# Synthesis and Studies of Some [2₄]Ferrocenophanetetraenes

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Ferrocenophanetetraenes *1–5*, in which the two cyclopentadienyl rings are linked by a conjugated chain of double bonds and *para*-substituted benzene rings, have been synthesized *via* multiple Wittig reactions. The extent of planarity and conjugation in these layered compounds and some of their dynamic processes have been studied.

As part of our work on the synthesis and studies of cyclophanetetraenes,[1] we have now synthesized a number of unsaturated macrocyclic compounds incorporating one or two 1,1'-disubstituted ferrocene units (compounds *1 – 5*).
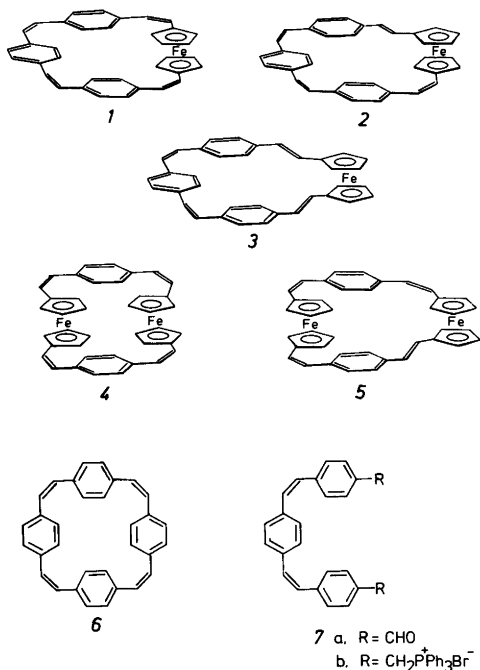
The synthetic route to these compounds, one-pot multiple Wittig reactions, has been developed and used in our laboratory for the preparation of a large number of cyclophanetetraenes and hexaenes incorporating various carbocyclic and heterocyclic ring systems.[2] So far, our studies of these cyclophanes have concentrated on their stereochemistry and dynamic processes,[1] photochemical ring-closures,[3] electrochemical reductions[4] and investigation of the extent of conjugation and aromaticity in these large ring compounds.[1] The ferrocenophanetetraene *1* could adopt a conformation with appreciable conjugation over the entire hydrocarbon moiety, thus exemplifying a layered molecule with conjugated "top" and "bottom" halves. Our interest in such a system lay in the nature of possible interactions between the ends of the conjugated chain, and in a comparison of this layered molecule with its more planar analogues (*e.g. 6*).[5] Comparison could also be made with known ferrocene systems such as [0.0]ferrocenophane (*8*)[6] and [2.2]ferrocenophane-1,13-diyne (*9*),[7] in which the top and bottom halves are linked *via* metal atoms only, and with the more closely related compounds *10* and *11* which have been reported recently.[8,9]
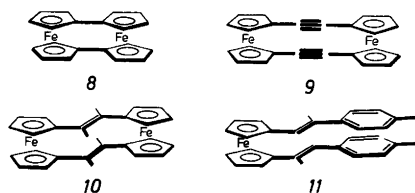
RESULTS AND DISCUSSION

The isomeric ferrocenophanetetraenes *1* and *3* were synthesized *via* a double Wittig reaction

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between the bis(triphenyl)phosphonium salt from 1,1'-bis(chloromethyl)ferrocene[10] and dialdehyde 7 (itself available from a double Wittig reaction; see Experimental for details). The best procedure for 1 proved to be in dry DMF at −5 °C, using solid potassium tert-butoxide as base. Under these conditions, compound 1 was obtained in 4 % yield, along with smaller amounts of 3 (<1 %) but by running the reaction at higher temperatures (+10 to +15 °C) the yield of 3 could be increased at the expense of the all-cis isomer. An unfortunate feature of this otherwise very straightforward synthesis is the extreme ease of reduction of the ferrocene bisphosphonium salt and corresponding ylids, often leading to large amounts of 1,1'-dimethylferrocene at the expense of ring-closed products. The yields of the ferrocenophanetetraenes were thus low (up to 4 %) but this is partly offset by the shortness and simplicity of the chosen route.

