Synthesis, Reactions, and Structural and NMR Features of [2.2]Metacyclophane Monoenes and Their Tricarbonylchromium and Cyclopentadienyliron(+) Complexes

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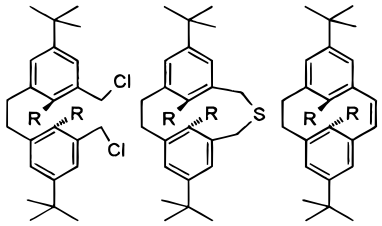
8,16-Dimethyl-, 5,8,13,16-tetramethyl-, and 4,6,8,12,14,16-hexamethyl[2.2]metacyclophanene have been synthesized from the corresponding methyl-substituted 3-thia[3.2]metacyclophane precursors via a Wittig rearrangement−Hofmann elimination procedure. Simple addition of bromine or similar electrophiles to the bridge double bond of the cyclophane monoenes did not occur; rather, the methyl-substituted dihydropyrenes were formed. However, mono- and bis-tricarbonylchromium and monocyclopentadienyliron complexes were obtained using ligand-exchange reactions. Addition of bromine to the cyclophane bridge double bond of the iron complex did occur, but unusually slowly. Surprisingly, debromination rather than dehydrobromination occurred when the dibromo addition product was treated with a variety of bases. Photoisomerization of the monoenes and nucleophilic substitution of the metal complexes was also investigated. The geometries of the monoenes and their complexes were compared to the cyclophanes and the cyclophanedienes and to the monothia- and dithiacyclophanes, by comparison of X-ray and calculated structural data and NMR spectroscopic data. Introduction of double bonds into the cyclophane bridges causes the cyclophane step to be less steep but increases distortion of the internal atoms out of the plane of the benzene rings. Making the bridges nonidentical also causes a sideways twist of the step.

Introduction

In contrast to the case of [2.2]paracyclophane,[1] the saturated bridges of [2.2]metacyclophane cannot be directly functionalized.[2] This led Boekelheide[3] to devise a rather lengthy synthesis of the cyclophane monoenes **1** (R = H, CH_3), in which the unsaturated bridge was formed first via a Wittig reaction. Closure of the second (saturated) bridge occurred by means of a Wurtz coupling, which proceeded rather poorly (10%) for R = CH_3, making study of the chemistry of the cyclophane monoenes difficult. Our synthesis[4] of metacyclophanedienes, **2**, using thiacyclophane intermediates gave much improved access to both these compounds and cyclophanes with unsaturated bridges in general.[5] However, study of the chemistry of [2.2]metacyclophane-1,9-dienes with internal alkyl substituents, **2**, was still not possible because of the thermal valence isomerization that readily occurred to the more stable and much more reactive dihydropyrenes **3**.[6] Tashiro[7] recognized that the thiacyclophane route might yield better quantities of the metacyclophane monoenes by first forming the saturated bridge to form a 1,2-diphenylethane, **4**, and then formation of the unsaturated bridge using the thiacyclophane **5** as intermediate, and so was able to obtain the *tert*-butyl-substituted examples **6** (R = Me, Et). However, the

1 **2** **3**



4 **5** **6**

tert-butyl substituents substantially change the chemistry of the [2.2]metacyclophanes, relative to those cyclophanes that lack such groups,[7,8] and thus, we thought the chemistry of the monoenes without such groups should also be explored, and as well we wanted to study some of their metal complexes, to complement our studies in cyclophanes with saturated bridges.[9]

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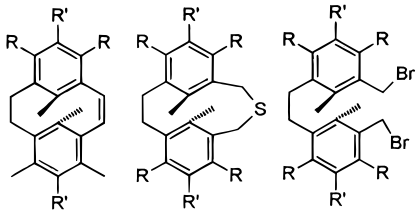
Syntheses

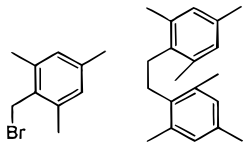
Since we knew we would want to investigate metal complexation of the cyclophane monoenes, we decided that **7a**−**c** would be appropriate targets, with different numbers of methyl substituents and, hence, different electron density in the benzene rings. To make use of the thiacyclophane intermediate, **8a**−**c**, we thus required the three diarylethanes **9a**−**c**. Unfortunately, each of these



7 **8** **9**

a: R=R'=H **b: R=H; R'=Me** **c: R=Me; R'=H**

required their own route. Only **9c** was attainable fairly directly: bromomethylation of mesitylene proceeded in 85% yield to form **10** when myristyltrimethylammonium bromide was used as phase-transfer catalyst[10] with trioxane and concentrated aqueous HBr at 80−90 °C. Coupling of **10** with Mg in refluxing THF was almost quantitative to give **11**, which on rebromomethylation as above, using 2 equiv of trioxane, gave 85% of the desired product **9c** and none of the isomer with both bromomethyl groups in the same benzene ring. All compounds

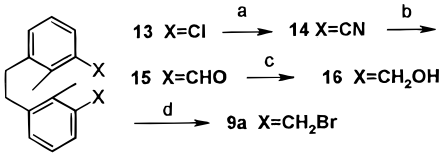


10 **11**

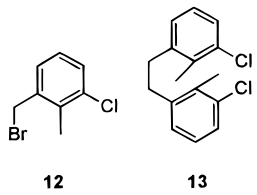
were fully characterized, and details are in the Experimental Section. To access **9a**, commercial 2,6-dichlorotoluene was converted to the bromide **12** in 79% yield in two steps[11] via the mono-Grignard reagent and formaldehyde, followed by HBr, and then **12** could be coupled in 88% yield to the dimer **13** using Mg in THF *at room temperature*, which avoided formation of the aryl Grignard and its subsequent coupling to byproducts. Dichloride **13** was converted to **9a** in 66% overall yield using the longer sequence shown in Scheme 1, rather than the shorter Grignard−formaldehyde−HBr sequence used above for **12**, which from **13** only gave **9a** in 25−35% overall yield.

To access **9b** was more difficult: commercial 2,5-dimethylaniline was brominated in 94% yield in aqueous alcohol to give **17A**, which was deaminated to **17B** in 75%

Scheme 1

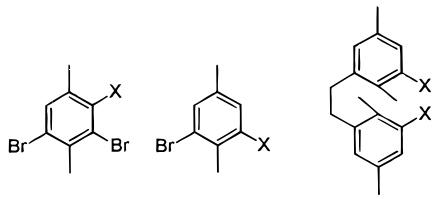


a: CuCN/N-methylpyrrolidone, 84%
b: DIBALH/benzene, 84%
c: $NaBH_4$/THF, 100%
d: 48% aq. HBr, reflux, 93%



12 **13**

yield via diazotization.[12] The latter failed to yield the alcohol **20** via the Grignard reagent and formaldehyde and so had to be put through a sequence, **18** → **21**, similar to that used in Scheme 1, to give the bromide **21**. To



17A X=NH_2
17B X=H

18 X=CN
19 X=CHO
20 X=CH_2OH
21 X=CH_2Br

22A X=Br
22B X=CN
22C X=CHO
22D X=CH_2OH
9b X=CH_2Br

achieve benzylic coupling of **21** without aryl-coupling interference, Mg in THF in the presence of $FeCl_3$ was used[2] and gave the dimer **22A** in 93% yield. Repeat of this four- step sequence on **22A** then yielded **9b** in 71% yield.

Thiacyclophanes 8. Thiacyclophanes can be obtained by coupling one molecule containing a bromide and one a thiol[4] or by coupling a dibromide and $Na_2S{\cdot}9H_2O$.[13] To obtain good yields in the latter coupling, the dibromide was placed in one dropping funnel and the sulfide in a second, and the drop rates from both funnels were kept as equal as possible. Typically, yields were 20−50%. Bodwell[14] has introduced sodium sulfide adsorbed on to alumina to improve yields in this reaction and has obtained yields as high as 65% in intermolecular cyclizations using this reagent. We took a slightly different approach. The dibromides **9** are not very soluble in benzene. We thus thought that by keeping most of the dibromide present as a suspended solid only a small amount would be dissolved to couple, and thus, we would achieve a high dilution process without the need for large volumes of solvent. After a few trials, a suitable solvent system was found for each of the dibromides **9a**−**c**, shown in Table 1, which gave very respectable yields of the thiacyclophanes **8**.

In each case, only the anti isomers were obtained, in which the internal methyl groups are shielded to δ 0.8 (from about 2.2) by the opposite benzene rings.

The Metacyclophane Monoenes 7. Wittig rearrangement[15] of the three thiacyclophanes **8** proceeded smoothly with *n*-BuLi or LDA in THF at room temper-

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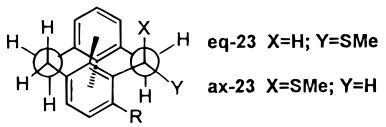
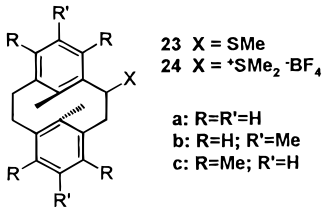


Figure 1. Equatorial and axial isomers of cyclophanes **23** (only one R group shown for clarity).

Table 1. Solvent System Used to Couple Dibromides 9 with Sodium Sulfide

bromide	product	yield (%)	solvent (water/ethanol/benzene)
9a	**8a**	66	23:77:0
9b	**8b**	83	16:70:14
9c	**8c**	72	12:63:25

ature, followed by MeI, and gave essentially quantitative yields of the [2.2]cyclophanes **23** as a mixture of equatorial and axial isomers, Figure 1.

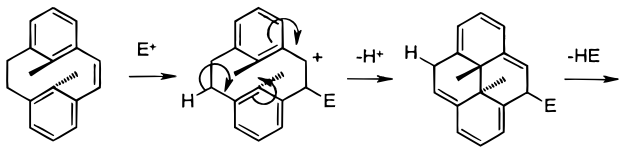


In the case of **23a**, the ratio of equatorial to axial isomers obtained was 91:9. These could be separated by chromatography and showed mp 95−96 °C and 156−157 °C, respectively. They are easily distinguished by ^{1}H NMR, since the internal methyl protons of **ax-23a** appear as two well-separated singlets at δ 0.53 and 0.88, the latter being deshielded by the adjacent −SMe group, while in **eq-23a** they appear at δ 0.57 and 0.59. In this case, the adjacent ring hydrogen, R in Figure 1, is deshielded to δ 7.70, while in **ax-23a** it appears at δ 7.26. For **23b**, the ratio of isomers was also 91:9, but for **23c** the ratio was 72:28. Less equatorial isomer was formed in this case, presumably because of the unfavorable steric interaction between the *eq*-Me and the ring-Me (R = Me in Figure 1). We were not able to separate these two isomers by chromatography; however, we did obtain a pure sample of **eq-23c**, because it reacts slower than the axial isomer in the next step (below). Methylation of **23a**−**c** with dimethoxycarbonium fluoroborate[16] gave the sulfonium salts **24** in high yield, which with *t*-BuOK in *t*-BuOH/DMF (1:1) at room temperature underwent Hofmann elimination to give the desired monoenes **7a**−**c** in 92, 72, and 52% yields, respectively. In the last case, 26% of **eq-23c** was returned. Evidently, the additional ring Me groups in **eq-23c** (R = Me in Figure 1) inhibit approach of the base to remove the β-*eq*-H in the syn transition state.

