and b, containing two irons, are produced when the dianion is combined with ferrous chloride, and only traces of sandwiches containing three iron atoms (presumably 9 with M=Fe) are detected in the corresponding reaction product of 6. A product hoped for, polymer 5, could not be identified. The trindene trianion, although it contains multiple charges in one π-electron system, is a favorable species because its rings are all five- and six-membered, because its highest occupied molecular orbital is low in energy, and because its lowest unoccupied molecular orbital is high in energy.

Introduction

With proper control of the hydrocarbon, it should be possible to circumvent the tendency of ions like 1,[1] 2,[2] and 3[3], when mixed with transition metal salts, from giving dimers like 4 (here M is the metal) rather than the novel and more interesting polymeric structures 5. One way is to cause the hydrocarbon to react with metals on opposite faces, at b rather than a in Scheme 1, a possibility considered in another publication.[4]



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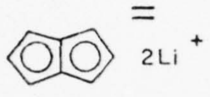

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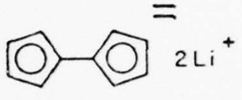

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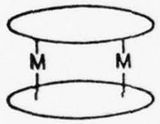

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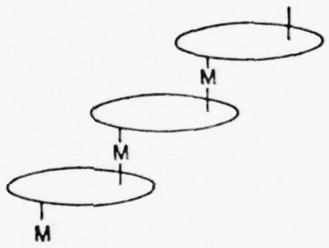
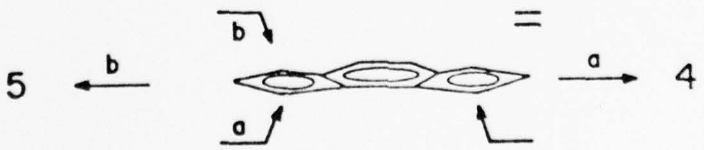


5

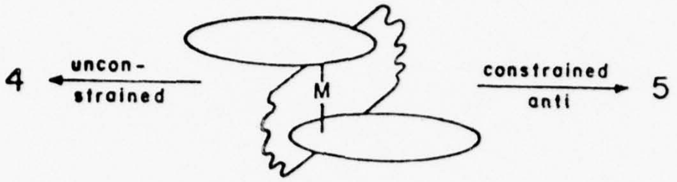
The other is to constrain the hydrocarbons bonded by the metals to anti-conformations, in which dimerization is impossible whether the metals attach to the same or to opposite faces of one ring system (Scheme 2), a possibility considered here.

Scheme 1

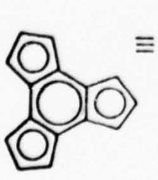


At first the means by which the hydrocarbons could be strapped

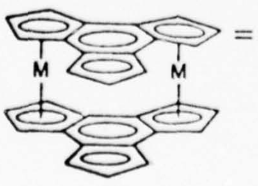
Scheme 2



together appropriately appeared obscure and the task seemed formidable, but motivating the work below was the thought that the trindene trianion, 6, could provide a simple solution. If it combined with two transition metal cations in the way that 1 does, the remaining centers of reactivity on adjacent ring systems are likely to be kept apart by steric and coulombic repulsive forces and to be locked in their positions by the bonds between the metals and the five-membered rings. Thus the reaction of trindene trianion with metal ions rather than giving 7 should give 8, which because it appears to be an example of the constrained ring system symbolized in Scheme 2 should react further with metal ions to give polymers like 5. Even if this hypothesis did not work, an investigation of the reaction of 6 with metal cations appeared worthwhile, for should 7 form instead, with additional metal ions it also might form polymers like 5, or it might give the first examples of an extraordinary structure, 9, in which two planar aromatic hydrocarbons are united by three metal atoms.



6



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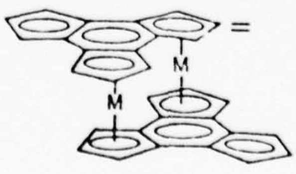

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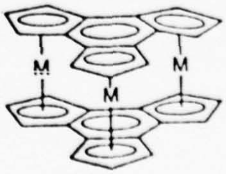
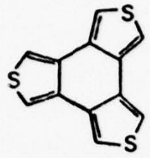


9

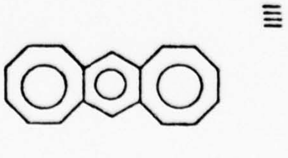
To study these possibilities 6 had to be synthesized, and as the only derivative that had been made before was the recently prepared molecule 10, related to it as thiophene is to cyclopentadienide,[5] a way to make 6 itself was developed and is described below.



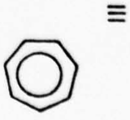
10

Another consideration motivating the work to make 6 was the possibility of finding out how difficult it is to form a conjugated polyanion, a structure in which coulombic repulsion might be severe and inescapable. The expectation that such repulsion might prove an insurmountable barrier to synthesis could account for the rarity of *tri-* and *tetra*-anions,[6] although there are some, notably 11[6a] and 12[6e] which are formed from the corresponding hydrocarbons by reduction with potassium in ethers, and 13, which is formed from appropriate hydrocarbons by deprotonation with *n*-butyllithium plus tetramethylethylenediamine.[6f] (Species like Li$_4$C$_3$,[7] lithiated propyne, might also be related to these ions.) However, there

11



12



13

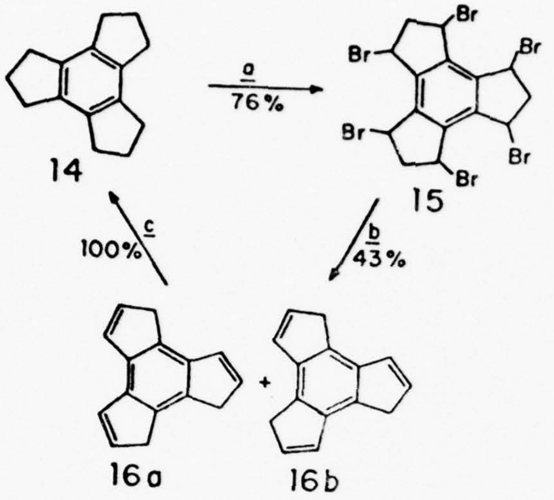
is a feature of 6's structure that distinguishes it from the polyanions made before and that should endow it with special stability: the energies of its Hückel molecular orbitals are distributed in such a way that only the bonding ones are occupied.[8] Streitwieser, Berke, and Robbers'[9] recent demonstration that the first and second pKa's of 9,10-dihydroanthracene differ by little (4 pK units) helps justify the belief in its stability.