The third isomer, 2, was prepared via successive double Wittig reactions starting from terephthalaldehyde (1 mol equiv.) and the bisphosphonium salt from 1,4-bis(bromomethyl)benzene (2 mol equiv.). Addition of lithium ethoxide in ethanol (2 mol equiv.) generated, in situ, the bisphosphonium salt 7b, and ferrocene-1,1'-dicarbaldehyde (1 mol equiv.) was then added and a second double Wittig reaction performed to yield compound 2. Isomers 1 and 3 were formed in only trace amounts under these conditions. The same result was obtained when the ferrocenedicarbaldehyde was reacted first, i.e. when terephthalaldehyde was used for final ring-closure. (The stereochemistry of the Wittig reactions described above is discussed in the next section.)

Thus, by simple variation of the reaction conditions or starting materials, the three isomers are easily available. Compounds 1 and 3 were obtained as orange-red solids which could be recrystallized from dichloromethane − methanol. Isomer 2, usually obtained as an oily orange-coloured solid, was more difficult to recrystallize. The related ferrocenophanetetraenes 4 and 5 were synthesized via fourfold Wittig reactions between ferrocene-1,1'-dicarbaldehyde and the bisphosphonium salt from 1,4-bis(bromomethyl)benzene in DMF at −30 °C, and were isolated as orange-coloured crystalline solids. Isomer 5 was the main ring-closed product under these conditions (5 %). Other isomers, containing more than one trans double bond, were not observed to be formed and this is probably due to the steric strain and crowding which would be present in such molecules.

STEREOCHEMISTRY OF THE WITTIG REACTIONS

The Wittig reaction between the ferrocene bisphosphonium salt and dialdehyde 7 yielded varying amounts of the all-cis isomer, 1, and the cis,cis,-trans,trans isomer, 3, depending on the reaction temperature, but only trace amounts of the cis,cis,-cis,trans isomer 2. Compound 2 was, however, the main ring-closed product from the stepwise Wittig reactions between ferrocene-1,1'-dicarbaldehyde, terephthalaldehyde, and the bisphosphonium salt from 1,4-bis(bromomethyl)benzene regardless of the order of reaction of the dialdehydes; isomers 1 and 3 were obtained in only trace amounts from these reactions. The relative thermodynamic stability of the three isomers, 3 > 2 > 1, was determined from isomerizations via ferricenium ions, as described below. We have tried to rationalize these observations by considering the mechanism of the Wittig reactions involved. The results confirm previous assumptions[11] and may be of some value for predictions of the course of similar Wittig reactions. Our interpretations are therefore treated in some detail here.

The experimental results show that there is not a constant cis/trans ratio in the Wittig reactions described above. The double bonds between the benzene rings must be cis in order for ring-closure to occur, and these can thus be excluded from the discussion, whereas the double bonds adjacent to the ferrocene unit can be cis or trans (the trans configuration being favoured thermodynamically). In the Wittig reactions performed with ferrocene-1,1'-dicarbaldehyde, one of the double bonds has the cis configuration and is formed first in a kinetically controlled reaction, whereas the formation of the second double bond is thermodynamically controlled and leads to the trans configuration. Since interannular electronic effects in substituted ferrocenes are well-known,[16] it seems reasonable to assume that ferrocene-1,1'-dicarbaldehyde is sufficiently activated to give irreversible betaine formation and fast elimination of triphenylphosphine oxide, thus mainly yielding a cis double bond, while the vinylferrocene-monoaldehyde thus formed is much less reactive and therefore betaine formation may become reversible to give a trans double bond.