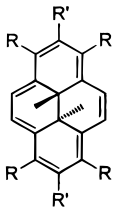
By this route, 1−2 g of **7a**,**b** and 10 g of **7c** could be obtained in a single run compared to the 90 mg of **7a** prepared in ref 3, such that the chemistry of the monoenes **7** can now be explored.

Electrophilic Addition Reactions of the Monoenes 7. One of the potentially more important synthetic utilities of the monoenes **7** would be to be precursors to the as yet unknown [2.2]metacyclophanynes, e.g., **24**. The [2.2]orthocyclophanyne **25** is known[17] and is a stable compound, and both the paracyclophanyne **26**[18] and the metaparacyclophanyne **27**[19] can be trapped with furan.

Scheme 2



7 a: R=R'=H b: R=H; R'=Me c: R=Me; R'=H



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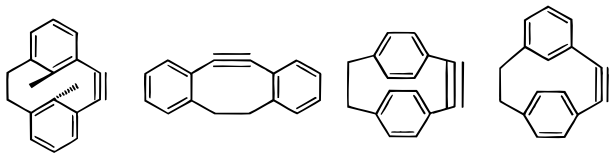

24 25 26 27

We thus first tried addition of bromine to the double bonds of the monoenes **7**. Even with a solution of bromine in dichloromethane at −78 °C, the monoenes **7a**−**c** *immediately* gave dark green solutions of the dihydropyrenes **28a**−**c** in essentially quantitative yield. The same result was obtained using the milder brominating reagents pyridinium bromide perbromide[20] and NBS[21] also in dichloromethane at 0 °C. Excess bromination reagents introduced further bromine substituents into the dihydropyrene ring. Both PhSeCl[22] and PhSeCl$_3$[23] also gave the dihydropyrenes, rather than addition product. Evidently, the monoenes **7** are extremely easily oxidized to the dihydropyrenes **28**. Because on addition of bromine, the green dihydropyrene color forms immediately, a reasonable mechanism would involve after attack by the electrophile, a very rapid loss of H^+ with formation of the interannular bond, such that a final loss of HBr gives the aromatic dihydropyrene. One possible mechanism is shown in Scheme 2.

Tashiro[7] reported the reaction of the monoene **6** (R=Me,Et) only with excess bromine in carbon tetrachloride, and found the tetrabrominated dihydropyrene, 4,5,9,10-tetrabromo-**28** (R = H; R′ = *t*-Bu) to be the product. With chlorine, a hexachloro derivative was obtained, while iodine chloride gave a tetrachloropyrene in which the internal alkyl groups were lost.[7] Even when nonoxidizing electrophiles, such as CF_3COOH, were used,

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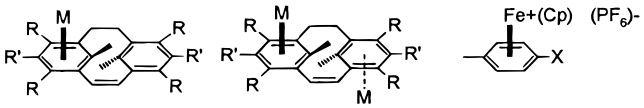
interannular bond formation to form a dihydropyrene was observed.[24] To overcome this problem, we thought constraining the π-electrons of the benzene ring as a metal complex might be useful and would make interannular bond formation less likely.

Metal Complex Formation of the Monoenes 7. Two metal complexes were chosen for study: the tricarbonylchromium derivatives and the cyclopentadienyl iron salts. The former was chosen both for comparison with our previously studied thia-[25] and saturated [2.2]cyclophane[9] examples, and as well as candidates for nucleophilic and electrophilic substitution; the latter was chosen to be subjected to bromination studies, since the cationic iron center is not removed by bromine as is a tricarbonylchromium group.



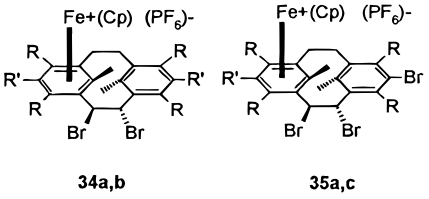
29 M=Cr(CO)$_3$ **30** M=Cr(CO)$_3$ **31** X=Me
32 M=Fe$^+$(Cp) $^-$PF$_6$ **33** X=Cl

a: R=R'=H b: R=H; R'=Me c: R=Me; R'=H

Reaction of the monoenes **7a**,**c** with a 3:1 molar excess of tricarbonylchromiumnaphthalene[26] in ether at 60 °C in a sealed tube gave the mono- and bis-chromium complexes **29a**,**c** and **30a**,**c**, respectively. The less substituted monoene **7a** gave a 2:3 ratio of mono/bis complexes **29a** and **30a** in 95% overall yield, while the more substituted monoene gave a 1:4 ratio of **29c**/**30c** in 82% overall yield. Their structures were given by their clear molecular ions in their mass spectra and by their proton and carbon NMR spectra. In the bis-complexes the aromatic ring protons were all shielded to δ 5.1−5.4, characteristic[9,25] of such protons, while in the mono complexes, one set was shielded and one set remained relatively normal at around δ 7; their spectra are discussed in detail below.

Several CpFe$^+$ complexes of [2.2]metacyclophanes were successfully prepared by Swann and Boekelheide,[27] using the photochemical exchange procedure of Gill and Mann,[28] in which η^6-*p*-xylene-η^5-cyclopentadienyliron hexafluorophosphate, **31**, is used as the CpFe$^+$ source. Indeed, irradiation of a 2:1 mixture of **31** and monoene **7c** in dry dichloromethane using a garden flood lamp gave the monoiron complex **32c** in 82% yield. However, using the less electron-rich monoene **7a** failed to exchange the *p*-xylene ligand of **31**. Thus, the *p*-chlorotoluene containing reagent **33** was used in place of **31**, and with monoene **7a** gave 78% of the iron complex **32a**. With monoene **7c** it gave the same yield of **32c** that **31** did. Interestingly, the yield with monoene **7b** was lower in both cases, 47% with **33** and 43% with **31**. There structures were proven by their NMR spectra (discussed below) and elemental analyses, and as well, an X-ray structure was obtained for **32a**.

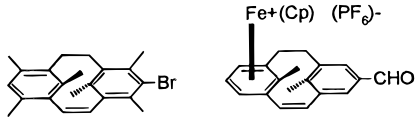
Bromination of the Iron Complexes 32. Surprisingly, reaction of the iron complexes **32** with bromine in dichloromethane in the dark was not instantaneous. In the case of **32b**, after 10 min, the expected dibromide **34b** was formed. This was easily verified by the disappearance of the vinylic proton doublets (J = 11.1 Hz) of **32b** at δ 7.08 and 6.49 and the appearance of two new sets of doublets (J = 5.0 Hz) at δ 5.57 and 5.23 for the −C*H*Br− protons of **34b**. A single trans isomer appeared to form.



34a,b **35a,c**

a: R=R'=H b: R=H; R'=Me c: R=Me; R'=H

Since the internal methyl groups of **34b** were slightly deshielded relative to those in **32b**, while the aryl hydrogens remained almost unchanged, the two bromines probably occupy the *pseudoaxial* positions, adjacent to the internal methyl groups as shown. The other hydrogens and carbons, though slightly shifted, all remained. In the case of **32c** however, not only did the vinylic proton doublets disappear but also the uncomplexed aromatic ring proton, and the product was the tribromide **35c**. As well, the ^{13}C NMR signals for the vinylic carbons of **32b** at δ 138.2 and 131.8 were replaced by −*C*HBr− carbons for **34b** at δ 54.2 and 51.1. In the unsubstituted case, **32a**, about equal amounts of the dibromide **34a** and the tribromide **35a** were obtained. Clearly, addition of bromine to the vinylic double bond is much slower for the complexed compounds than for the uncomplexed, such that ring bromination competes. We have previously reported[9] that the bis-Cr(CO)$_3$-complexed derivative of *syn*-**2** (R = H) could not be catalytically hydrogenated, even though uncomplexed examples reduce rapidly. Taken together, this suggests that metal complexation of the metacyclophanenes substantially reduces the available electron density in the bridge double bond, even though the π-orbital overlap between the aromatic ring and the bridge double bond must only be partial. Surprisingly when the tribromide **35c** was treated with base, (NaOMe/MeOH or KOBu-*t*/HOBu-*t*/THF or DBU or NaNH$_2$/THF), *debromination* and decomplexation occurred to give the monoene **36** and none of the vinyl bromide and none of the dihydropyrene.



36 **37**

Formylation of the complex **32a** with TiCl$_4$ and Cl$_2$CHOMe proceeded poorly and gave only 2% of the aldehyde **37** while returning 32% of unchanged starting material.

Nucleophilic Substitution of 29a. It is well-known that reaction of *n*-BuLi with η^6-tricarbonylchromiumbenzene abstracts a ring proton to give a species that reacts with electrophiles to yield a substituted benzene.[29] Reac-

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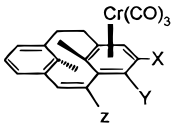
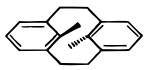
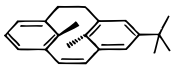
tion of **29a** with *n*-BuLi in THF at −78 °C and subsequent quenching with D_2O gave an 87% yield of a mixture of the ring monodeuterium-substituted complexes **38a**,**b** together with a minor amount of the vinyl substituted complex **38c**. No benzylic substitution at the saturated



38a X=D, Y=Z=H
b Y=D, X=Z=H
c Z=D, X=Y=H



39



40

ethano bridge occurred, unlike nonmetacyclophane cases.[30] This was easily shown from the ^2H NMR spectrum, where the only peaks seen were at δ 5.43 and 5.24 for the new deuterium atoms on the complexed ring and a very small peak at δ 6.37 for the vinyl-deuterium. Mass spectroscopy indicated only one deuterium was incorporated. No selectivity between the ring hydrogens was found. Oxidation of the intermediate anionic species with $FeCl_3$/DMF gave equal amounts of uncomplexed monoene **7a** and saturated cyclophane **39**. When *t*-BuLi in THF at −78 °C was used, addition[29] to the ring occurred, and then with $FeCl_3$/DMF, 62% of the *tert*-butyl substituted cyclophanene **40** was obtained.

Geometry and NMR Features of the Cyclophanenes and Their Metal Complexes

The numbering system used is shown in Figure 2.

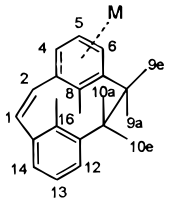


Figure 2. Numbering system used for the cyclophanenes and their metal complexes.