Results

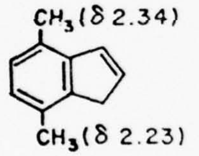
The dihydro-1H-trindenes (16a and 16b), the conjugate acids of the trindene trianion were prepared simply (Scheme 3) from "trindane" (octahydro-1H-trindene, 14), the condensation trimer of cyclopentanone.[10] Thus bromination in the way previously developed to make hexa(α-bromoethyl)benzene[11] and debromination in a way previously found to give indene[12] produce the dihydrotrindenes in 43% yield. That this product is a mixture of nearly statistical amounts of the two isomers, 16a and 16b, is indicated by its ^{1}H NMR spectrum showing two methylene resonances, at δ3.42 and 3.28, with similar intensities. The difference in the chemical shifts of these resonances is similar to the analogous difference in 4,7-dimethylindene (17),[13] and accordingly the resonance at δ3.42 is assigned to the methylenes in 16b and to one of the methylenes in 16a, while that at δ3.28 is assigned to the other two in 16a.[14]

With 3.5 equivalents of n-butyllithium in tetrahydrofuran (THF) at -78°C, the dihydro-1H-trindenes (16) form the trianion 6, identified by its reaction with deuterated water (D_2O) giving back 16 (in 88% yield) with three deuterium atoms incorporated in the allylic positions. The number and location of the deuteriums were identified by the ratio of the intensities of the methylene and vinyl proton resonances, which in the precursor is 1.00 but in the deuterated product is 0.48 in one experiment and 0.49

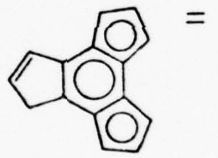
Scheme 3



(a) Br_2/CCl_4, hν; (b) Zn/DMF; (c) H_2/PtO_2



17



18

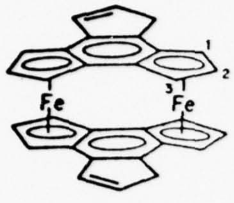
in another.

Mass spectrometric analyses[15] of the deuterated product also showed three deuterium atoms per molecule, implying again that the trianion was its precursor. Thus upon chemical ionization with isobutane only two major peaks were observed: m/e 196 (M+1, base peak), corresponding to proton addition, and 252 (M+57, 77% of the base peak), corresponding to addition of $C_4H_9^+$. To measure the ratios of deuterated products the M+57 peaks were used rather than the M+1's, for in the mass spectrum of 16-d_0, measured under the same conditions, the ratio of the intensities of the peaks at M and M+1 was larger (0.14) than that of M+56 and M+57 (0.03). The ratios of the deuterated molecules calculated from a spectrum in which 77 scans were summed were 0.6% 16-d_0, 1.4% 16-d_1, 2.8% 16-d_2, and 95.2% 16-d_3. A second series of measurements (67 scans) made on the same sample gave results that were almost identical, and measurements on an independently prepared sample gave results that were similar: 2% 16-d_0, 0% 16-d_1, 6% 16-d_2, and 92% 16-d_3.

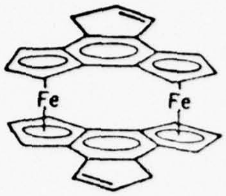
Attempts to measure the ^{1}H NMR spectrum of 6 were not successful.[16] In THF the lithium derivative is too insoluble, and its spectrum could not be recognized when attempts were made to dissolve it in hexamethylphosphoric triamide (HMPA)[17] or to prepare and identify the sodium salt by combining 16 with dimsylsodium in dimethylsulfoxide.[18]

With two, rather than three, equivalents of *n*-butyllithium in THF at -78°C, hydrocarbons 16 give the dianion (18), which was identified by its reaction with D_2O returning 16 in 88% yield with deuterium atoms incorporated in two of the allylic positions. Thus the ratio of methylene and vinyl resonances in the ^{1}H NMR spectrum was 0.66, and the distribution of deuterium atoms implied by the mass spectrum was 1.4% d_0, 6.7% d_1, 85.7% d_2, and 6.3% d_3. (The experiment, incidentally, shows that, as expected, the dianion does not disproportionate appreciably to the mono- and trianions.)

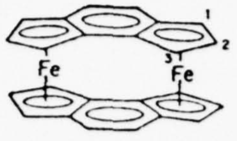
With ferrous choride, 18 gives in 53% yield bis(trindenylene)diiron, assigned for the reasons discussed below structures 19 (a and b). The ferrocene is an auburn solid, which although slightly soluble in CS_2, THF, CH_2Cl_2, and benzene, resisted crystallizing. Its mass spectrum on electron impact at low voltage (15V) consists only of the parent peaks.[19] Its ^{1}H NMR spectrum, summarized in the experimental section and displayed and analyzed in the supplementary material, resembles that of the bis(*as*-indacenyl)diiron, 20a and 20b,[20] complicated by additional AMXX' reonances due to the extra ring. The similarity in the chemical shifts,



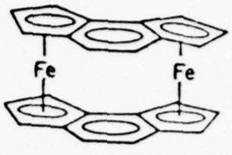
19a



19b



20a



20b

summarized in Table 1, is especially close for the resonances of 19 and those assigned to 20a, suggesting that the hydrocarbon rings in

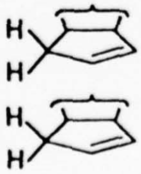
Table 1. Chemical Shifts[a] of Protons in 19 and 20a and 20b

	H_1	H_2	H_3
19a and b[b]	4.04 and 4.13	3.71	5.16 and 5.11
20a[c]	4.00	3.65	5.33
20b[c]	4.00	3.16	6.08

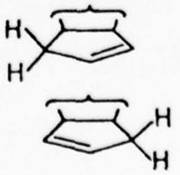
[a] Ppm from tetramethylsilane.