The Wittig reaction between the bisphosphonium salt from 1,1'-bis(chloromethyl)ferrocene (1 mol equiv.) and benzaldehyde (2 mol equiv.) in DMF at −5 °C yielded the expected 1:1 mixture of

cis,cis and cis,trans isomers, the products being characterized by their 270 MHz ^{1}H NMR spectra ($J_{cis}=12$ Hz and $J_{trans}=16$ Hz, respectively). However, the reaction between equimolar amounts of the same bisphosphonium salt and dialdehyde 7 under the same experimental conditions yielded the cis,cis and the trans,trans isomers 1 and 3 but no cis,trans isomer 2. The final Wittig reaction, which completes the ring, thus gives a cis double bond if all the other double bonds are cis, and a trans double bond if the previously-formed double bond is trans. The final stereochemistry is determined by the conformation of the betaine involved in the final ring-closure step. Molecular models (CPK) show that the large aromatic groups of the betaine prefer to be mutually anti. It is further assumed that, in the highly polar solvent used (DMF), the positively-charged phosphorus and negatively-charged oxygen (both surrounded by solvent molecules) will also prefer to be mutually anti if possible. This anti conformation leads to formation of a cis double bond from the erythro betaine shown in Fig. 1. A gauche relation between phosphorus and oxygen is sterically less favourable, and leads to a trans double bond from the threo betaine depicted in Fig. 1.

Molecular models (CPK) of the cyclic betaines A and B depicted in Fig. 2 reveal that in A the phosphorus and oxygen can be anti, whereas they can at best be gauche in B. In the latter case, the substituent anti to phosphorus will interfere sterically with the trans double bond already formed, and it is thus favourable to have the smallest substituent (H) in this position.
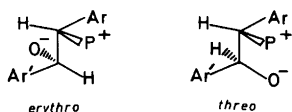

Fig. 1. Betaines with the erythro and threo configurations.

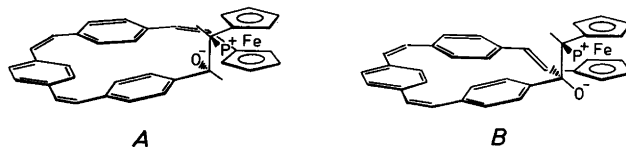The main product at -5 °C is the cis,cis isomer 1, while at $+10$ to $+15$ °C the trans,trans isomer 3 predominates. This result indicates that for the initial Wittig reaction at -5 °C the rate of elimination of triphenylphosphine oxide is higher than that of erythro−threo betaine interconversion, and a cis double bond results; at the higher temperatures, however, erythro−threo betaine interconversion is faster and the threo betaine leads to the thermodynamically more stable trans double bond. In each case, the subsequent (and final) Wittig reaction is subject to the steric control described above. It should be noted that all the Wittig reactions and subsequent work-up were conducted in the dark, and the products protected as far as possible from light in order to avoid cis−trans photoisomerization.

cis−trans ISOMERIZATION, AND OXIDATIONS

Of the cyclophanes containing one ferrocene unit, isomers 1 and 3 appear to be stable to daylight. The cis,cis,cis,trans isomer (2), however, isomerizes slowly to 1 on exposure to sunlight, the course of the reaction being monitored easily by TLC and ^{1}H NMR. We have also oxidized compounds 1, 2, and 3 with iodine to yield the corresponding paramagnetic radical cations. On re-reduction of these species with bisulfite, it was observed (TLC, ^{1}H NMR) that compound 1 had isomerized to a mixture of compounds 2 and 3 (mostly 3) and that compound 2 had isomerized totally to 3. Compound 3 was itself recovered unchanged after the oxidation-reduction sequence. (All these operations were conducted in the dark.) These results imply that oxidation leads to a common radical cation in which the odd electron is, to some extent, delocalized over the hydrocarbon chain thus lowering the energy of the transition state for cis−trans isomerization. (See Fig. 3.)

