groups as proton donors are found frequently, e.g., in $CHCl_3$,[10-12] the role of methyl groups as proton donors for hydrogen bonds is controversial. They were postulated by Sutor[13] for 1,3,7,9-tetramethyluric acid and caffeine, where C–H⋯O distances of 3.00 and 3.24 Å and C–H⋯O angles of 120.8 and 109.1° were observed. In contrast, the C–H⋯Cl and C–H⋯O groups of the title compound are nearly linear.

Recently methylene-hydrogen⋯O hydrogen bonds were found in $Cl_2(O)PCH_2P(O)Cl_2$.[14] The methyl group in I, however, differs from those in most methyl compounds; it is highly activated because it is bound directly to a phosphorus atom with a formal positive charge; furthermore, the phosphorus atom is additionally bound to three strongly electron-withdrawing groups. The strong influence that this environment exerts at phosphorus can also be seen in the extraordinarily short P–C(1) bond, one of the shortest phosphorus-carbon single bonds so far determined.

Supplementary Material Available: Temperature factors and structure factor listing (26 pages). Ordering information is given on any current masthead page.

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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 III, convert trindane (octahydro-1*H*-trindene, **14**) into the dihydro-1*H*-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,b**. When only 2 mol of *n*-butyllithium is used, the dianion **18** forms instead, as evidenced by reaction with deuterated water yielding molecules of **16a,b** containing two allylic deuterium atoms. Sandwich molecules, assigned structures **19a,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
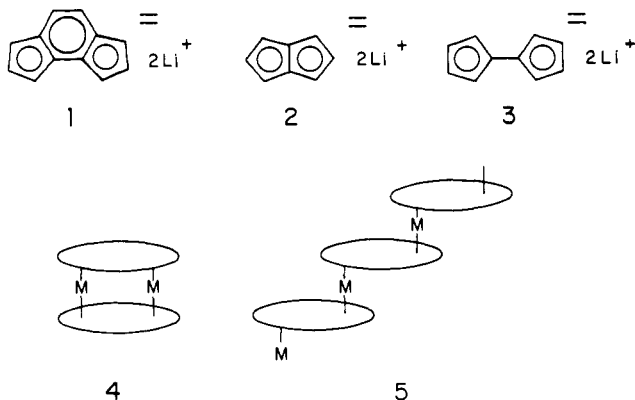

mixed with transition-metal salts, from giving dimers like **4** (here M is the metal) rather than the novel polymeric structures **5**. One way is to cause the hydrocarbon to react with metals on opposite faces, at b rather than a in Scheme I, a possibility considered in another publication.[4] The 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 a one ring system (Scheme II), a possibility considered here.

At first the means by which the hydrocarbons could be strapped 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
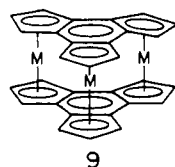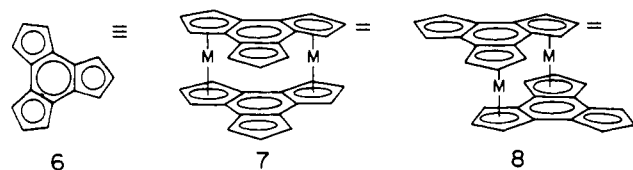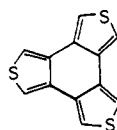
Scheme I
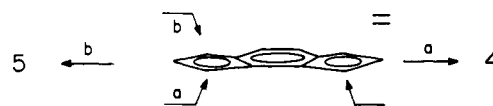
Scheme II
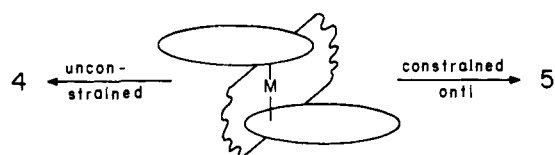
solution. If it combined with two transition-metal cations in the way that **1** does, the remaining centers of reactivity on adjacent ring systems are likely to be kept apart by steric and Coulombic repulsive forces and to be locked in their positions by the bonds between the metals and the five-membered 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 II, should react further with metal ions to give polymers like **5**. Even if this hypothesis were incorrect, 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.

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 **6** as thiophene is to cyclo-


pentadienide,[5] a way to make **6** itself was developed and is described below.