The C_2 rotation axis passing through the midpoints of the C1−C2 and C9−C10 bonds for each of **7a**−**c** makes protons H-1 and H-2 magnetically equivalent, and they thus appear as singlets at about δ 6.6 (±0.06 ppm), Table 2. The bridge protons however, are not equivalent and show a typical[31] AA′XX′ multiplet, which can be analyzed with two chemical shifts and four coupling constants. The values were refined by simulation, and the iterated values are reported in Table 2.

The axial protons (δ 2.5) are more shielded than the equatorial protons (δ 2.9), presumably by the ring current of the opposite ring; however, in **7c**, they are even more so, δ 2.2, possibly because of additional twisting caused by the C-6(Me)−H-9e steric interaction, not present in **7a**,**b**. This is supported also by a small (0.1 ppm) increase in shielding of the internal methyl (Me-8,16) protons in **7c** relative to those in **7a**,**b**. As well, there is a small change in the coupling constants in **7c** from those of **7a** and **7b**, which are almost identical. In ^{13}C NMR spectra of [2.2]metacyclophanes, substitution of a methyl group on the ring, ortho to the bridge, causes a pronounced shielding of the bridge carbon of about 5 ppm per adjacent methyl group,[32] and indeed the bridge carbons, C-9,10, of **7c** are shielded by 6 ppm from those of **7a** and **7b** (Table 2). The symmetry is maintained in the bis-chromium complexes, **30a**,**c**, and again the axial hydrogens and bridge carbons of **30c** are shielded from those in **30a** (Table 2). Interestingly, the chemical shifts of all (etheno and ethano) bridge hydrogens (compare **30c** and **7c**, for example) are hardly changed on bis-complexation. This suggests that there are several effects that cancel each other out. In general, a bridge hydrogen of **30** will be subject to a deshielding by the ring current of the adjacent benzene ring, a shielding by the ring current of the opposite benzene ring, and an anisotropic effect caused by the chromium tricarbonyl group on the adjacent benzene ring (the opposite one is too far away).[33] Since tricarbonylchromium complexation in effect reduces the ring current of the ring that is complexed,[25,34] and both the adjacent and opposite rings are complexed, then on bis-complexation, both the shielding and the deshielding of the benzene rings change (from that in **7**), together with the new through space anisotropic effect of the closer $Cr(CO)_3$. Evidently in total, these just balance. This is not true for the internal methyl groups, Me-8 and Me-16, which are approximately 0.5 ppm (H) and 7 ppm (C) less shielded in the complexes than the parents. In general,[35] the proton and carbon chemical shifts of any substituent methyl groups of arenes are hardly changed (<1 ppm) upon complexation. This is indeed found to be so for the other (C-4,6) methyl groups of **30c** and so suggests that for the internal methyl groups *the dominant effect is the reduction in shielding by the opposite benzene ring*, with the other two effects canceling each other. The monocomplexes **29a**,**c** can then be understood. H-2 and both H-9 protons of **29a**,**c** are assigned the shielded ones of each pair, by about 0.3−1.0 ppm, again primarily because the opposite uncomplexed ring causes full shielding of these. Again, this is especially evident for the internal methyl groups, where C-8 is 0.6−0.8 ppm shielded from C-16, while the external methyl groups, Me-6,12 are hardly affected. The three iron complexes, **32a**−**c** show very similar results (Table 2). For substituent methyl or methylene groups, complexation shifts in such iron complexes[35] are small and very similar to those of the chromium complexes; however, the shielding effect on the aromatic ring carbons is larger for iron complexes. The results for **32c** and **29c** are consistent; for example, the chemical shifts of C-5 are δ 85.5 and 91.2, respectively.

Calculated and Experimental Structural Features

The molecules shown in Figure 3 present an interesting and relevant series to compare structural features. The X-ray structure of the [2.2]metacyclophane **39** has been reported by Hanson.[36] We have obtained the X-ray

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(36) Hanson, A. W. *Acta Crystallogr.* **1962**, *15*, 956.

Table 2. Selected NMR Data for the Monoenes and Their Complexes

	^{1}H NMR			J_{H-H} (Hz)		^{13}C NMR (δ)			
compd	δ(H-1) δ(H-2)	δ(H-9$_{eq}$) δ(H-10$_{eq}$)	δ(H-9$_{ax}$) δ(H-10$_{ax}$)	J_{9e-9a} J_{9e-10e}	J_{9e-10a} J_{9a-10a}	δ(Int-CH$_3$)	C-9 C-10	C-8(Me) C-16(Me)	Ext-CH$_3$
7a	6.59	2.89	2.50	−12.2 2.8	3.9 12.1	0.76	39.2	17.3	
7b	6.54	2.81	2.48	−12.1 2.8	3.9 12.2	0.73	39.0	17.0	20.6
7c	6.64	3.06	2.17	−13.1 4.0	3.0 12.0	0.63	33.0	17.8	19.16 19.13
30a	6.65	2.97	2.52			1.20	37.7	24.2	
30c	6.69	3.12	2.17			1.11	32.5	24.4	19.0
29a	6.68 6.35	2.77 3.07	2.19 2.77	−13.4	3.9	0.51 1.31	39.4	20.5	
29c	6.95 6.36	2.94 3.20	1.92 2.43	−13.0 3.1	3.1 12.7	0.49 1.11	33.2 32.1	21.1 21.0	19.1 18.9
32a	7.13 6.53	3.00 3.11	2.42 2.58	−13.1 4.1	3.6 12.3	0.67 0.92	38.4 37.4	20.9 22.3	
32b	7.08 6.49	2.95 3.05	2.42 2.54	−12.9 3.9	3.4 12.0	0.62 0.90	38.2 37.0	20.7 22.1	20.4 20.2
32c	7.24 6.58	3.17 3.25	2.18 2.18			0.49 0.86	32.6 32.4	21.1 22.5	19.2 19.1

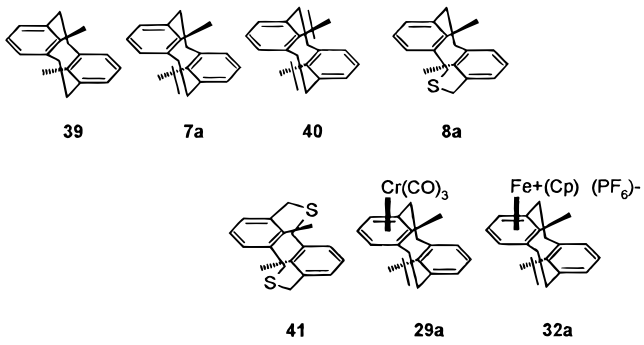


Figure 3. Molecules selected for comparison.

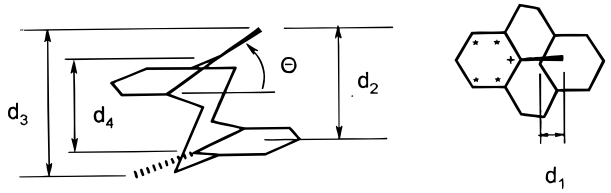


Figure 4. Structural features referred to in Table 3. θ = angle that the internal benzene carbon (+) is bent out of the plane of the benzene carbons (*). d_1 = distance (Å) the internal methyl carbon projects over the opposite benzene ring; 0.0 would be over the opposite internal benzene carbon, 1.4 would be over the center of the ring. d_2 = distance (Å) from the internal methyl carbon to the plane (* carbons) of the opposite benzene ring. d_3 = distance (Å) between internal methyl carbons. d_4 = distance (Å) between internal benzene carbons.

structures of **8a**, **41**, and **32a**, and they are deposited as Supporting Information. Unfortunately, as yet, we have not successfully determined the structures of **7a**, **40**, or **29a**. Nevertheless, we have carried out PCMODEL[37] (an MM2 + π) and AM1[38] calculations on these molecules, so that comparisons can be made between each other and with the X-ray data. We have given both PCMODEL and AM1 data because the latter do not contain the parameters for metals, and a comparison between the two is thus useful to give confidence in the PCMODEL values for metal containing systems.[33] Selected data (see Figure 4 for an explanation) are compared in Table 3.

In our experience, calculations such as PCMODEL and AM1 on the cyclophanes give geometries good enough for discussion, though not necessarily agreeing with all the X-ray-derived data. For example, in the [2.2]metacyclophane **39** the bond lengths of bonds in or attached to the benzene rings all agree very well (<0.01 Å), whereas the bond length between the two bridge carbons is calculated at 1.549 Å but found to be 1.573 Å. Since the $\pi-\pi$ compression between the rings is hard to model, one might expect the biggest differences between calculation and experiment to be in the distances and angles between opposite rings, and in the distortion of the benzene rings out of the plane. Some of the possible values are presented in Table 3 for discussion. For **39**, it can be seen that the experimental values for d_4, d_3, and d_2 lie between

Table 3. Comparison of Calculated and Experimental Values for Selected Structural Features of the Molecules in Figure 3

	compd						
	39	**7a**	**40**	**8a**	**41**	**29a**	**32a**
δ(int-C$^1H_3$)	0.56	0.76	1.52	0.85	1.30	0.51/ 1.31	0.67/ 0.92
δ(int-^{13}CH$_3$)	14.8	17.3	20.0	14.3	14.7	20.5/ 20.9	20.9/ 22.3
d_1 (PCM)	1.0	0.4	0.0	0.8	0.75	0.7	0.6/0.8
d_1 (AM1)	1.0	0.7	0.4	1.0	1.3		
d_1 (exp)	1.0			1.1	1.0		
d_2 (PCM)	3.4	3.0	2.8	3.5	3.5	3.0	3.1
d_2 (AM1)	2.9	2.9	2.7	3.2	3.5		
d_2 (exp)	3.1			3.2	3.1		3.0
d_3 (PCM)	4.792	4.336	4.158	4.709	4.709	4.353	4.345
d_3 (AM1)	4.243	4.175	4.063	4.373	4.718		
d_3 (exp)	4.394			4.325	4.429		4.226
d_4 (PCM)	3.058	2.851	2.753	3.217	3.446	2.867	2.849
d_4 (AM1)	2.681	2.703	2.660	3.049	3.371		
d_4 (exp)	2.819			3.014	3.243		2.687
θ (PCM)	14.8	16.3	18.9	10.9	7.3	16.5/ 14.9	17.1/ 13.4
θ (AM1)	9.4	11.0	12.0	7.1	4.6		
θ (exp)	8.7			3.6	3.4		10.3/10.4

the PCMODEL and AM1 values. PCMODEL appears to overestimate the repulsion between the rings, while AM1 underestimates it. To decide whether the calculated data can be used for cases in which X-ray data is lacking, independent data are required. The NMR data in Table 3 provide some: From calculations of d_1, it is predicted in all cases that the internal methyl carbon (e.g., on C-16) lies within the perimeter of the carbons of the opposite

(37) PCMODEL v. 5.13 for WINDOWS was used from Serena Software, Box 3076, Bloomington, IN, 47402−3076.

(38) Hyperchem v 4.5; Hypercube, Inc., 419 Phillip St., Waterloo, Ontario, Canada, N2L 3X2.