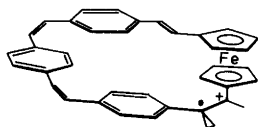The cis,cis,cis,cis and the cis,cis,cis,trans isomers are thus converted to the thermodynamically more

Fig. 2. The cyclic betaines A and B.

Fig. 3. One form of the common radical cation obtained on oxidation of *1*, *2* or *3*.

stable *cis,cis,trans,trans* isomer, the overall order of stability being *3*>*2*>*1*. The I_3^- salt of the radical cation (as obtained from oxidation of *2*) crystallizes as brown needles (m.p. >300 °C) from chloroform and is rather insoluble in common organic solvents. Further investigations of the oxidation and oxidized species are now in progress.

SPECTROSCOPIC STUDIES AND DYNAMIC PROCESSES

In previous studies of cyclophanetetraenes and their derivatives, we have made use of ^{1}H NMR and UV spectroscopy to determine the extent of planarity and conjugation in these compounds.[1] In some favourable cases, dynamic processes can also be studied (using NMR) and the energetic barriers to these processes approximated by simple calculation.[1] We have now made a variable-temperature ^{1}H NMR study of some of the ferrocenophanes described here, and used the results in conjunction with the UV spectra to make some proposals regarding the possible structures of these compounds.

Each of the ferrocenophanes *1* through *3* can exist in helix-like conformations which interconvert rapidly on the NMR time-scale, as apparent from
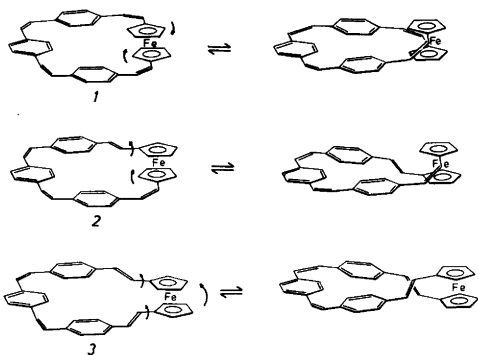

Scheme 1. Interconversions within each of the ferrocenophanes *1*, *2* and *3*.

the simplicity of the ferrocene part of the spectra. (See Scheme 1.)

For *1*, this interconversion must occur by a rotation of the entire ferrocene unit through the central cavity of the molecule. In *2*, the process is confined to a similar rotation of the cyclopentadienyl group adjacent to the *cis* double bond. The mirror-image forms of compound *3* can interconvert by a rotation of the entire ferrocene unit around the single bonds to the hydrocarbon bridge. The NMR spectra of *1* and *2* are temperature-dependent, whereas no barrier could be observed from the spectrum of *3*.