[b] This work. [c] Reference 20.

bis(trindenylene)diiron are disposed *trans*, as in structures 19, rather than *cis*, as in 21 (a or b). This assignment is supported by the ^{1}H NMR spectrum



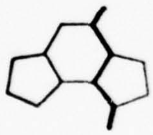
21a



21b

displaying only one set of AMXX' resonances, for if, as seems likely, both a and b isomers are present, the overlap of the resonances of the five-membered rings not bonded to the metal probably reflects the similarity of the local environments in the two isomers. This is apparent in 19a and 19b where the cyclopentenes are remote and not in 21a and 21b where they are proximate.

The assignments displayed in Table 1 for the resonances of protons 1 and 3 in the bis(*as*-indacenyl)diirons are, incidentally, the reverse of those published previously,[20] a revision made because the long-range proton-proton spin coupling that was the basis for the assignment is probably transmitted more efficiently through the five bonds outlined on structure 22, a zig-zag arrangement,[21] than through the shorter four-bond path outlined on structure 23.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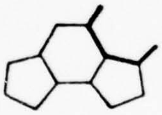
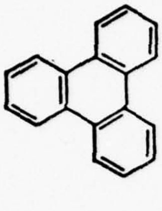

23

A few attempts were made to convert trilithium trindenide into a polymer like 5 using ferrous chloride, but they were not successful. They gave an auburn solid that is insoluble in CS$_2$ and THF at room temperature and in toluene, chlorobenzene, and *o*-dichlorobenzene at their boiling points. It does not change noticeably when stored under argon, but in the air it turns black for a few hours. Its elemental analyses for carbon, hydrogen, and iron total to only 74-85%. Its infrared spectra exhibit strong peaks at 3400, 1010, and 785 cm^{-1} (the latter two similar to peaks in 19, 20,[1b] and related ferrocenes[4]). The properties of a product formed when 19 in THF is treated first with two moles of *n*-butyllithium and then with ferrous chloride are similar. The dianion 8 (M=Fe) is probably an intermediate in this sequence, but was not characterized except to the extent that it was shown with D_2O to give 19 that according to mass spectrometric analysis is substantially dideuterated.[22] The most interesting observation during the course of the experiments to prepare 5 was of small amounts of material isolated by extraction with CS_2 from the reaction of trilithium trindenide with ferrous chloride. This material exhibits the mass spectrometric peaks expected for 9 when M is iron: a cluster around m/e 546, intensities for the peaks at m/e 547 and 548 that are 44% and 12% of that at 546 (considering the abundance of the isotopes the figures should have been 41% and 12%), and no other peaks in the vicinity. Undoubtedly some molecules with structure 9 are present, but the amount must be very small, for the samples that exhibit these mass spectra also exhibit many peaks at low mass, implying that the bulk of even these small samples are simpler impurities.

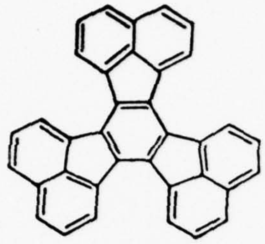
Discussion

While the objective to characterize materials like 5 and 9 was not attained, 9 (with M=Fe) appearing to form in only minuscule amounts and 5 (with M=Fe), if present, not being purifiable, the experiments lead the way to other such molecules by showing how the trindene trianion can be made.

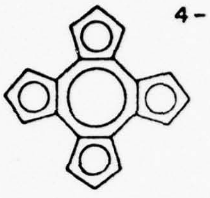
The trindene trianion (6) is the smallest polycyclic conjugated hydrocarbon with a three-fold axis of symmetry to be synthesized. That axis should preserve almost all the orbital degeneracies characteristic of annulenes with the same number of carbon atoms, the exceptions being degeneracies derived from the kth pair in the annulene where k is divisible by three. Triphenylene (24) is the prototype of such a molecule,[23] and there are other more complicated examples, like 25, that are related to it.[5a, 24]



24



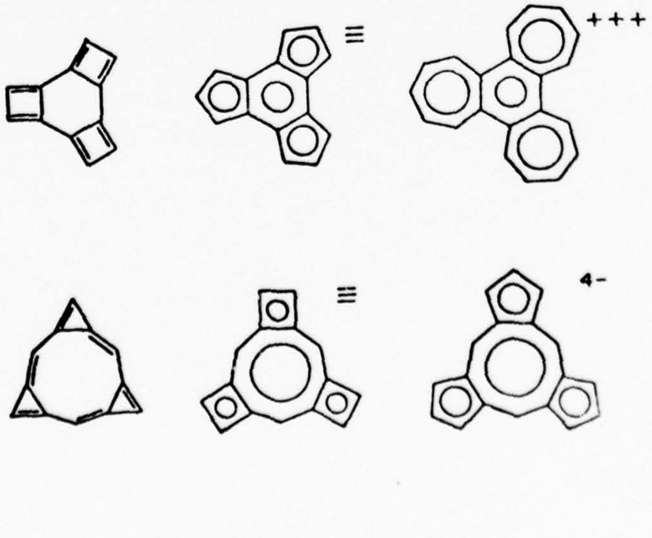
25



26

The trindene trianion (6) is the first to be made in which the rings comprising the framework are not all benzenes, and it represents a variety of such molecules like those imagined and pictured in Chart I. Analogous structures having four-fold axes of symmetry, 26 being an example, can also be imagined to evolve. Yet except for the trindene trianion, no such structures have been made, and the synthesis described here suggests that attempts to make at least some of the others be tried.