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 tetraanions,[6] although there are some, notably **11**[6a] and **12**,[6e] which are formed from the corresponding hydrocarbons by reduction with potassium
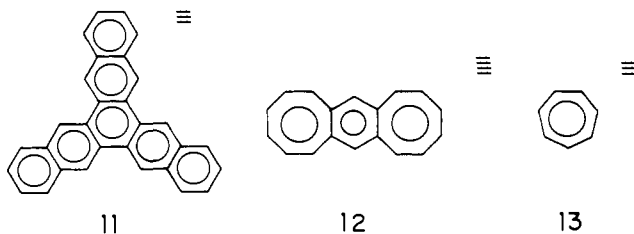

Scheme III
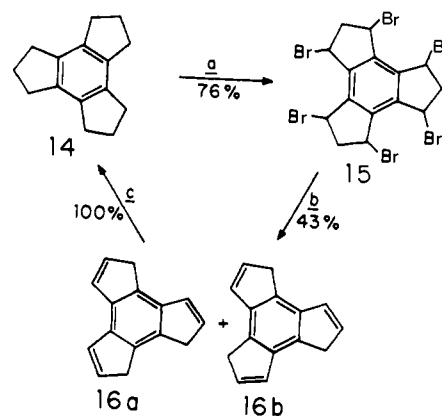
(a) Br_2/CCl_4, hv; (b) Zn/DMF; (c) H_2/PtO_2

in ethers, and **13**, which is formed from appropriate hydrocarbons by deprotonation with *n*-butyllithium plus tetramethylethylenediamine.[6f] (Species like Li_4C_3,[7] lithiated propyne, might also be related to these ions.) However, there is a feature of the structure of **6** that distinguishes it from the tri- and tetraanions 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 pK_a's of 9,10-dihydroanthracene differ by little (4 pK units) helps justify the belief in its stability.

Results

The dihydro-1*H*-trindenes (**16a** and **16b**), the conjugate acids of the trindene trianion, were prepared simply (Scheme III) from "trindane" (octahydro-1*H*-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 δ 3.42 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 δ 3.42
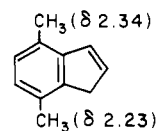
is assigned to the methylenes in **16b** and to one of the methylenes in **16a**, while that at δ 3.28 is assigned to the other two in **16a**.[14]

With 3.5 equiv of *n*-butyllithium in tetrahydrofuran (THF) at −78 °C, the dihydro-1*H*-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 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 dimethyl sulfoxide.[18]

With 2, rather than 3, equiv of *n*-butyllithium in THF at -78 °C, hydrocarbons **16** give the dianion (**18**), which was

18
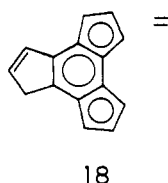
identified by its reaction with D_2O returning **16** in 88% yield with deuterium atoms incorporated in two of the allylic positions. Thus the ratio of methylene and vinyl resonances in the ^{1}H NMR spectrum was 0.66, and the distribution of deuterium atoms implied by the mass spectrum was 1.4% d_0, 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 chloride, **18** gives in 53% yield bis(trindene)-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 (15 V) 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
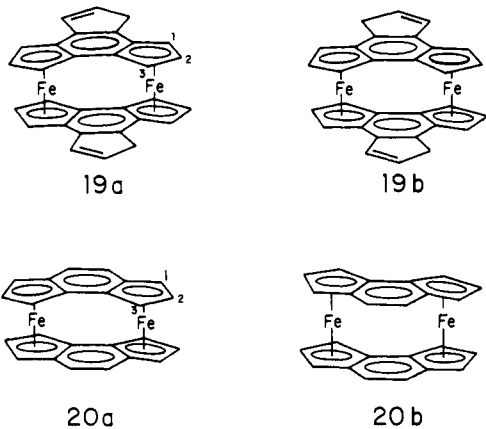
by additional AMXX' resonances due to the extra ring. The similarity in the chemical shifts, summarized in Table I, is especially close for the resonances of **19** and those assigned to **20a**, suggesting that the hydrocarbon rings in bis(trindene)-

Table I. Chemical Shifts[a] of Protons in **19** and **20a,b**

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

[a] Parts per million from tetramethylsilane. [b] This work. [c] Reference 20.