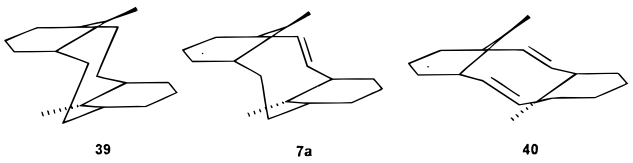


Figure 5. Sketch of the relative geometries of **39**, **7a**, and **40**.

benzene ring, being closest to the center of the opposite ring for **39** ($d_1 = 1$) and closest to the edge (C-8) for **40** ($d_1 \sim 0$). We would expect the chemical shift of the internal carbon (and its protons) to decrease (i.e., become more shielded) as d_1 goes from 0 to 1.4 and the carbon approaches the center of the ring current of the opposite ring. The observed ^{13}C and ^{1}H shifts for **40**, **7a**, and **39** clearly are in the correct order to that expected for the calculated values of d_1. These chemical shift shieldings also depend on d_2, the distance from the internal carbon to the plane of the opposite benzene ring. However, in these three compounds this is reasonably constant at 3 Å. Using the Johnson−Bovey tables,[39] the predicted shieldings caused by the opposite benzene's ring current at this value for d_2 are from about 1.9 ppm over the center of the ring to 0.7 ppm over its edge, similar to the range found for the protons in Table 3. Note: an aryl methyl is normally at δ 2.3. From Table 3, θ, the bending of the internal benzene carbon out of the plane of the rest of the benzene carbons is calculated most poorly. Clearly PCMODEL allows the benzene to bend out of plane too much, as does AM1, though to a lesser extent. This leads to larger distances for d_3 and d_4 in PCMODEL than in AM1.

Taking all of the data together, it suggests that on progression from the cyclophane **39** to the monoene **7a** to the diene **40**, the geometry of the molecule changes such that the two benzene rings both slide away from each other along the long axis of the molecule (the C-5−C-13 distance goes from 6.488 to 6.828 to 7.063 Å, and d_1 decreases) but move so that the distance between the planes of the rings decreases from 2.4 to 2.2 to 1.8 Å, such that as a result d_3 and d_4 decrease and θ increases. We have attempted to sketch this in Figure 5.

For the metal complexes **29a** and **32a**, there appears to be very little geometry change on complexation from that of the monoene **7a**. In fact, PCMODEL predicts the geometry of **32a** quite well compared to its X-ray structure, with the exception of the overestimate of the bending of the benzene ring out of plane. From calculation and X-ray data, the sulfides **8a** and **41** appear to have geometry closest to **39** of the three shown in Figure 5. This is consistent with the chemical shift data for the internal methyl carbon atoms.

Finally, the relative orientation of the rings to the C5−C13 axis is of interest: for **39** both X-ray and calculations have the two benzene rings parallel, i.e., projected on to a plane, carbons 13−16−8−5 form a straight line, likewise for 14−15−3−4 and 12−11−7−6, see A in Figure 6. The diene **40** is calculated to be the same. For the disulfide **41**, both X-ray and calculations have the rings parallel as for **39**, but shifted sideways off the axis; see B in Figure 6. All of the remaining molecules have the rings twisted off the C5−C13 axis as well as sideways

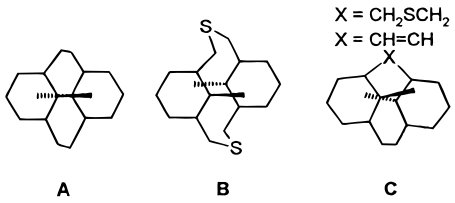


Figure 6. Sketch of the axial alignments A−C.

Table 4. Thermodynamic Parameters for the Thermal Return of 42 to 7 in Acetonitrile

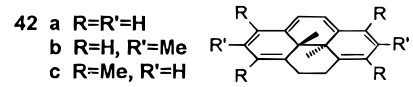
compd	rate at 25 °C (10^3k, min^{-1})	E_{act}[a] (kcal/mol)	$\Delta H^{\ddagger}$[ThinSpace]a (kcal/mol)	$\Delta S^{\ddagger}$[ThinSpace]b (cal/K)	ΔH_f(42−7) [AM1] (kcal/mol)
42a	52.5 (±0.8)	21.3	20.7	−14.3	7.33
42b	6.42 (±0.1)	22.2	21.6	−12.8	7.00
42c	2.04 (±0.1)	24.6	24.0	−18.7	7.63

[a] Estimated error is ±0.5 kcal/mol. [b] Estimated error is ±2 cal/K.

displaced; see C in Figure 6. The sideways displacement follows the order **41** > **8a** > **7a** ≈ 32a ≈ 29a. The twist follows the order **29a** ≈ **7a** > **32a** > **8a**.

Photovalence Isomerization of the Monoenes 7a−c

In the same way that **2** and **3** are valence isomers that are photochemically reversibly interconvertible, and as well thermally from **2** to **3**,[6,40] the monoenes **7a**−**c** can be converted by irradiation with light of wavelength 254 nm to their photoisomers **42a**−**c**, which thermally revert



to the monoenes on standing. The thermal return reaction has been studied for **1** (where R = H, H; H, Me; Me, Me),[41] where it was found that substitution of the internal hydrogens by methyl groups speeded the thermal return reaction. Study of **7a**−**c** would show the effect of external methyl groups. The thermal return of **42** to **7** in acetonitrile was thus followed by UV spectroscopy at six temperatures between 15 and 40 °C to obtain the thermodynamic parameters of Table 4.

As can be seen, the rates of thermal return to the cyclophane monoene follow the order **42a** > **42b** > **42c**, and thus, external methyl groups *slow* the rate of thermal return. Blattmann and Schmidt[40] found that for the thermal return of **2** → **3**(R = Me), four similarly substituted external methyl groups, raised $\Delta H^{\ddagger}$ and E_{act} by about 1.5 kcal/mol and changed $\Delta S^{\ddagger}$ by 5 cal/K, consistent with our results, but overall did not change the rates much. From the calculated ΔH_f values, as expected, the cyclophane monoenes are the more stable, but adding external methyl groups does not favor thermally one or other isomer much at all, and thus, perhaps the main factor reducing the rate with increasing substitution is in the organization involved to get to the transition state.[42]

Conclusions

This study of three cyclophane monoenes and two of their metal complexes has made clear their structural

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(41) Ramey, C. E.; Boekelheide, V. *J. Am. Chem. Soc.* **1970**, *92*, 3681.
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relationship to the saturated cyclophanes and the cyclophanedienes, and the mono- and dithiacyclophanes, by detailed examination of NMR and X-ray data and calculation results. As well, we have shown that some exploration of their chemical reactions is possible, unlike the cyclophanedienes, which too easily thermally convert to the dihydropyrenes, or the saturated cyclophanes, which have essentially inert bridges.

Experimental Section

Melting points were determined on a Reichert 7905 melting point apparatus integrated to a chrome-alumel thermocouple. UV−vis spectra were recorded in acetonitrile. Proton and carbon NMR spectra were recorded in $CDCl_3$ as solvent. Mass spectra were recorded either using methane gas for chemical ionization (CI) or using electron impact (EI) at 70 eV. Exact mass measurements used perfluorokerosene as calibrant. Elemental analyses were carried out by Canadian Microanalytical Services Ltd, Vancouver, BC. All evaporations were carried out under reduced pressure on a rotary evaporator, and all organic extracts were washed with water and dried over anhydrous $MgSO_4$. SiGel refers to Merck silica gel, 70−230 mesh. PE refers to distilled petroleum ether, bp 30−60 °C.

2-Bromomethyl-1,3,5-trimethylbenzene, (10). A mixture of mesitylene (120 g, 1 mol), trioxane (30 g, 0.33 mol), aqueous HBr (48%, 500 mL), and myrystyltrimethylammonium bromide (5 g, 15 mmol) was heated at 80−90 °C with vigorous mechanical stirring for 8 h. PE (50 mL) was then carefully added, and the mixture was left open to cool overnight without further stirring. The solid that collected on top was collected by filtration, washed with water, and air dried. Recrystallization from PE gave bromide **10** as white crystals: mp 49−50 °C (lit.[43] mp 49−50 °C); ^{1}H NMR (250 MHz) δ 6.84 (br s, 2), 4.55 (s, 2), 2.36 (s, 6), 2.25 (s, 3); ^{13}C NMR (62.9 MHz) δ 138.4, 137.4, 131.0, 129.2, 29.6, 21.0, 19.1.

1,2-Bis(2′,4′,6′-trimethylphenyl)ethane (11). A portion (about 5 mL) of a solution of bromide **10** (106 g, 0.5 mol) in dry THF (400 mL) was added to Mg (6.03 g, 0.25 mol) in dry THF (500 mL) under N_2 with gentle warming to initiate the reaction, and then the remainder of the bromide solution was added at such a rate to keep the mixture at reflux. After the addition, the reaction mixture was heated at reflux for a further 2 h, and then the solvent was evaporated, the residual solid was extracted with ether (800 mL) and water, and the ether layer was washed well with water, dried, and evaporated to give 66 g (99%) of dimer **11** as a fluffy white solid, suitable for use in the next step. A portion was recrystallized from hexane: mp 113−114 °C; ^{1}H NMR (250 MHz) δ 6.86 (s, 4), 2.77 (s, 4), 2.36 (s, 12), 2.26 (s, 6); ^{13}C NMR (62.9 MHz) δ 136.3, 135.7, 135.2, 129.1, 29.0, 20.8, 20.1; EI MS *m*/*z* 266 (M^+). Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.26; H, 9.67.

1,2-Bis(3′-bromomethyl-2′,4′,6′-trimethylphenyl)ethane (9c). A mixture of dimer **11** (133 g, 0.5 mol), trioxane (33 g, 0.37 mol), aqueous HBr (48%, 300 mL), myrystyltrimethylammonium bromide (4 g), and heptane (250 mL) were heated at reflux with vigorous mechanical stirring for 20 h. After cooling, the solid was collected by filtration, washed well with water, and then dried to give 193 g (85%) of the bromide **9c**, suitable for use in the next step. A portion was recrystallized from benzene as white crystals: mp 244−246 °C; ^{1}H NMR (360 MHz) δ 6.85 (s, 2), 4.57 (s, 4), 2.80 (s, 4), 2.35 (s, 6), 2.33 (s, 6), 2.26 (s, 6); ^{13}C NMR (90.6 MHz) δ 137.3, 136.9, 136.1, 135.1, 132.1, 130.6, 30.9, 29.4, 20.5, 19.2, 15.1; CI MS *m*/*z* 451 (MH^+). Anal. Calcd for $C_{22}H_{28}Br_2$: C, 58.43; H, 6.24. Found: C, 58.50; H, 6.03.