Chart I



Among these structures the trindene tranion is a particularly favorable one because its rings are all five- and six-memberd so that strain is minimal, because the highest occupied π-molecular orbital is particularly low in energy,[7] and because the lowest unoccupied π-molecular orbital is particularly high in energy.[8] Although these effects should be counteracted by the accumulation of multiple charges in the same π-electron system, the preparation of the trindene trianion shows that it can be made easily available for the synthesis of new materials, as well as for other studies.

Experimental

General

Infrared spectra (IR) were determined using a Perkin-Elmer 621 Spectrometer, ^{1}H NMR spectra using Varian HA100 and Perkin-Elmer R32, mass spectra (MS) using Jeol MS-07 and Finnigan 3300, and UV spectra using a Cary 17. EI means electron impact and CI chemical ionization. Melting points (Thomas Hoover apparatus) are not corrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

1,3,4,6,7,9-hexabromotrindanes (15).

Trindane (14) was prepared from 500 g cyclopentanone by the Mayer procedure.[10a] Yield 68.8 g (17.5%, lit[10a] 18-20%). Mp 95-96°C (lit[10a] 97.5-98.0°C). ^{1}H NMR (CCl_4): δ2.71 (t, 12.05 H), 2.01 (quint., 5.95 H). MS (EI, 13 V, only peaks $\geq$3% are listed) m/e (rel int): 170 (3), 196 (3), 197 (6), 198 (100, M), 199 (32.5).

Trindane (10 g, 50.5 mmol) and 300 mL CCl_4 were placed in a 1 L round-bottomed, 3-necked flask fitted with an addition funnel, a mechanical stirrer, and a condenser equipped with a tygon tube to vent HBr to the hood. To the solution, cooled in an ice-salt bath and illuminated with a 300 W incandescent bulb, a solution of 50 g (313 mmol) of bromine dissolved in 200 mL CCl_4 was added in drops over a period of 4.3 h. (After ca. 70% of the bromine solution had been added, a precipitate appeared.) To complete the reaction, the flask contents were stirred and illuminated for an additional 1 h, and then gently refluxed for 1.5 h while flushing with nitrogen to remove traces of bromine and HBr. Filtration, washing with ether (3 x 5 mL), and drying in vacuo over P_2O_5, yielded 10.39 g of off-white powder. The filtrate was evaporated, giving an oil that on addition of 100 mL ether solidified. The solid was collected, washed with ether (4 x 10 mL), and dried in vacuo over P_2O_5 for 2 h, yielding another 15.53 g of off-white powder. The total yield was 25.92 g (38.57 mmol, 76%). In 3 similar experiments the yields were 70, 73 and 75%. A 0.9 g sample of the product was purified by dissolving it in boiling THF, filtering, and adding dry ether to precipitate 146 mg of white crystals. This product did not melt, but decomposed at 190°C, emitting white fumes. ^{1}H NMR ($CDCl_3$): δ 5.47-5.97 (m, 5.77 H), 2.92-3.38 (m, 6.23 H). IR (KBr, cm^{-1}): 3440 broad w, 2984 w, 2917 w, 1415 m, 1307 w, 1214 m, 1185 shoulder, 1171 s, 987 m, 917 m, 890 s, 808 w, 759 w, 717 w, 700 w, 560 m, 536 w, 515 shoulder, 480 w. MS (EI, 30 V, except for the parents, only peaks with intensities >25% are listed) m/e (rel int): 79 (33), 80 (100), 81 (38), 82 (100), 189 (33), 190 (43), 191 (55), 192 (41), 271 (26), 591 (25), 593 (25), 671 (<1), 673 (<1). UV [CH_3CN, λ[nm], (log ε)]: 243 (5.033). Anal. Calcd for $C_{15}H_{12}Br_6$: C, 26.82; H, 1.80; Br, 71.38. Found: C, 26.09, 26.99; H, 1.67, 2.03; Br, 67.45, 68.25.

Dihydro-1H-trindenes (16a and b).

Activated zinc dust[25] (15 g) and argon-purged dry dimethylformamide (DMF) were placed in a 1 L, 3-necked, round-bottomed flask fitted with a mechanical stirrer and an addition funnel, and equipped with an argon inlet. To this mixture, stirred and cooled in a water-ice bath, solid **15** (25.34 g, 37.71 mmol) and triethylamine (6 mL) were added simultaneously during 15 min. The resulting dark mixture was stirred at 0°C for 1/2 h and at room temperature for 18 h, filtered through Celite, and poured into 500 mL ice-water. The precipitate was collected, washed with water, and taken up in 400 mL ether, and the aqueous filtrate was extracted with petroleum ether (3 x 400 mL). The combined extracts were washed, dried over $MgSO_4$, and evaporated. Chromatography (60 g silica, petroleum ether) and crystallization from petroleum ether at -78°C yielded 3.01 g (15.68 mmol; 43%) of colorless needles, mp 108-110°C. In numerous similar experiments the yields were approximately 35%. A sample for analysis was sublimed at 45°C/10^{-6} torr.

Anal. Calcd for $C_{15}H_{12}$*:* C, 93.71; H, 6.29. *Found:* C, 93.88; H, 6.14.