The protons on the cyclopentadienyl rings of compound *1* appear as an AA'XX' system (two distorted triplets at δ 4.12 and 4.04) at room temperature. On cooling the sample (CD_2Cl_2 solvent) these peaks broaden (−30 to −40 °C, the lower-field "triplet" collapsing faster) coalesce (about −60 and −70 °C, respectively) and finally appear, at −95 °C, as an ABCD pattern consisting of four broad peaks at δ 4.37, 4.22, 3.96 and 3.85, respectively. The olefinic doublet originally at δ 5.87 is very broad at −60 °C and shifts progressively upfield on further cooling, appearing as a doublet at 5.64 at −95 °C. At this temperature, the remaining olefinic protons appear as a broad, featureless peak at δ 6.71, while the benzene rings appear as a very broad AA'BB' pattern (7.20 and 7.07) partially overlapping a broad singlet at 7.05. From these data, we conclude that the dynamic process with the highest observable barrier is rotation of the ferrocene unit through the central cavity of the molecule, and we have used the data to perform a very simple calculation of the barrier height, assuming two-site exchange and taking the coalescence temperatures as −60 and −70 °C, respectively. This gives an average value of 40 kJ mol^{-1}. The behaviour of the doublet originally at δ 5.87 (which is assigned to the olefinic protons adjacent to the ferrocene unit by comparison with a series of [2₄]cyclophanetetraenes[2] and 1,1′-distyrylferrocenes)[12] cannot be explained by the simple process of rotation of the ferrocene unit, but rather indicates that, even at low temperature, more than one conformation is present. A second conformation, of higher energy, which is present to the extent of only a few percent at low temperature may be difficult to observe directly but its presence may be indicated by line-broadening near the coalescence temperature. Molecular models (CPK) reveal that such a conformation could exist, and the idealized Scheme 2 would account for our observations.
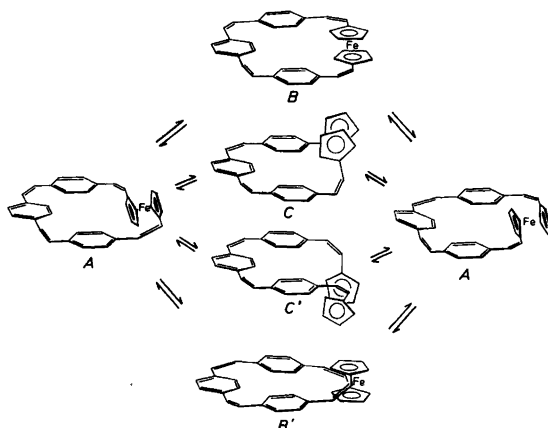
Scheme 2. Idealized conformational interconversions of *1*.

We assume that *B* is the most stable conformer, with maximum planarity (supported by UV data) whereas *A* represents the barrier to interconversion. Conformer *C* is of somewhat higher energy than *B* and can be reached from the latter only *via A*.

Isomer *2* was studied in acetone-d_6 at temperatures between -30 and $+105$ °C (in a sealed NMR tube). At room temperature, the spectrum consists of the expected pattern of sharp peaks for the aromatic and olefinic protons (three AA'BB' patterns and four AB systems, all with the expected coupling constants) while the protons of the ferrocene unit appear as a series of broad, overlapping peaks between δ 4.52 and 3.76. Cooling the sample leads to a gradual sharpening of these peaks and at -30 °C these cyclopentadienyl protons give rise to two ABCD systems which appear as seven well-resolved multiplets at δ 4.50 (1H), 4.44 (1H), 4.39 (1H), 4.31 (1H), 4.23 (1H), 4.17 (2H) and 3.79 (1H), respectively. On warming the sample, these peaks broaden, collapse, then (between $+60$ and $+70$ °C) begin to re-sharpen and finally appear as a rather broad singlet at δ 4.35 (4H) and an AA'XX' system (two distorted triplets) at 4.25 (2H) and 4.10 (2H). By a decoupling of the highest-field multiplet at -30 °C, and from a plot of chemical shift *vs.* temperature for all the multiplets observed, the multiplets can be assigned to two sets of four. (The multiplets at δ 4.39, 4.23, one of the multiplets at 4.17 and the multiplet at 3.79 observed at -30 °C eventually giving rise to the AA'XX' system observed at $+105$ °C). Calculation of the barrier to rotation, performed in a manner similar to that for isomer *1*, and taking the coalescence temperatures

as $+25$ and $+35$ °C, respectively, gives a value of 60 kJ mol^{-1}. The higher barrier in this case reflects the enhanced rigidity which the *trans* double bond endows on the molecule. It is assumed that the preferred conformation is that in which the *trans* double bond is coplanar with the attached benzene and cyclopentadienyl rings, thus allowing maximum π electron overlap. This assumption is supported by the UV spectrum (λ_{max} 302 nm, log ε 4.58, ethanol) which implies considerable conjugation, as for the all-*cis* isomer *1*.