1,2-Bis(3′-chloro-2′-methylphenyl)ethane (13). A mixture of 2-chloro-6-hydroxymethyltoluene[11] (30.2 g, 0.2 mol) in benzene (150 mL) and aqueous HBr (48%, 60 mL) was stirred under reflux for 16 h. The organic layer was separated, washed, and dried by azeotropic distillation, which was continued to remove most of the benzene. The resulting bromide **12** was diluted with dry THF (150 mL), and a portion (5 mL) was added to Mg (2.43 g, 0.1 mol) in dry THF (200 mL) under N_2. The reaction was initiated by warming, but then the rest of the bromide was added at such a rate to maintain the reaction mixture close to room temperature (*not reflux)*. The mixture was then stirred for a further 6 h, and then water and dichloromethane were added. The organic layer was washed, dried, and evaporated to yield 26.1 g (95%) of the dichloride **13** as a white powder, suitable for use in the next step. A portion was recrystallized from hexane as white crystals: mp 108−109 °C; ^{1}H NMR (250 MHz) δ 7.24 (dd, J = 7.5, 1.7 Hz, 2), 7.05 (t, J = 7.5 Hz, 2), 6.99 (dd, J = 7.5, 1.7 Hz, 2), 2.87 (s, 4), 2.36 (s, 6); ^{13}C NMR (62.9 MHz) δ 141.6, 135.1, 133.9, 127.6, 127.3, 126.6, 35.1, 15.8; EI MS *m*/*z* 278 (M^+). Anal. Calcd for $C_{16}H_{16}Cl_2$: C, 68.83; H, 5.78. Found: C, 68.71; H, 5.61.

1,2-Bis(3′-cyano-2′-methylphenyl)ethane (14). Copper(I) cyanide (20.0 g, 0.26 mol) was added to a hot (∼100 °C) solution of the dichloride **13** (27.9 g, 0.1 mol) in *N*-methyl-2-pyrrolidinone (70 mL), and the mixture was heated to reflux with mechanical stirring for 10 h. It was then cooled to ∼100 °C, a further portion of CuCN (13 g, 0.17 mol) was added, and the mixture was then stirred and refluxed for a further 14 h. This was then cooled to ∼100 °C, and a solution of ethylenediamine (50 mL) in water (100 mL) was added, with vigorous stirring, which was continued for 15 min. The precipitated solid was collected by filtration, was washed thoroughly with ethylenediamine solution and then water, and then was extracted with dichloromethane (800 mL). The extract was washed, dried, and evaporated to give crude dinitrile. This was preabsorbed on to silica gel and chromatographed on SiGel using dichloromethane as eluant to yield 21.9 g (84%) of the dinitrile **14** as a white solid. A portion was recrystallized from hexane as white crystals: mp 204−205 °C; ^{1}H NMR (360 MHz) δ 7.48 (dd, J = 7.4, 1.8 Hz, 2), 7.22 (dd, J = 7.4, 1.8 Hz, 2), 7.18 (t, J = 7.4 Hz, 2), 2.89 (s, 4) 2.48 (s, 6); ^{13}C NMR (90.6 MHz) δ 140.4, 139.6, 133.4, 131.0, 126.5, 118.4, 113.7, 33.7, 17.3; IR (KBr) 2224 cm^{-1}; CI MS *m*/*z* 261 (MH^+). Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.05; H, 6.19; N, 10.76. Found: C, 82.98; H, 6.20; N, 10.69.

1,2-Bis(3′-formyl-2′-methylphenyl)ethane (15). Diisobutylaluminum hydride (0.25 mol in hexane 200 mL) was added dropwise under N_2 with good stirring to a solution of the dinitrile **14** (26.0 g, 0.1 mol) in dry benzene (350 mL) at 20 °C. The stirring was continued overnight, and then the mixture was cooled in an ice bath and decomposed by slow addition of methanol (frothing) (100 mL) and then aqueous HCl (400 mL, 1:1). The mixture was then extracted with dichloromethane (∼ 1 L), and the organic layer was washed, dried, and evaporated. The residue was preabsorbed and filtered through a column (6 × 15 cm) of SiGel using 1:1 PE/dichloromethane as eluant to give 22.3 g (84%) of the dialdehyde **15** as a pale yellow powder. A small sample was recrystallized from acetone−hexane: mp 116−117 °C; ^{1}H NMR (360 MHz) δ 10.29(s, 2), 7.67 (dd, J = 6.5, 2.7 Hz, 2), 7.30−7.26 (m, 4), 2.94 (s, 4), 2.61 (s, 6); ^{13}C NMR (90.6 MHz) δ 192.9, 141.0, 138.2, 134.6, 134.7, 130.5, 125.9, 33.8, 14.0; IR (KBr) 2768, 1688 cm^{-1}; CI MS *m*/*z* 267 (MH^+). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.32; H, 6.89.

1,2-Bis(3′-hydroxymethyl-2′-methylphenyl)ethane (16). A solution of the dialdehyde **15** (43.6 g, 164 mmol) in THF (450 mL) was added dropwise to a stirred suspension of $NaBH_4$ (4 g, 100 mmol) in THF (150 mL) and water (10 mL) at 20 °C. After the suspension was stirred for 20 h, aqueousaqueous HCl (60 mL of concentrated acid + 120 mL water) was added slowly to decompose the reaction mixture. Filtration then gave the first batch of product. The aqueous layer was extracted with dichloromethane until it became clear, and then the combined organic extracts were dried and evaporated to give a second batch of product. The two batches were combined and dried under vacuum to yield 43.5 g (98%) of the diol **16**, suitable for use in the next step, as a white powder: mp 156−158 °C (lit.[2]

(43) Hauser, C. R.; Van Eenam, D. N. *J. Am. Chem. Soc.* **1957**, *79*, 5512.

mp 158−160 °C); ^{1}H NMR (360 MHz) δ 7.26−7.15 (m, 6), 4.72 (d, J = 4 Hz, 4), 2.89 (s, 4), 2.30 (s, 6), 1.58 (bs, 2); ^{13}C NMR (90.6 MHz) δ 140.7, 139.0, 134.4, 129.0, 126.2, 125.9, 64.3, 34.8, 14.1; IR (KBr) 3320, 3240 cm^{-1}.

1,2-Bis(3′-bromomethyl-2′-methylphenyl)ethane (9a). A suspension of the diol **16** (8.78 g, 32.5 mmol) in benzene (100 mL) and concentrated aqueous HBr (48%, 60 mL) and concentrated H_2SO_4 (0.5 mL) was refluxed for 24 h. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed well with water, aqueous $NaHCO_3$, and water and then were dried and evaporated. The residue (CAUTION: lacrimator) was filtered through a column of SiGel (5 × 15 cm) using PE/dichloromethane (5:1) as eluant to yield 11.95 g (93%) of dibromide **9a** as a white solid: mp 140−142 °C (lit.[2] mp 142−143 °C); ^{1}H NMR (250 MHz) δ 7.24−7.09 (m, 6), 4.54 (s, 4), 2.88 (s, 4), 2.30(s, 6); ^{13}C NMR (90.6 MHz) δ 140.9, 136.1, 135.3, 130.1, 128.3, 126.1, 34.7, 33.4, 14.3.

2,6-Dibromo-*p*-xylene (17B). This procedure is adapted from a similar one in *Organic Syntheses*.[12] A rapid stream of air saturated with bromine vapor (500 g, 3.12 mol) was pulled by suction through a well stirred solution of 2,5-dimethylaniline (189 g, 1.56 mol) in 95% aqueous ethanol (1.7 L) and water (1.4 L) at 20 °C in the dark (∼6 h). The solid 2,4-dibromo-3,5-dimethylaniline[44] (**17A**) was collected by filtration, washed well with water, and used directly in the next step. A small quantity was dried, indicated a yield of 94%, and gave ^{1}H NMR (90 MHz) δ 7.22 (s, 1), 3.37 (bs, 2), 2.51 (s, 3), 2.15 (s, 3). The damp crude dibromide was dissolved in benzene (400 mL) and 95% aqueous ethanol (1.7 L), and then concentrated H_2SO_4 (200 mL) was added with stirring. $NaNO_2$ (200 g) was then added to this hot mixture in small portions as quickly as the violence of the reaction would permit (∼1 h). After the addition, the mixture was refluxed for 3 h and then was kept at ∼50 °C for 14 h. The mixture was then cooled, and concentrated H_2SO_4 (200 mL) that had been diluted with water (1.4 L) was added followed by PE (1.5 L). The organic layer was washed with water, aqueous $NaHCO_3$, and water and then was dried and evaporated. The residue was distilled under vacuum (133−136 °C/13 Torr) to give 289 g (75%) of the dibromide **17B**: mp 32−34 °C (lit.[42a,b] mp 32,36 °C); ^{1}H NMR (90 MHz) δ 7.32 (s, 2), 2.47 (s, 3), 2.22 (s, 3).

3-Bromo-2,5-dimethylbenzonitrile (18). Cu(I)CN (29.5 g, 0.33 mol) was added to a mechanically stirred, hot (∼80 °C) solution of 2,6-dibromo-*p*-xylene (**17B**) (174 g, 0.66 mol) in DMF (100 mL). The mixture was then stirred at reflux for 4 h, and while still hot a solution of ethylenediamine (80 mL) and water (240 mL) was added and, after some cooling, dichloromethane (400 mL). After the mixture was stirred for 30 min, insoluble material was filtered, and the organic layer was separated, washed, dried, and evaporated. The residue was preabsorbed and chromatographed on SiGel using first PE as eluant to elute 92 g (53%) of unreacted **17B**. Elution with PE/dichloromethane (3:1) then gave 61 g (44%) of the mononitrile **18** as a white solid: mp 74−75 °C; ^{1}H NMR (360 MHz) δ 7.57 (s, 1), 7.35 (s, 1), 2.56 (s, 3), 2.31 (s, 3); ^{13}C NMR (90.6 MHz) δ 138.4, 137.9, 137.6, 132.1, 125.5, 117.6, 114.0, 21.1, 20.3; IR (KBr) 2230 cm^{-1}; CI MS m/z 212,210 (1:1, MH$^+$). Anal. Calcd for C_9H_8BrN: C, 51.46; H, 3.84; N, 6.67. Found: C, 51.10; H, 3.81; N, 6.51.

Eluted last was 2.6 g (3%) of 2,5-dimethyl-1,3-phthalodinitrile: mp 171−172 °C; ^{1}H NMR (360 MHz) δ 7.61 (s, 2), 2.69 (s, 3), 2.38 (s, 3); ^{13} C NMR (90.6 MHz) δ 142.4, 137.6, 136.9, 116.4, 114.5, 20.3, 18.9; IR (KBr) 2220 cm^{-1}; CI MS m/z 157 (MH$^+$).

Use of a full equivalent of CuCN gave 16−17% unreacted dibromide, 50% of nitrile **18**, and 20% of dinitrile, but the reaction mixture was more difficult to separate.