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

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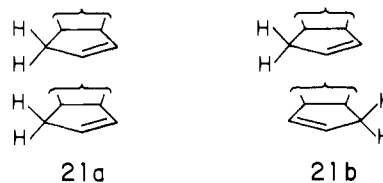
spectrum displaying only one set of AMXX' resonances, for if, as seems likely, both **a** and **b** isomers are present, the overlap of the resonances of the five-membered rings not bonded to the metal probably reflects the similarity of the local environments in the two isomers. This is apparent in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

The assignments displayed in Table I 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 zigzag arrangement,[21] than through the shorter four-bond path outlined on structure **23**.

22   **23**
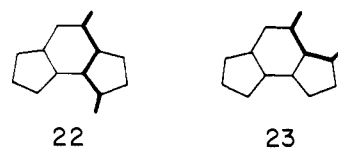
A few attempts were made to convert trilithium trindenide into a polymer like **5** using ferrous chloride, but they were not successful. They gave an auburn solid that is insoluble in CS_2 and THF at room temperature and in toluene, chlorobenzene, and *o*-dichlorobenzene at their boiling points. It does not change noticeably when stored under argon, but in the air it turns black after 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 2 mol 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 m/e 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 their number must be very small, for the samples that exhibit these mass spectra also exhibit

Chart I
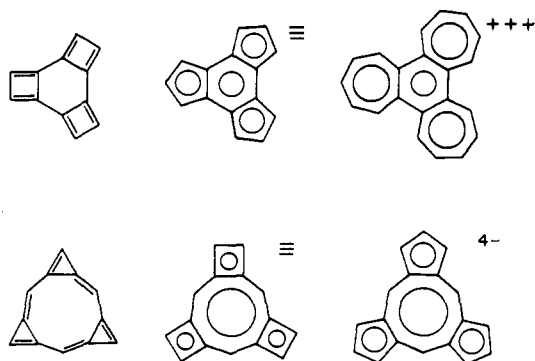
many peaks at low mass, implying that the bulk of even these small samples are simpler impurities.

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 threefold 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

24   25   26
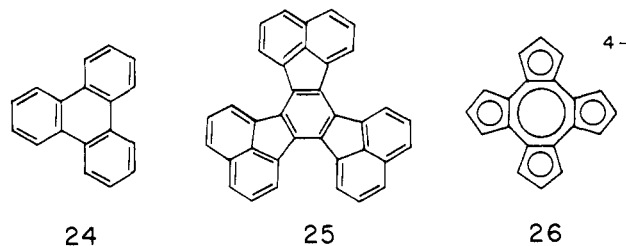
there are other more complicated examples, like **25**, that are related to it.[5a,24]

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 pictured in Chart I. Analogous structures having fourfold axes of symmetry, **26** being an example, can also be imagined. The synthesis of the trindene trianion suggests that attempts to make at least some of these others be tried.

Among these structures the trindene trianion is a particularly favorable one because its rings are all five and six membered so that strain is minimal, because the highest occupied π molecular orbital is particularly low in energy,[6] 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. It should now be available for the synthesis of new materials, as well as for other studies.

Experimental Section

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 of 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$_4$) δ 2.71 (t, 12.05 H), 2.01 (quintet, 5.95 H); MS (EI, 13 V, only peaks ⩾3% are listed) m/e (rel intensity) 170 (3), 196 (3), 197 (6), 198 (100, M), 199 (32.5).

Trindane (10 g, 50.5 mmol) and 300 mL of CCl$_4$ were placed in a 1-L, round-bottomed, three-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 of 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 × 5 mL), and drying in vacuo over P$_2$O$_5$ yielded 10.39 g of off-white powder. The filtrate was evaporated, giving an oil that on addition of 100 mL of ether solidified. The solid was collected, washed with ether (4 × 10 mL), and dried in vacuo over P$_2$O$_5$ for 2 h, yielding another 15.53 g of off-white powder. The total yield was 25.92 g (38.57 mmol, 76%). In three 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 intensity) 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$_3$CN, 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,b). Activated zinc dust[25] (15 g) and argon-purged dry dimethylformamide (DMF) were placed in a 1-L, three-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 0.5 h and at room temperature for 18 h, filtered through Celite, and poured into 500 mL of ice-water. The precipitate was collected, washed with water, and taken up in 400 mL of ether, and the aqueous filtrate was extracted with petroleum ether (3 × 400 mL). The combined extracts were washed, dried over MgSO$_4$, and evaporated. Chromatography (60 g of 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 intensity) 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). ^{1}H NMR (CCl$_4$): δ 6.95 (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 was the yield 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 of absolute ethanol over PtO$_2$ (20 mg, 0.088 mmol) absorbed 52.7 mL of 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 ^{1}H NMR spectrum.