UV [cyclohexane, λ_{max}[nm] (log ε)]: 220 (4.125), 227 (4.088), 257 (4.378), 265 (4.379), 282 (3.992), 297 (4.046), 308 (3.961), 329 (2.887). IR (CCl_4, cm^{-1}): 3109 w, 3092 w, 3054 m, 2881 m, 2763 w, 1614 w, 1430 w, 1396 m, 1387 m, 1335 m, 1314 w, 1236 w, 1118 w, 1110 m, 939 s, 921 m, 914 m, 902 m, 724 m, 709 s, 686 s, 634 w, 610 m. MS (EI, 75 V, only intensities >10% are listed) m/e (rel int): 39 (21), 50 (10), 51 (11), 63 (18), 95 (12), 165 (28), 189 (30), 190 (17), 191 (69), 192 (M, 100), 193 (16.5), 194 (3.5). ^1H NMR (CCl_4) δ6.95 (broad m, 2.95 H), 6.41 (broad m, 3.05 H), 3.42 (m, 3.05 H), 3.28 (m, 2.95 H).

Attempts to debrominate **15** using zinc in dimethyl sulfoxide or hexamethylphosphoric triamide instead of DMF, or using Zn-Cu couple[25] in DMF or Zn-Ag couple[26] in DMF all gave **16**, but in none of these variations were the yields improved. Debromination with lithium amalgam[27] in dioxane gave 16 in low yield (14%).

Hydrogenation of 16.

A solution of 16 (125 mg, 0.651 mmol) in 25 mL absolute ethanol over PtO_2 (20 mg, 0.088 mmol) absorbed 52.7 mL hydrogen (calcd 52 mL) at room temperature and atmospheric pressure during 30 min. Filtration and evaporation gave 130 mg (0.657 mmol, 100%) of colorless needles mp 94-95°C, identified as 14 by its ^1H NMR spectrum.

Trilithium trindenide (6).

To a solution of 500 mg (2.6 mmol) of 16 in 12 mL THF cooled to -78°C, 4.34 mL of 2.1 M n-butyllithium in n-hexane (9.12 mmol) was injected in drops through a serum cap. The solution turned yellow and some precipitate appeared. The mixture was stirred cold for 1/2 h, warmed to room temperature, and then stirred for an additional 45 min. At ca. 0°C a thick yellow suspension formed, which gradually turned off-white during the stirring at room temperature. This suspension separated to an off-white precipitate and a slightly yellow supernatant liquid only after prolonged standing. The salt could be filtered and did not noticeably decompose when stored overnight in an argon atmosphere. Attempts to measure its ^1H NMR spectrum in THF or HMPA failed because of its insolubility in the former and its apparent decomposition in the latter.

Reaction of trilithium trindenide (6) with deuterium oxide.

The salt prepared as above from 50 mg (0.26 mmol) of 16 was quenched with an excess (5 mL) of deuterium oxide. The organic layer was separated and the aqueous layer extracted with n-pentane (2 x 15 mL). Drying ($MgSO_4$), evaporation, and chromatography on 18 g silica gel with n-pentane yielded 44.2 mg of white crystals (0.23 mmol, 88%). ^1H NMR (CCl_4): δ 6.95 (m, 3.05 H), 6.45 (m, 3.05 H), 3.35 (m, 2.90 H). The mass spectrometric analysis (Table 2) shows the distribution of deuteriums to be 0.6% d_0, 1.4% d_1, 2.8% d_2, 95.2% d_3.

Table 2. Mass Spectrometric Analysis of Deuterated Dihydro-1H-trindene Prepared from 6.[a]

Undeuterated Sample[b]		Deuterated Sample[c]	
m/e	%	m/e	%
247	2.01	248	0.41
248	0.69	249	0.61
249	100	250	1.62
250	21.38	251	3.30
251	3.04	252	100
		253	22.06
		254	2.42
		255	0.27

[a] Chemical ionization with isobutane. Only the M+57 region is displayed. *Spectra are corrected for background noise.*

[b] 80 Scans. [c] 77 Scans.

A second measurement (67 scans) gave similar results: 0.3% d_0, 1.4% d_1, 2.7% d_2, 95.5% d_3. The preparation of the deuterated material from dihydro-1H-trindene was repeated, and mass spectrometric analysis showed the distribution of deuteriums in it to be 2% d_0, 0% d_1, 6% d_2, 92% d_3, while ^{1}H NMR analysis (CCl_4) showed the distribution of hydrogens: δ6.95 (2.99 H), 6.45 (3.07 H), 3.35 (2.95 H).

Reaction of trilithium trindenide with ferrous chloride.

The apparatus consisted of a double Schlenk tube[28] connected to a source of argon and fitted with two magnetic stirring bars and two stopcocks equipped with serum caps. In the left compartment was placed 254 mg ferrous chloride (2 mmol) and 2 mL THF and in the right compartment a solution of 16 (150 mg, 0.78 mmol) in 3 mL THF. The trilithium trindenide was prepared as above using 2.4 mL (2.34 mmol) of 0.97 M *n*-butyllithium in *n*-hexane and poured in portions onto the ferrous chloride slurry. The transfer was completed with 4 x 1 mL of THF. After stirring at room temperature for 20 min, the solvents were evaporated and the solid residue was extracted with CS_2 (4 x 40 mL). The extracts were filtered and evaporated leaving 47 mg of a sticky solid containing mostly starting material 16 (TLC analysis, silica gel, 2% ether in petroleum ether). Its mass spectrum (EI, 75V) is similar to that of bis (trindenylene)diiron (19) (see below), the main difference being the presence of a pronounced peak at m/e 546 suggesting the presence of bis(trindenetriyl)triiron (9, M=Fe). The relative intensities of the peaks in the parent group were: m/e 544 (24), 545 (18), 546 (100, M), 547 (44, M+1), 548 (12). Another sample prepared similarly exhibited these peaks (EI, 20 V) with the following intensities: m/e 546 (100), 547 (43.2), 548 (9.7).[29] There were no other peaks in the range $208 \leq m/e \leq 560$. The intensities required, considering the natural abundances of isotopes, are 546 (100), 547 (44), and 548 (12%). Attempts to measure an ^{1}H NMR spectrum by Fourier transform spectroscopy did not show peaks recognizably attributable to 9 with M=Fe.