Introduction of a second *trans* double bond, as in compound *3*, further increases the rigidity of the molecule and rotation of the ferrocene unit through the central cavity is rendered impossible. The mirror-image forms of *3* can still, however, interconvert by the rotation depicted in Scheme 1. The barrier to this process is low and thus the room-temperature NMR spectrum of *3* consists of the expected well-resolved AA'XX' pattern for the protons on the ferrocene unit, and temperature-dependent behaviour such as that observed for *1* and *2* is not observed in this case. The further increase in conjugation in *3* as compared to *1* and *2* is apparent from the bathochromic shift in the UV spectrum of *3* (λ_{max} 312 nm, log ε 4.60, ethanol). As an indication of the extent of planarity and conjugation in compounds *1* through *3*, their UV spectra can be compared with that of cyclophane *6*, which is known to be relatively planar[13] (λ_{max} 303 nm, log ε 4.76, ethanol).[5] Inspection of models shows that the ferrocenophanes incorporating two ferrocene units are unable to be as planar as compounds *1* through *3*, and this is borne out by their
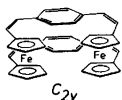
C_{2v}

Fig. 4. Possible, but less likely, conformation of the all-*cis* isomer *4*.

UV spectra (see Experimental). For the all-*cis* isomer *4*, the conformation of C_{2v} symmetry shown in Fig. 4 is also possible but, for steric reasons, we think the conformer of C_{2h} symmetry to be more likely.

According to UV data compound *5*, containing one *trans* double bond, is somewhat more conjugated than *4* as expected. Models reveal that many conformations are possible, and it is difficult to decide which one is of lowest energy. Further studies of these compounds are now in progress.

Finally, the mass spectra of all the ferrocenophanetetraenes described here are very simple, showing the molecular ion as the base peak and very little fragmentation. Doubly-charged ions are also observed. These features are also typical of the analogous cyclophenatetraenes described elsewhere.[2]

EXPERIMENTAL

^{1}H NMR spectra were obtained on a Bruker WH 270 instrument, using $CDCl_3$ as solvent and TMS as internal standard unless otherwise stated. UV spectra were obtained on a Beckman DK-2A, IR spectra on a Beckman IR9, and mass spectra (70 eV) on an AEI MS 902 instrument. Melting points were determined on a Reichert hot-stage apparatus. All the Wittig reactions and subsequent work-up were conducted in the dark, and isolated products protected from light. Reactions were run in dry DMF under nitrogen atmosphere, and worked up as described earlier.[5] The products were isolated by PLC on silica gel, using carbon tetrachloride as eluent unless otherwise stated.

Ferrocene-1,1'-dicarbaldehyde[14] and 1,1'-bis-(chloromethyl)ferrocene[10] were prepared according to the literature. The bisphosphonium salt from 1,1'-bis(chloromethyl)ferrocene was prepared in dry DMF at room temperature from the bis(chloromethyl) compound and two equivalents of triphenylphosphine. The salt was dried 12 h *in vacuo* before use. (Yield 90 %). The preparation of the bisphosphonium salt from 1,4-bis(bromomethyl)benzene has been described earlier.[15] Commercial benzene-1,4-dicarbaldehyde was recrystallized before use.

Dialdehyde *7* was prepared *via* Wittig reaction of benzene-1,4-dicarbaldehyde (2 mol equiv.) and the bisphosphonium salt from 1,4-bis(bromomethyl)benzene (1 mol equiv.). The reaction was run at −40 °C, using LiOEt in ethanol or solid potassium *tert*-butoxide as base. After usual work-up, the dialdehyde was isolated by column chromatography on silica gel, using dichloromethane as eluent. Yield 40−50 %, m.p. 111−115 °C. NMR: δ 9.94 (2H, s) aldehyde, 7.72 (4H, m) and 7.38 (4H, m) *para*-disubstituted benze rings carrying the aldehyde groups, 7.06 (4H, s) remaining benzene ring, 6.63 (4H, m, J_{AB} 12 Hz) double bonds. The dialdehyde is easily photoisomerized and oxidized, and it was therefore reacted as soon as possible after isolation.