3-Bromo-2,5-dimethylbenzaldehyde (19). Diisobutylaluminum hydride (75 mmol in hexane (60 mL)) was added dropwise over 1.5 h under N_2 to a solution of nitrile **18** (10.5 g, 50 mmol) in dry benzene (60 mL) at 20 °C. After the mixture was stirred for 14 h, methanol (15 mL) was slowly added followed by aqueous methanol (1:1, 40 mL)and aqueous 10% HCl (120 mL). The mixture was filtered, the organic layer was separated, and the aqueous layer was further extracted with ether (2 × 100 mL). The combined organic layers were washed, dried, and evaporated to give 10.33 g (97%) of the aldehyde **19** as a yellowish liquid suitable for use in the next step. Vacuum distillation gave colorless liquid: bp 116−117°/2.5 mmHg; ^{1}H NMR (250 MHz) δ 10.19 (s, 1), 7.59 (s, 1), 7.54 (s, 1), 2.66 (s, 3), 2.34 (s, 3); IR (film) 2730, 1690 cm^{-1}; CI MS m/z 215, 213 (MH$^+$, Br$_1$).

1-Bromo-2,5-dimethyl-3-hydroxymethylbenzene (20). A solution of the aldehyde **19** (30.0 g, 140 mmol) in THF (not dried, 350 mL) was added dropwise to a stirred suspension of $NaBH_4$ (2.65 g, 70 mmol) in THF (300 mL) at 20 °C. After the mixture was stirred for 20 h, aqueous 10% HCl (180 mL) was added, followed by ether (250 mL). The organic layer was separated, and the aqueous layer was re-extracted with ether (2 × 200 mL). The combined organic layers were washed, dried, and evaporated to give 30.3 g (100%) of the alcohol **20** as a white solid: mp 89−90 °C; ^{1}H NMR (360 MHz) δ 7.33 (s, 1), 7.11 (s, 1), 4.67 (d, J = 5.7 Hz, 2), 2.36 (s, 3), 2.28 (s, 3), 1.54 (t, J = 5.7 Hz, 1); ^{13}C NMR (90.6 MHz) δ 140.1, 137.0, 132.5, 132.4, 127.7, 125.9, 64.1, 20.5, 17.9; IR (KBr) 3240 (w) cm^{-1}; EI MS m/z 216, 214 (M$^+$, small, Br$_1$). Anal. Calcd for C_9H_{11}-BrO: C, 50.26; H, 5.15. Found: C, 50.20; H, 5.15.

1-Bromo-3-bromomethyl-2,5-dimethylbenzene (21). A mixture of the alcohol **20** (28.8 g, 134 mmol), benzene (120 mL), and concentrated aqueous 48% HBr (100 mL) was refluxed with stirring for 40 h. The organic layer was separated, washed with water, aqueous $NaHCO_3$, and water, and then dried and evaporated. The residue was preabsorbed and filtered through a short column of SiGel using PE as the eluant and gave 36.3 g (97%) of the bromide **21** as a white solid. A portion was recrystallized from pentane as colorless crystals: mp 51−52 °C; ^{1}H NMR (360 MHz) δ 7.34 (s, 1), 7.05 (s, 1), 4.47 (s, 2), 2.41 (s, 3), 2.26 (s, 3); ^{13}C NMR (90.6 MHz) δ 137.2, 137.1, 133.8, 133.7, 130.0, 126.2, 32.8, 20.4, 18.3; CI MS m/z 281, 279, 277 (MH$^+$, Br$_2$). Anal. Calcd for $C_9H_{10}Br_2$: C, 38.89; H, 3.63. Found: C, 39.02; H, 3.62.

1,2-Bis-(3′-bromo-2′,5′-dimethylphenyl)ethane (22A). A solution of dibromide **21** (21.5 g, 7.7 mmol) in dry ether (50 mL) was warmed (to reflux if necessary) with Mg (0.95 g, 3.9 mmol) under N_2. Once the reaction initiated, anhyd $FeCl_3$ (50 mg, 0.3 mmol) was added, which caused vigorous reaction that subsided after about 20 min. The reaction was then refluxed for 1 h, and then cold water was added, followed by aqueous HCl and dichloromethane. The organic layer was washed, dried, and evaporated to give 14.2 g (93%) of the diphenylethane **22A** as a white powder. A portion was recrystallized from ethyl acetate as white crystals: mp 169−170 °C; ^{1}H NMR (360 MHz) δ 7.26 (br s, 2), 6.85 (br s, 2), 2.79 (s, 4), 2.34 (s, 6), 2.25 (s, 6); ^{13}C NMR (90.6 MHz) δ 141.4, 136.9, 132.3, 131.1, 129.1, 125.9, 35.7, 20.5, 18.6; CI MS m/z 399, 397, 395 (MH$^+$, Br$_2$). Anal. Calcd for $C_{18}H_{20}Br_2$: C, 54.57; H, 5.09. Found: C, 54.83; H, 5.06.

1,2-Bis(3′-cyano-2′,5′-dimethylphenyl)ethane (22B). Cu(I)CN (26.9 g, 0.3 mol) was added to a hot solution of the dibromide **22A** (39.6 g, 0.1 mol) in *N*-methyl-2-pyrrolidinone (150 mL), and the mixture was mechanically stirred under reflux for 20 h. The mixture was then cooled to 80 °C, aqueous 25% ethylenediamine (280 mL) was added, and the mixture was vigorously stirred for 30 min. The solid was collected by filtration, and the filtrate was extracted with dichloromethane (2 × 100 mL). The solid was dissolved in dichloromethane (∼800 mL) and was filtered. The organic layers were combined, washed, dried, and evaporated. The residue was preabsorbed and filtered through a column of SiGel using PE/dichloromethane (1:1) as eluant to give 27.6 g, (96%) of the dinitrile **22B** as a yellowish solid. A portion was recrystallized from acetone as white crystals: mp 206−207 °C; ^{1}H NMR (360 MHz) δ 7.28 (s, 2), 7.05 (s, 2), 2.80 (s, 4), 2.43 (s, 6), 2.28 (s, 6); ^{13}C NMR (90.6 MHz) δ 140.4, 136.5, 136.3, 134.4, 131.1, 118.0, 113.5, 33.9, 20.6, 16.9; IR (KBr) 2223 cm^{-1}; CI MS m/z 289

(44) (a) Blanksma, J. J. *Chem. Weekblad*, *10*, 136−141; *Chem. Abstr.* **1913**, *7*, 1493. (b) Bures, E.; Meskan, F. *Casopis Ceskoslov. Lekarnicta* **1937**, *17*, 149; *Chem. Abstr.* **1937**, *31*, 7857.

(MH^+). Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.23; H, 7.16; N, 9.56.

1,2-Bis(3′-formyl-2′,5′-dimethylphenyl)ethane (22C). Diisobutylaluminum hydride (0.25 mmol in hexane (200 mL)) was added dropwise under N_2 to a solution of the dinitrile **22B** (28.84 g, 0.1 mol) in dry benzene (500 mL) at 20 °C. The mixture was then stirred for 14 h and then decomposed cautiously with methanol (100 mL) and aqueous HCl (1:1, 400 mL). The mixture was extracted with dichloromethane (800 mL), washing the solids well with dichloromethane, and then the organic layers were combined, washed, dried, and evaporated. The residue was preabsorbed and chromatographed on SiGel using PE/CH_2Cl_2/ethyl acetate (5.5:4:0.5) as eluant to give 24.2 g (82%) of the dialdehyde **22C** as a yellowish solid. A portion was recrystallized from acetone as white crystals: mp 142−144 °C; ^{1}H NMR (360 MHz) δ 10.28 (s, 2), 7.49 (s, 2), 7.13 (s, 2), 2.86 (s, 4), 2.57 (s, 6), 2.33 (s, 6); ^{13}C NMR (90.6 MHz) δ 193.3, 141.2, 135.7, 135.6, 135.3, 134.6, 130.9, 34.1, 20.7, 13.7; IR (KBr) 2766, 1670 cm^{-1}; CI MS *m*/*z* 295 (MH^+). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.44; H, 7.68.

1,2-Bis(3′-hydroxymethyl-2′,5′dimethylphenyl)ethane (22D). A solution of the dialdehyde **22C** (21.0 g, 71.3 mmol) in THF (not dried, 500 mL) was added slowly to a stirred suspension of $NaBH_4$ (1.90 g, 50 mmol) in THF (75 mL) and water (5 mL) at 20 °C. After 24 h, the mixture was decomposed by addition of aqueous HCl (10%, 90 mL), and the first batch of product was collected by filtration. A further batch was obtained by extracting the aqueous layer with ether (3 × 200 mL), which was then washed, dried, and evaporated. The combined batches of diol **22D** were dried and gave 20.2 g (95%) of white solid. A portion was recrystallized from acetone as colorless crystals: mp 174−175 °C; ^{1}H NMR (360 MHz) δ 7.04 (s, 2), 6.98 (s, 2), 4.68 (d, J = 5.7 Hz, 4), 2.81 (s, 4), 2.30 (s, 6), 2.27 (s, 6), 1.48 (t, J = 5.7 Hz, 2); IR (KBr) 3280 (br) cm^{-1}. Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 79.86; H, 8.24.

1,2-Bis(3′-bromomethyl-2′,5′-dimethylphenyl)ethane (9b). A mixture of the diol **22D** (19.0 g, 64 mmol), benzene (200 mL), and concentrated aqueous HBr (48%, 120 mL) was refluxed for 36 h. On cooling, some product crystallized, which was collected. The organic layer was washed, dried, and evaporated, and the combined solids were preabsorbed and filtered through a short column of SiGel using PE/CH_2Cl_2 (2:1) as eluant to give 25.7 g (95%) of dibromide **9b** as a white solid. A portion was recrystallized twice from acetone as white crystals: mp 178−179 °C; ^{1}H NMR (360 MHz) δ 7.03 (s, 2), 6.96 (s, 2), 4.51 (s, 4), 2.81 (s, 4), 2.28 (s, 12); ^{13}C NMR (90.6 MHz) δ 141.0, 135.9, 135.5, 132.1, 130.9, 128.9, 34.9, 33.6, 20.8, 13.9. Anal. Calcd for $C_{20}H_{24}Br_2$: C, 56.63; H, 5.70. Found: C, 56.64; H, 5.57.

***anti*-9,17-Dimethyl-2-thia[3.2]metacyclophane (8a).** A solution of $Na_2S{\cdot}9H_2O$ (3.7 g, 15 mmol) in N_2-purged water (120 mL) and aqueous 95% ethanol (380 mL) was added dropwise over 48 h to a well-stirred suspension of the dibromide **9a** (5.55 g, 14 mmol) in N_2-purged aqueous 95% ethanol (618 mL) and water (182 mL) under N_2. Stirring was continued for a further 2 h, and then the solvents were evaporated. Dichloromethane and water were added to the resultant solids, and the organic layer was separated, washed, dried, and evaporated. The residue was preabsorbed on and chromatographed over SiGel using PE/CH_2Cl_2 (3:1) as eluant to yield 2.32 g (66%) of the thiacyclophane **8a**. A portion was recrystallized from hexane as white crystals: mp 171−173 °C; ^{1}H NMR (360 MHz) δ 7.13−7.10 (m, 4), 6.98 (t, J = 7.5 Hz, 2), 3.85 (*A*B, J = 13.8 Hz, 2, H_{eq}), 3.73 (A*B*, J = 13.8 Hz, 2, H_{ax}), 2.94 (*AA*′XX′, $J_{AA'}$ = 2.6 Hz, J_{AX} = −12.6 Hz, $J_{AX'}$ = 4.5 Hz, 2, H_{eq}), 2.64 (AA′*XX*′, $J_{XX'}$ = 12.4 Hz, H_{ax}), 0.85 (s, 6); ^{13}C NMR (90.6 MHz) δ 139.7, 137.6, 135.1, 129.1, 128.7, 125.6, 35.6, 34.1, 14.3; EI MS *m*/*z* 268 (M^+). Anal. Calcd for $C_{18}H_{20}S$: C, 80.55; H, 7.51. Found: C, 79.73; 7.24.