The CS_2 insoluble material (prepared in another experiment) was a red-brown material that was washed under argon with 1:1 THF-H_2O (3 x 4 mL) and then THF (3 x 4 mL) and dried *in vacuo* at room temperature for 14 h. Anal. Calcd. for $(C_{30}H_{18}Fe_3)_x$: C, 65.9; H, 3.3; Fe, 30.8. Found: C, 59.38, 45.72; H, 3.87, 3.05; Fe 22.06, 25.21. IR (KBr, cm^{-1}): 3400 broad, 3065 w, 3010 vw, 2910 m, 2845 shoulder, 1610 broad, 1490 m, 1450 m, 1370 m, 1010 s, 785 broad, 685 s. The IR spectrum of another sample that was powdered using an agate mortar and dried for 16 h at 100°C *in vacuo* was identical. The product was insoluble in THF at room temperature and in toluene, chlorobenzene, or o-dichlorobenzene at their boiling points. Attempts to purify this material by washing it with 5% aqueous HCl or by drying it with thionyl chloride (it turned black) or by oxidizing it to a ferricenium salt all failed.

Dilithium Trindenide (18).

n-Butyllithium in n-hexane (0.50 mL, 1.1 mmol) was injected in drops into a stirred solution of 16 (100 mg, 0.521 mmol) in 2 mL THF that was cooled to -78°C. The yellow solution when stirred at -78°C for 1/2 h and at room temperature for 1/2 h deposited a yellow precipitate.

Reaction of 18 with Deuterium Oxide.

The above salt was quenched with D_2O and the product isolated exactly as when 6 was quenched; yield 89 mg. ^1H NMR (CCl_4): δ6.95 (m, 2.97 H), 6.41 (m, 3.10 H), 3.35 (m, 3.93 H). The distribution of deuterium atoms calculated from the analyses summarized in Table 3 is 1.4% d_0, 6.7% d_1, 85.7% d_2, and 6.3% d_3.

Table 3. Mass Spectrometric Analysis of Deuterated Dihydro-1H-trindene Prepared from 18.[a]

Undeuterated Sample[b]		Deuterated Sample[c]	
m/e	%	m/e	%
247	0.73	247	0.30
248	0.47	248	0.19
249	100	249	1.58
250	21.00	250	7.96
251	2.61	251	100
		252	28.04
		253	3.91
		254	0.41

[a] Chemical ionization with isobutane. Only the M+57 region is displayed. Spectra are corrected for background noise.

[b] 22 Scans. [c] 20 Scans.

Preparation of Bis(trindenylene)diiron (19).

The apparatus, consisting of connected 100 mL and 250 mL round bottomed flasks capped by serum caps and flushed with argon, was flame dried. The salt of 18 was prepared by adding in drops 5.4 mL (11.26 mmol) 2.1 M n-butyllithium in n-hexane to a solution of 1.08 g (5.63 mmol) 18 in 15 mL THF at -78° in the 100 mL flask. It was then poured in portions into the 250 mL flask which contained 900 mg (7.08 mmol) $FeCl_2$ and 10 mL THF at room temperature. A slightly exothermic reaction occurred, the precipitate became dark red-purple, and the supernatant liquid turned red. Additional THF (2 x 4 mL) was used to complete the transfer, and the mixture was stirred at room temperatrue for 8 h, stripped, extracted with argon-purged carbon disulfide (250 mL), and filtered under argon. Removing the solvent left 740 mg (1.51 mmol, 53% yield) of crude brownish-red 19. The yields in other experiments conducted on smaller scales (three experiments with 0.5 mmol 18 and one with 1 mmol) were in the range 52-86%. The product was purified by washing it under argon with 4 x 4 mL of argon-purged n-pentane to remove unreacted starting material. The compound is insoluble in dimethylsulfoxide, very slightly soluble in n-pentane or the hexanes, and slightly soluble in CS_2, benzene, CH_2Cl_2, $CHCl_3$ and THF. Solutions in air deposit a black precipitate. The ferrocene does not melt, but it darkens at ca. 260°C. ^1H NMR (CS_2, sealed tube, after 30 scans with a time-averaging computer): an AMXX' system, δ7.27 (A part, two broad signals, J_{AM} = 5 Hz), 6.81 (M part, d of t, J_{AM} = 5 Hz, J_{MX} = $J_{MX'}$ = 1.5 Hz), 4.18 (X part, $J_{XX'}$ = 23 Hz), 3.45 (X' part, $J_{XX'}$ = 23 Hz; and multiplets at 5.16, 5.11, 4.13, 4.04 and 3.71. A very small peak at δ6.41 is attributed to dihydrotrindene impurity and another small one at 6.17 to an unknown impurity. The spectrum is displayed and analyzed in the supplementary material. IR (KBr, cm^{-1}): 3089 broad m, 2961 w, 2925 w, 2874 w, 1624 broad m, 1372 m, 1333 w, 1309 w, 1270 w, 1232 w, 1109 w, 1094 w, 1049 m, 1018 s, 968 w, 941 s, 894 m, 826 s, 799 s, 736 w, 695 s, 651 m, 630 m, 521 s, 502 s, 474 w. MS (EI, 15 V) m/e (rel int): 490 (17), 491 (3), 492 (100), 493 (14), 494 (8), 495 (<1). The only other peak whose intensity was greater than 10% of the base peak was one at m/e 192 that is probably attributable to dihydro-1H-trindene, present as an impurity. In a spectrum measured using an ionizing voltage of 70 V, the base peak was that at m/e 246 (1/2 M or M^{++}) and the intensities in the parent region were 490 (25), 491 (15), 492 (83), 493 (32), 494 (7), 495 (10. Visible spectrum (CS_2, λ(nm) [log ε]): shoulder 512 (2.89), maximum 527 (2.83).