Trilithium Trindenide (6). To a solution of 500 mg (2.6 mmol) of **16** in 12 mL of THF cooled to −78 °C, 4.34 mL of 2.1 M n-butyl-

Table II. Mass Spectrometric Analysis of Deuterated Dihydro-1*H*-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.

Table III. Mass Spectrometric Analysis of Deuterated Dihydro-1*H*-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.

lithium 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 0.5 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 ^{1}H 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 × 15 mL). Drying ($MgSO_4$), evaporation, and chromatography on 18 g of silica gel with *n*-pentane yielded 44.2 mg of white crystals (0.23 mmol, 88%): ^{1}H 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 II) shows the distribution of deuteriums to be 0.6% d_0, 1.4% d_1, 2.8% d_2, 95.2% d_3.

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-1*H*-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: δ 6.95 (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 were placed 254 mg of ferrous chloride (2 mmol) and 2 mL of THF and in the right compartment was placed a solution of **16** (150 mg, 0.78 mmol) in 3 mL of 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 × 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 × 40 mL). The extracts were filtered and evaporated leaving 47 mg of a sticky solid containing mostly starting material **16** (thin layer chromatographic analysis, silica gel, 2% ether in petroleum ether). Its mass spectrum (EI, 75 V) is similar to that of bis(trindene)diiron (**19**) (see below), the main difference being the presence of a pronounced peak at *m/e* 546 suggesting the presence of bis(trindene)triiron (**9**, M = Fe). The relative intensities of the peaks in the parent group follow: *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 ≤ *m/e* ≤ 560. The intensities required, considering the natural abundances of isotopes, are *m/e* 546 (100), 547 (44), and 548 (12). Attempts to measure a ^{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 × 4 mL) and then THF (3 × 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, 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 of THF that was cooled to −78 °C. The yellow solution when stirred at −78 °C for 0.5 h and at room temperature for 0.5 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. ^{1}H NMR (CCl_4): δ 6.95 (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 III is 1.4% d_0, 6.7% d_1, 85.7% d_2, and 6.3% d_3.

Preparation of Bis(trindene)diiron (19). The apparatus, consisting of connected 100- and 250-mL round-bottomed flasks capped by serum caps and flushed with argon, was flame dried. The salt **18** was prepared by adding in drops 5.4 mL (11.26 mmol) of 2.1 M *n*-butyllithium in *n*-hexane to a solution of 1.08 g (5.63 mmol) of **16** in 15 mL of THF at −78 °C in the 100-mL flask. It was then poured in portions into the 250-mL flask which contained 900 mg (7.08 mmol) of $FeCl_2$ and 10 mL of THF at room temperature. A slightly exothermic reaction occurred, the precipitate became dark red-purple, and the supernatant liquid turned red. Additional THF (2 × 4 mL) was used to complete the transfer, and the mixture was stirred at room temperature 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 of **18** and one with 1 mmol) were in the range 52–86%. The product was purified by washing it under argon with 4 × 4 mL of argon-purged *n*-pentane to remove unreacted starting material. The compound is insoluble in dimethyl sulfoxide, 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. ^{1}H NMR (CS_2, sealed tube, after 30 scans with a time-averaging computer): an AMXX′ system, δ 7.27 (A part, two broad signals, J_{AM} = 5 Hz), 6.81 (M part, d of t, J_{AM} = 5, 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 δ 6.41 is attributed to dihydrotrindene impurity and another small one at δ 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 intensity) 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^{2+}) and the intensities in the parent region were m/e 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 of THF while the reaction mixture was stirred at −78 °C under argon, and after 0.5 h at −78 °C the mixture was warmed to room temperature for 0.5 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 0.5 h. The solvents were then evaporated, and, after 19 mg of starting material, **19**, had been extracted with CS_2 (identification by ^{1}H 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 intensity) 490 (10), 491 (22), 492 (68), 493 (44), 494 (100), 495 (48), 496 (24), 497 (4).

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.

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