[2](1,1')Ferroceno[2]para[2]para[2]paracyclo-phane-cis,cis,cis,cis-*tetraene (1).* The Wittig reaction between dialdehyde *7* (0.68 g, 2 mmol) and the bisphosphonium salt from 1,1'-bis(chloromethyl)ferrocene (1.6 g, 2 mmol) was run at −5 °C, using solid potassium *tert*-butoxide as base. Usual work-up followed by PLC yielded cyclophane *1* which crystallized as red needles from dichloromethane−methanol. (40 mg, 4 %, m.p. 207−208 °C). UV (ethanol): λ_{max} 300 nm, log ε 4.53. NMR: δ 7.12 (8H, m) benzene rings adjacent to ferrocene unit, 7.00 (4H, s) remaining benzene ring, 6.66 (2H, d, J 12 Hz), 6.60 (2H, d, J 12 Hz), 6.55 (2H, d, J 12 Hz), 5.87 (2H, d, J 12 Hz) *cis* double bonds, 4.12 (4H, m) and 4.03 (4H, m) cyclopentadienyl. MS (70 eV) m/e 516 (M^+, 100 %) 514 (8) 258 (M^{2+}, 2). Abs. mass 516.154±0.005, calc. for $C_{36}H_{28}Fe$ 516.154. IR (KBr): 3000 (m), 2950 (m), 1640 (w), 1600 (m), 1400 (m), 800 (s), and 740 (s) cm^{-1}.

[2](1,1')Ferroceno[2]para[2]para[2]paracyclo-phane-cis,cis,trans,trans-*tetraene (3).* The Wittig reaction was run as for *1*, but at +10 °C. Usual work-up and PLC yielded cyclophane *3* which crystallized as orange-red plates from dichloromethane−methanol. [31 mg, 3 %, m.p. 260 °C (dec.)]. UV see text. NMR: δ 7.24 (4H, m) and 7.13 (4H, m) benzene rings adjacent to ferrocene unit, 7.18 (4H, s) remaining benzene ring, 6.81 (2H, d, J 16 Hz) and 6.66 (2H, d, J 16 Hz) *trans* double bonds, 6.72 (2H, d, J 12 Hz) and 6.54 (2H, d, J 12 Hz) *cis* double bonds, 4.43 (4H, m) and 4.26 (4H, m) cyclopentadienyl. MS (70 eV): m/e 516 (M^+, 100 %) 514 (10) 258 (M^{2+}, 2). Abs. mass 516.156±0.005, calc. for $C_{36}H_{28}Fe$ 516.154. IR (KBr): 3000 (m), 2900 (m), 1640 (w), 1600 (m), 1440 (m), 950 (s), 820 (s), and 740 (s) cm^{-1}.

[2](1,1')Ferroceno[2]para[2]para[2]paracyclo-phane-cis,cis,cis,trans-*tetraene (2).* The Wittig reaction between terephthalaldehyde (0.134 g, 1 mmol) and the bisphosphonium salt from 1,4-bis(bromomethyl)benzene (1.58 g, 2 mmol) was run at −40 °C, using LiOEt in ethanol (2 mmol) as base. Ferrocene-