Reaction of 19 with n-Butyllithium and $FeCl_2$.

n-Butyllithium in *n*-pentane (0.21 mL, 1.3 M, 0.27 mmol) was added to **19** (60 mg, 0.12 mmol) in 12 mL THF while the reaction mixture was stirred at -78°C under argon, and after 1/2 h at -78°C the mixture was warmed to room temperature for 1/2 h. The solution, originally clear and auburn, turned brown and cloudly, and at room temperature deposited a precipitate. This was poured onto a slurry of $FeCl_2$ (20 mg, 0.16 mmol) and stirred at room temperature for 1/2 h. The solvents were then evaporated, and after 19 mg of starting material, **19**, had been extracted with CS_2 (identification by ^1H NMR analysis), the insoluble product was washed with THF and dried *in vacuo* for 16 h. The IR spectrum of this material closely resembles that of the insoluble product prepared from trilithium trindenide and $FeCl_2$.

When after a similar preparation the $FeCl_2$ was replaced by D_2O, the CS_2 extract yielded **19** (*ca.* 79% recovery), in whose mass spectrum (EI, 30 V) parent peaks were prominent that were displaced by two mass units from those in the spectrum of undeuterated **19**: m/e (rel int): 490 (10), 491 (22), 492 (68), 493 (44), 494 (100), 495 (48), 496 (24), 497 (4).

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Supplementary Material Available: ^{1}H NMR spectrum of **19** and results and analyses of decoupling experiments (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Katz, T. J.; Schulman, J. *J. Am. Chem. Soc.* **1964**, *86*, 3169; (b) Katz, T. J.; Balogh, V.; Schulman, J. *ibid.* **1968**, *90*, 734; (c) Katz, T. J.; Acton, N. Unpublished experiments in this laboratory.

(2) (a) Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1972**, *94*, 3281; (b) Katz, T. J.; Acton, N.; McGinnis, J. *ibid.* **1972**, *94*, 6205.

(3) (a) 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; (b) Davison, A.; Smart, J. C. *J. Organometal. Chem.* **1973**, *49*, C43; (c) Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 956; (d) Smart, J.C.; Curtis, C.J. *Inorg. Chem.* **1977**, *16*, 1788.

(4) T.J. Katz and W. Ślusarek, manuscript submitted for publication (1978).

(5) Hart, H.; Sasaska, M. *J. Am. Chem. Soc.* **1978**, *100*, 4326.

(6) (a) Sommerdijk, J. L.; de Boer, E.; Pipers, F. W.; van Willigen, H. Z. Phys. Chem. (Frankfurt am Main) 1969, 63, 183; (b) Bauld, N. L.; Chang, C.-S.; Eilert, J. H. Tetrahedron Lett. 1973, 153; (c) Bates, R. B.: Beavers, W. A.; Greene, M. G.; Klein, J. H. J. Am. Chem. Soc. 1974, 96, 5640; (d) Paquette, L. A.; Ewing, G. D.; Traynor, S. G. ibid., 1976, 98, 279; (e) Paquette, L. A.; Ewing, G. D.; Traynor, S.; Gardlik, G. M. ibid. 1977, 99, 6115; (f) Bahl, J. J.; Bates, R.B.; Beavers, W. A.; Launer, C. R. ibid. 1977, 99, 6126.

(7) (a) West, R.; Carney, P. A.; Mineo, I. C. J. Am. Chem. Soc. 1965, 87, 3788; (b) West, R.; Jones, P. C. ibid. 1969, 91, 6156.

(8) HOMO: $\alpha + 0.21\beta$; LUMO: $\alpha - 1.34\beta$

(9) Streitwieser, A.; Berke, C. M.; Robbers, K. J. Am. Chem. Soc. 1978, 100, 827.

(10) (a) Mayer, R. Chem. Ber. 1956, 89, 1443; (b) Petrů, F.; Galík, V. Chem. Listy 1957, 51, 2371; (c) Wallach, O. Chem. Ber. 1897, 30, 1094.

(11) Hopff, H.; Wick, A. K. Helv. Chim. Acta 1961, 44, 19.

(12) Alder, K.; Fremery, M. Tetrahedron 1961, 14, 190.

(13) Elvidge, J. A.; Foster, R. G. J. Chem. Soc. 1964, 981.

(14) The ratio of the intensites of the resonances at δ3.42 and 3.28 is 1.03. Accordingly, the ratio of the amounts of 16a and 16b is 3/[2(1.03)-1] = 2.8, while the statistical ratio is 3.

(15) Biemann, K. "Mass Spectrometry", McGraw-Hill: New York, New York, 1962.

(16) Anion 11 has also been reported to be too insoluble for its ^{1}H NMR spectrum to be measured [reference 6e].

(17) Stevenson, G. R.; Ocasio, I. J. Phys. Chem. 1975, 79, 1387.

(18) Grimme, W.; Kaufhold, M.; Dettmeier, U.; Vogel, E. *Angew. Chem. Int. Ed. Engl*. **1966**, *5*, 604.

(19) The ratio of the intensities of the peaks at m/e 493 and 492 in this spectrum is 14%, not the required 38%. Possibly this is because too much background noise was subtracted before the spectrum was displayed. The ratio in a spectrum in which the electrons were accelerated through 70 V, however, was perfect (39%).