An X-ray structure was obtained on a crystal 0.45 × 0.77 × 0.68 mm in size and was found to be orthorhombic, space group *P*ccn, with a = 28.790 Å, b = 12.922 Å, c = 7.575 Å, and $\alpha = \beta = \gamma = 90°$. The structure was refined to R = 0.082. Full details of the X-ray determination can be found in the Supporting Information.

***anti*-6,9,14,17-Tetramethyl-2-thia[3.2]metacyclophane (8b).** A solution of $Na_2S{\cdot}9H_2O$ (2.64 g, 11 mmol) in N_2-purged water (60 mL), aqueous 95% ethanol (250 mL), and benzene (50 mL) was added dropwise over 20 h to a well-stirred suspension of the dibromide **9b** (4.24 g, 10 mmol) and Cs_2CO_3 (0.65 g) in N_2-purged benzene (150 mL), aqueous 95% ethanol (800 mL), and water (140 mL) under N_2. Stirring was continued for a further 2 h, and then the solvents were evaporated. Dichloromethane and water were added to the resultant solids, and the organic layer was separated, washed, dried, and evaporated. The residue was preabsorbed on and chromatographed over SiGel (4 × 40 cm) using PE/CH_2Cl_2 (4:1) as eluant to yield 2.46 g (83%) of the thiacyclophane **8b**. A portion was recrystallized from hexane as white crystals: mp 175−176 °C; ^{1}H NMR (360 MHz) δ 6.915 (s, 2), 6.905 (s, 2), 3.80 (*AB*, J = 13.8 Hz, 2, H_{eq}), 3.71 (A*B*, J = 13.8 Hz, 2, H_{ax}), 2.85 (*AA*′XX′, $J_{AA'}$ = 2.7 Hz, J_{AX} = −12.5 Hz, $J_{AX'}$ = 4.4 Hz, 2, H_{eq}), 2.60 (AA′*XX*′, $J_{XX'}$ = 12.5 Hz, 2, H_{ax}), 2.24 (s, 6), 0.84 (s, 6); ^{13}C NMR (90.6 MHz) δ 137.6, 136.7, 134.9, 134.5, 129.8, 129.3, 35.5, 34.2, 20.6, 13.9; CI MS *m*/*z* 297 (MH^+). Anal. Calcd for $C_{20}H_{24}S$: C, 81.03; H, 8.16. Found: C, 81.13; H, 8.02.

***anti*-5,7,9,13,15,17-Hexamethyl-2-thia[3.2]metacyclophane (8c).** A solution of $Na_2S{\cdot}9H_2O$ (26.4 g, 0.11 mol) in N_2-purged water (440 mL) to which aqueous 95% ethanol (760 mL) was added was then added dropwise over about 48 h to a well stirred suspension of the dibromide **9c** (45.2 g, 0.10 mol) in N_2-purged benzene (560 mL), aqueous 95% ethanol (1425 mL), and water (200 mL) under N_2. Stirring was continued for a further 4 h, and then the solvents were evaporated. Dichloromethane (1200 mL) and water (600 mL) were added to the resultant solids, and the organic layer was separated, washed, dried, and evaporated. The residue was preabsorbed on and filtered through SiGel (12 × 30 cm) using PE/CH_2Cl_2 (3:1) as eluant to yield 23.8 g (72%) of the thiacyclophane **8c**. A portion was recrystallized from hexane as colorless crystals: mp 208−210 °C; ^{1}H NMR (360 MHz) δ 6.73 (s, 2), 3.82 (*AX*, J = 13.5 Hz, 2, H_{eq}), 3.70 (A*X*, J = 13.5 Hz, 2, H_{ax}), 3.02 (*AA*′XX′, J_{AX} = −13.3 Hz, $J_{AX'}$ = 4.2 Hz, $J_{AA'}$ = 3.0 Hz, 2, H_{eq}), 2.51 (AA′*XX*′, $J_{XX'}$ = 12.8 Hz, 2, H_{ax}), 2.39 (s, 6), 2.34 (s, 6), 0.81 (s, 6, int-Me); ^{13}C NMR (90.6 MHz) δ 140.1, 135.0, 134.8, 133.1, 130.9, 129.2, 29.6, 27.9, 19.9, 19.7, 15.0; CI MS *m*/*z* 325 (MH^+). Anal. Calcd for $C_{22}H_{28}S$: C, 81.42; H, 8.70. Found: C, 81.09; H, 8.63.

***anti*-8,16-Dimethyl-1-methylthio[2.2]metacyclophane (23a).** *n*-Butyllithium (5 mmol in hexane (2 mL)) was added via syringe to a stirred solution of thiacyclophane **8a** (1.07 g, 4.0 mmol) in dry THF (120 mL) under N_2 at 20 °C. After 5 min, methyl iodide (0.34 mL, 5.5 mmol) was added, and then after a further 2 min, aqueous HCl and PE were added. The organic layer was separated, washed, dried, and evaporated to give a mixture of the two isomers of **23a** as 1.14 g (100%) as a yellowish solid. For synthetic purposes, this crude mixture could be used directly in the next step. To separate the isomers, a small portion (130 mg) was chromatographed over SiGel (2 × 80 cm) using PE as eluant. Eluted first was 113 mg (91%) of **eq-23a** as a white solid: mp 95−96 °C; ^{1}H NMR (COSY) (360 MHz) δ 7.70 (br d, J = 7.3 Hz, H-14), 7.17 (d, J = 7.4 Hz, H-12), 7.13 (2d, H-4,6), 6.97 (t, H-13), 6.84 (t, H-5), 4.02 (dd, J = 11.3, 4.2 Hz, H-1_{ax}), 3.18 (dd, J = 12.5, 4.2 Hz, H-2_{eq}), 2.98−2.94 (m, H-9_{eq},10_{eq}), 2.76−2.70 (m, H-9_{ax},-10_{ax}), 2.64 (t, J = ∼11.9 Hz, H-2_{ax}), 2.12 (s, 3), 0.59 (s, 3), 0.57 (s, 3); ^{13}C NMR (90.6 MHz) δ 143.0, 142.5, 137.2, 136.9, 135.6, 135.1, 128.1, 127.6, 127.3, 124.7, 124.4, 124.2, 43.2, 36.3, 36.1, 15.5, 14.9, 14.8; CI MS *m*/*z* 283 (MH^+). Anal. Calcd for $C_{19}H_{22}S$: C, 80.80; H, 7.85. Found: C, 81.10; H, 7.76.

Eluted next was 11.5 mg (9%) of **ax-23a** as a white solid: mp 156−157 °C; ^{1}H NMR (360 MHz) δ 7.26 (d, J = 7.2 Hz, 1), 7.16 (d, J = 7.2 Hz, 1), 7.15 (d, J = 7.2 Hz, 1), 7.07 (d, J = 7.3 Hz, 1), 6.88 (t, J = 7.3 Hz, 1), 6.83 (t, J = 7.3 Hz, 1), 4.41 (br d, J = 5.8 Hz, H-1_{eq}), 3.28 (dd, J = 14.0, 6.9 Hz, H-2_{eq}), 3.04 (br d, J = 14.0 Hz, H-2_{ax}), 2.96−2.81 (m, H-9_{eq},10_{eq}), 2.78−2.70 (m, H-9_{ax},10_{ax}), 2.18 (s, 3), 0.88 (s, C-16(Me)), 0.53 (s, C-8(Me)); ^{13}C NMR (90.6 MHz) δ 144.3, 142.3, 137.1, 136.9,

134.7, 133.9, 128.8, 128.7, 128.5, 128.1, 124.0, 123.9, 57.6, 41.1, 36.2, 36.0, 17.2, 14.7, 14.4; CI MS *m*/*z* 283 (MH^+).

***anti*-1-Methylthio-5,8,13,16-tetramethyl[2.2]-metacyclophane (23b).** A solution of LDA (freshly prepared from *n*-butyllithium (6 mmol in hexane (4 mL)) and *i*-Pr_2NH (0.85 mL, 6 mmol)) in dry THF (10 mL) was added via syringe to a stirred solution of thiacyclophane **8b** (1.19 g, 4 mmol) in dry THF (120 mL) under N_2 at 20 °C. After 30 min, methyl iodide (0.40 mL, 6.5 mmol) was added, followed after 2 min by aqueous HCl and diethyl ether. The organic layer was separated, washed, dried, and evaporated. The residue was preabsorbed and filtered through a column of SiGel using PE/dichloromethane (4:1) as eluant and gave 1.24 g (100%) of the two isomers (91:9) of cyclophane **23b** as a semisolid. For synthetic purposes, this was used in the next step. A portion (100 mg) was chromatographed through a column (2 × 65 cm) of SiGel, using PE/dichloromethane (10:1) as eluant. Eluted first was 90 mg (91%) of **eq-23b** as a white crystals from ether: mp 114−115 °C; ^{1}H NMR (360 MHz) δ 7.47 (s, 1, H-14), 6.96, 6.93, 6.90 (s, 1 each), 3.99 (dd, J = 11.3, 4.3 Hz, 1, H-1_{ax}), 3.11 (dd, J = 12.4, 4.2 Hz, 1, H-2_{eq}), 2.90−2.85 (m, 2, H-9_{eq},-10_{eq}), 2.73−2.67 (m, 2, H-9_{ax},10_{ax}), 2.61 (t J = ∼11.9 Hz, 1, H-2_{ax}), 2.26 (s, 3), 2.20 (s, 3), 2.13 (s, 3), 0.60 (s, 3), 0.58 (s, 3); ^{13}C NMR (90.6 MHz) δ 140.4, 139.9, 137.3, 137.0, 135.6, 135.1, 133.6, 133.2, 128.9, 128.3, 128.0, 124.8, 52.3, 43.2, 36.2, 36.0, 20.9, 20.6, 15.5, 14.7, 14.5; CI MS *m*/*z* 311 (MH^+). Anal. Calcd for $C_{21}H_{26}S$: C, 81.23; H, 8.44. Found: C, 81.32; H, 8.38.