1,1'-dicarbaldehyde (0.242 g, 1 mmol) was then added and addition of base continued. Usual work-up followed by PLC yielded cyclophane 2, usually as an oily, orange-coloured solid. This was dissolved in dichloromethane and most of the solvent allowed to evaporate slowly to yield orange crystals m.p. 201–202 °C (13 mg, 2.5 %). UV see text. NMR δ 7.18 (2H, m), 7.14 (2H, m), 7.05 (2H, m), 6.98 (2H, m), 6.91 (2H, m) and 6.89 (2H, m) benzene rings, 6.80 (1H, d, J 16 Hz) and 6.60 (1H, d, J 16 Hz) trans double bonds, 6.72 (1H, d, J 12 Hz), 6.68 (1H, d, J 12 Hz), 6.64 (1H, d, J 12 Hz), 6.49 (1H, d, J 12 Hz), 6.47 (1H, d, J 12 Hz) and 6.39 (1H, d, J 12 Hz) cis double bonds, 4.48 (1H, broad m), 4.35 (1H, broad m), 4.33 (2H, broad m), 4.18 (3H, broad m) and 3.97 (1H, broad m) cyclopentadienyl. NMR (acetone-d_6, +105 °C, sealed NMR tube): aromatic and olefinic signals are unchanged, while the cyclopentadienyl protons appear at δ 4.35 (4H, s), 4.25 (2H, m) and 4.10 (2H, m). See text for discussion of temperature-dependence. MS (70 eV): m/e 516 (M$^+$, 100 %) 514(7) 258 (M^{2+}, 6). Abs. mass 516.152±0.005, calc. for $C_{36}H_{28}Fe$ 516.154. IR (KBr): 3050 (m), 2900 (m), 1630 (w), 1600 (m), 1400 (m), 950 (s), 810 (s), and 740 (s) cm^{-1}.

[2](1,1')Ferroceno[2]para[2](1,1')ferroceno[2]-paracyclophane-cis,cis,cis,cis-tetraene (4), and [2]-(1,1')ferroceno[2]para[2](1,1')ferroceno [2]paracyclophane-cis,cis,cis,trans-tetraene (5) were both isolated from the Wittig reaction between ferrocene-1,1'-dicarbaldehyde (0.484 g, 2 mmol) and the bisphosphonium salt from 1,4-bis(bromomethyl)-benzene (1.58 g, 2 mmol). The reaction was run at −30 °C, using LiOEt in ethanol as base. Usual work-up was followed by PLC on silica gel using light petroleum (40°–60°)−diethyl ether (95:5) as eluent. This eluted 4 (orange crystals from dichloro-methane−methanol, m.p. >300 °C, 12 mg, 2 %) followed by 5 (orange-red crystals from dichloro-methane−methanol, m.p. >300 °C, 30 mg, 5 %). Spectral data: (4): UV (ethanol): λ_{max} 270 nm, log ε 4.06; λ_{max} 300 nm, log ε 3.97. NMR: δ 7.36 (8H, s) benzene rings, 6.54 (4H, d, J 12 Hz) and 6.04 (4H, d, J 12 Hz) cis double bonds, 4.25 (4H, m) and 4.11 (4H, m) cyclopentadienyl. MS (70 eV): m/e 624 (M$^+$, 100 %) 622(10) 312 (M^{2+}, 20). Abs. mass 624.120±0.005, calc. for $C_{40}H_{32}Fe_2$ 624.119. IR (KBr): 3000 (m), 2950 (m), 1630 (w), 1600 (m), 1450 (m), 810 (s), and 740 (s) cm^{-1}.

(5): UV (ethanol): λ_{max} 305, log ε 4.09. NMR: δ 7.39 (4H, m) and 7.27 (4H, m) benzene rings, 6.88 (1H, d, J 16 Hz) and 6.69 (1H, d, J 16 Hz) trans double bonds, 6.46 (1H, d, J 12 Hz), 6.42 (1H, d, J 12 Hz), 6.38 (1H, d, J 12 Hz), 6.26 (1H, d, J 12 Hz), 6.11 (1H, d, J 12 Hz) and 6.01 (1H, d, J 12 Hz) cis double bonds, 4.29 (4H, m), 4.25 (2H, m), 4.21 (8H, m) and 4.10 (2H, m) cyclopentadienyl. MS (70 eV): m/e 624 (M$^+$, 100 %) 622(9) 312 (M^{2+}, 30). Abs.

mass 624.122±0.005, calc. for $C_{40}H_{32}Fe_2$ 624.119. IR (KBr): 3000 (m), 2950 (m), 2900 (w), 1640 (m), 1460 (m), 960 (m), 800 (s), and 740 (s) cm^{-1}.

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