(20) Gitany, R.; Paul, I.C.; Acton, N.; Katz, T. J. *Tetrahedron Lett*. **1970**, 2723.

(21) Jackman, L. M.; Sternhell, S. "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press: New York, 1969.

(22) Difficulty suppressing fragmentation prevented quantitative analysis.

(23) van Willigen, H.; van Broekhoven, J. A. M.; de Boer, E. *Mol. Phys*. **1967**, *12*, 533.

(24) (a) Jesse, R. E.; Biloen, P.; Prins, R.; van Voorst, J. D. W.; Hoijtink, G. J. *Mol. Phys*. **1963**, *6*, 633; (b) Glasbeek, M.; van Voorst, J. D. W.; Hoijtink, G. J. *J. Chem. Phys*. **1966**, *45*, 1852; (c) Laarhoven, W. H.; van Broekhoven, J. A. M. *Tetrahedron Lett*. **1970**, 73.

(25) Corbin, T. F.; Hahn, R. C.; Shechter, H. *Org. Synth. Coll. Vol. V* **1973**, 328.

(26) Dennis, J. M.; Girard, C. *Synthesis* **1973**, 549.

(27) Wiberg, K. B.; Connor, D. S. *J. Am. Chem. Soc*. **1956**, *88*, 4437.

(28) Shriver, D. V. "The Manipulation of Air-Sensitive Compounds", McGraw-Hill: New York, New York, 1969, p.153.

(29) We are grateful to Donald Hou for measuring this spectrum.

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"The Trindene Trianion"

Supplementary Material

Supplementary Material

^{1}H NMR of 19.

The ^{1}H NMR spectrum of bis(trindenylene)diiron, 19, measured in CS_2 at room temperature using a 100 MHz spectrometer and a computer of average transients (CAT), is displayed and assigned in Figure 1.

The peaks at δ7.27 (a broad doublet) and 6.81 (a doublet of triplets with the small coupling $|J| = 1.5$ Hz) were assigned to olefinic protons H_7 and H_8, $|J_{7,8}| = 5.5$ Hz. These and the allylic protons should form an AMXX' system, and to find the allylic protons' peaks, the olefin resonances were simultaneously irradiated with the aid of two oscillators. The multiplets at 433, 356, and 334 Hz thereupon collapsed to singlets and the middle part of a broad multiplet at 409 Hz became sharper, identifying the chemical shifts of the X and X' protons as δ4.18 and 3.45 ($|J_{gem}| = 23\pm1$ Hz). To check this, the irradiation frequency was set at 345 Hz, whereupon the peaks at 433 and 409 Hz broadened and a singlet appeared at δ4.18. Because the chemical shift δ3.45 is similar to that of the methylene protons in dihydro-1H-trindene (δ3.42 and 3.28), it was assigned to the exo proton, H_9, and therefore δ4.18 was assigned to H_{10}.

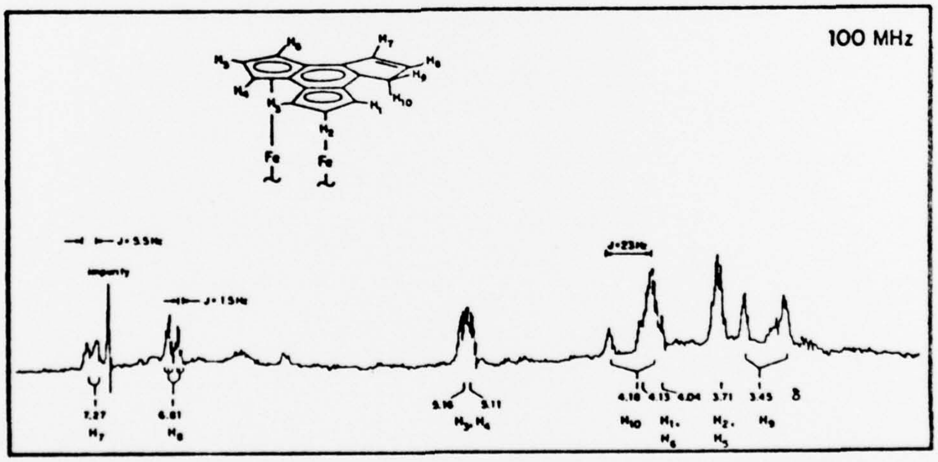

Figure 1. ^{1}H NMR spectrum (30 accumulated scans) of 19 in CS_2.

Irradiation at 371 Hz resolved the multiplet at 514 Hz into a pair of singlets, at δ5.16 and 5.11, and although the multiplet at 409 Hz was too close to the irradiated region to see exactly what effect the decoupling had on it, it seemed to simplify into three singlets, at 413, 409, and 404 Hz, the middle one being a part of the XX' system discussed above. Thus, the resonance at δ3.71 was attributed to protons H_2 and H_5. An interesting source of support for this assignment is the observation that irradiation at 371 Hz also simplifies the resonance at δ7.27, suggesting that the corresponding protons although distant are coupled appreciably because of the zig-zag arrangement of the bonds between them.

Irradiation at 409 Hz removed fine structure on the multiplet at 514 Hz, reducing it to a pair of doublets, and similarly irradiation at 514 Hz removed fine splitting around 409 Hz. Both irradiations simplified the peaks at δ3.71.

Although it is difficult to tell which pair, H_1 and H_6 or H_3 and H_4, produce the peaks at δ5.16 and 5.11 and which those at δ4.13 and 4.04, we speculate that H_3 and H_4 are associated with those at lower fields because their smaller differences in chemical shift (0.05 vs 0.09 ppm) might reflect their greater distance from the symmetry-destroying cyclopentadiene ring. This assignment is also supported by the analogy with H_4 and H_5 in phenanthrene resonating at much lower fields than the other protons in the molecule.