Eluted next was 9 mg (9%) of **ax-23b** as a white solid: mp 176−177 °C; ^{1}H NMR (360 MHz) δ 7.05 (s, 1, H-14), 6.94 (s, 2, H-4,6), 6.86 (s, 1, H-12), 4.34 (dd, J = 7.0, 0.8 Hz, 1, H-1_{eq}), 3.26 (dd, J = 14.0, 7.1 Hz, 1, H-2_{eq}), 2.97 (dd, J = 13.9, 0.8 Hz, 1, H-2_{ax}), 2.88−2.69 (m, 4, H-9,10), 2.23 (s, 3), 2.20 (s, 3), 2.16 (s, 3), 0.89 (s, 3), 0.54(s, 3); ^{13}C NMR (90.6 MHz) δ 141.7, 139.7, 137.0, 136.9, 134.6, 133.8, 132.79, 132.77, 129.5, 129.3, 129.2, 128.7, 57.5, 41.0, 36.2, 35.9, 20.7, 20.4, 17.1, 14.4, 14.1.

***anti*-4,6,8,12,14,16-Hexamethyl-1-methylthio[2.2]-metacyclophane (23c).** A solution of LDA (freshly prepared from *n*-butyllithium (48 mmol in hexane (32 mL)) and *i*-Pr_2-NH (7.0 mL, 50 mmol)) in dry THF (100 mL) was added over 30 min to a stirred solution of thiacyclophane **8c** (13.0 g, 40 mmol) in dry THF (600 mL) under N_2 at 20 °C. After 30 min, methyl iodide (3.2 mL, 52 mmol) was added, followed after 2 min by aqueous HCl and diethyl ether (500 mL). The organic layer was separated, washed, dried, and evaporated. The residue was filtered through a short column of SiGel using PE/dichloromethane (3:1) as eluant and gave 13.4 g (99%) of the two isomers (72-eq/28-ax) of cyclophane **23c** as a white solid, CI MS *m*/*z* 339 (MH^+). The ratio of the isomers was obtained from the internal methyl proton integrations, **ax-23c** at δ 0.79 and 0.41; **eq-23c** at δ 0.57 and 0.56. We were not able to separate these isomers by chromatography. For synthetic purposes, the mixed isomers were used directly in the next step.

Some pure **eq-23c** was returned in the elimination step below (to give monoene **7c**) and thus could be characterized as white plates from hexane/methanol: mp 142−143 °C; ^{1}H NMR (360 MHz) δ 6.58 (s, 1), 6.57 (s, 1), 3.68 (dd, J = 11.4, 2.7 Hz, 1, H-1_{ax}), 3.25 (dd, J = 12.9, 2.7 Hz, 1, H-2_{eq}), 3.10−3.03 (m, 2, H-9_{eq},10_{eq}), 2.85 (dd, J = 12.7, 11.6 Hz, 1, H-2_{ax}), 2.57 (s, 3), 2.46−2.36 (m, 2, H-9_{ax},10_{ax}), 2.34 (s, 3), 2.33 (s, 3), 2.31 (s, 3), 2.25 (s, 3), 0.57 (s, 3), 0.56 (s, 3); ^{13}C NMR (90.6 MHz) δ 142.4, 141.9, 134.6, 134.5, 133.6, 133.5, 132.7, 131.4, 130.5, 127.9, 52.0, 37.4, 29.9, 29.6, 21.1, 19.2, 17.2, 15.7.

By subtraction of these peaks from those of the mixed isomers, the ^{1}H NMR spectrum of **ax-23c** was indicated: δ 6.65 (s, 1), 6.64 (s, 1) 4.88 (dd, J = 6.5, 1.0 Hz, H-1_{eq}), 3.40 (dd, J = 14.5, 1.4 Hz, H-2_{eq}), 3.12−3.04 (m, H-9_{eq},10_{eq}), 2.93 (dd, J = 14.7, 6.9 Hz, H-2_{ax}), 2.52 (s, 3), 2.44−2.37 (m, H-9_{ax},-10_{ax}), 2.36 (s, 3), 2.21 (s, 3), 0.79 (s, 3), 0.41 (s, 3).

Sulfonium Salts 24a−c. Dimethoxycarbonium fluoroborate (Borch reagent)[16] (0.88 g, 80% oil, 5.4 mmol) was added to a stirred solution of mixed isomers of **23a** (1.02 g, 3.6 mmol) in dichloromethane (20 mL) at −30 °C and was stirred for 4 h with warming to 20 °C. The solvent was then decanted, and ethyl acetate (10 mL) was added and stirring continued for 4 h until clean powdery solid was obtained (this step can be repeated if necessary), which was collected, 1.24 g (90%) of sulfonium salt **24a**, used directly in the elimination step below.

Likewise, from **23b** (2.48 g, 8 mmol), Borch reagent (2.0 g, 80% oil, 10 mmol), dichloromethane (25 mL), and ethyl acetate (40 mL) was obtained **24b**, 3.28 g, (99%) and from **24c** (13.5 g, 40 mmol), Borch reagent (10 g, 80% oil, 50 mmol), dichloromethane (120 mL), and ethyl acetate (60 mL) was obtained **24c**, 16.5 g, (94%).

***anti*-8,16-Dimethyl[2.2]metacyclophan-1-ene (7a).** Potassium *tert*-butoxide (0.62 g, 5.5 mmol) was added to a stirred solution of the sulfonium salts **24a** (1.10 g, 2.87 mmol) in DMF/*tert*-butyl alcohol (1:1, 26 mL) at 20 °C under N_2. After 30 min, PE (300 mL) and water were added. The organic layer was separated, washed, dried, and evaporated. The residue was preabsorbed and filtered through a short column of SiGel using PE as eluant and gave 0.62 g (92%) of monoene **7a** as white crystals from methanol−hexane: mp 148−150 °C (lit.[3] mp 151−152 °C); ^{1}H NMR (360 MHz) δ 7.00−6.95 (m, 4), 6.88−6.84 (m, 2), 6.59 (s, 2), 2.89 (*AA′*XX, $J_{AA'}$ = 2.8, J_{AX} = −12.2, $J_{AX'}$ = 3.9 Hz, 2, H-9_{eq},10_{eq}), 2.50 (AA′*XX′*, $J_{XX'}$ = 12.1 Hz, 2, H-9_{ax},10_{ax}), 0.76 (s, 6); ^{13}C NMR (90.6 MHz) δ 140.4, 138.5, 135.9, 132.1, 128.1, 125.8, 123.7, 39.2, 17.3; UV (CH_3CN) λ_{max} (ϵ_{max}) nm 212 (36 300), 255 (24 300), 307 (1980); CI MS *m*/*z* 235 (MH^+).

***anti*-5,8,13,16-Tetramethyl[2.2]metacyclophan-1-ene (7b).** From potassium *tert*-butoxide (1.6 g, 14.3 mmol), sulfonium salts **24b** (2.35 g, 5.7 mmol), and DMF/*t*-BuOH (1:1, 50 mL), exactly as described for **7a** above, there was obtained 1.08 g (72%) of monoene **7b** as white crystals from methanol: mp 151−152 °C; ^{1}H NMR (360 MHz) δ 6.77 (s, 2), 6.66 (s, 2), 6.54 (s, 2), 2.81 (*AA′*XX, $J_{AA'}$ = 2.8, J_{AX} = −12.1, $J_{AX'}$ = 3.9 Hz, 2, H-9_{eq},10_{eq}), 2.48 (AA′*XX′*, $J_{XX'}$ = 12.2 Hz, 2, H-9_{ax},10_{ax}), 2.22 (s, 6), 0.73 (s, 6); ^{13}C NMR (90.6 MHz) δ 138.4, 137.9, 135.9, 134.8, 132.1, 128.8, 124.2, 39.0, 20.6, 17.0; UV (CH_3CN) λ_{max} (ϵ_{max}) nm 214 (37,000), 260 (28,400), 301 (1,930); CI MS *m*/*z* 263 (MH^+). Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.42; H, 8.38.

***anti*-4,6,8,12,14,16-Hexamethyl[2.2]metacyclophan-1-ene (7c).** From potassium *tert*-butoxide (13.8 g, 124 mmol), sulfonium salts **24c** (27.2 g, 62 mmol), and DMF/*t*-BuOH (1:1, 400 mL), exactly as described for **7a** above, there was obtained 9.36 g (52%) of monoene **7c**, as white crystals from methanol: mp 220 °C dec; ^{1}H NMR (360 MHz) δ 6.68 (s, 2), 6.64 (s, 2), 3.06 (*AA′*XX′, $J_{AA'}$ = 4.0, J_{ax} = −13.1, $J_{AX'}$ = 3.0 Hz, 2, H-9_{eq},-10_{eq}), 2.28 (s, 6), 2.22 (s, 6) 2.17 (AA′*XX′*, $J_{XX'}$ = 12.0 Hz, 2, H-9_{ax},10_{ax}), 0.63 (s, 6); ^{13}C NMR (90.6 MHz) δ 139.5, 135.3, 133.9, 132.6, 131.5, 129.8, 129.2, 33.0, 19.16, 19.13, 17.8; UV (CH_3CN) λ_{max} (ϵ_{max}) nm 217 (44,600), 260 (29,100), ∼315 (2,-400); CI MS *m*/*z* 291 (MH^+). Anal. Calcd for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 90.91; H, 8.76.

Eluted after **7c** from the column was the equatorial isomer **eq-24c**, 5.3 g (26%), characterized above.

Reaction of the Monoene 7c with Bromine To Give Dihydropyrene 28c. A solution of Br_2 (0.1 M in dichloromethane, 10 mL) was added at −78 °C to a solution of monoene **7c** (290 mg, 1 mmol) in dichloromethane (10 mL). The solution turned dark green immediately. Water was added, and the organic layer was washed, dried and evaporated and filtered through a short column of SiGel using PE as eluant to give 280 mg (97%) of dihydropyrene **28c**, identical (TLC, NMR) to an authentic sample.[45]

^{1}H NMR of **28c** (360 MHz) δ 8.55 (s, 4), 7.79 (s, 2), 3.15 (s, 12), −4.02 (s, 6); ^{13}C NMR (90.6 MHz) δ 134.0, 128.7, 118.7, 31.7, 19.8, 14.6.

Similar results were obtained from **7a** to give **28a**[4] and from **7b** to give **28b**.[46]

When pyridinium bromide perbromide (320 mg, 1 mmol) instead of bromine was used, essentially the same amount of product **28c** was obtained.

(45) Renfroe, H. B., Gurney, J. A.; Hall, L. A. R. *J. Org. Chem.* **1972**, *20*, 3045.

Tricarbonylchromium(0) Complexes 29c and 30c of the Monoene 7c. A solution of monoene **7c** (87 mg, 0.3 mmol) and tricarbonylchromiumnaphthalene[26] (164 mg, 1 mmol) in N_2-purged ether (1 mL) and THF (0.2 mL) was stirred in a small heavy-walled screw cap vial in an oil bath at 60 °C for 20 h. The insoluble bis-complex **30c** was collected by filtration and recrystallized from hexane/dichloromethane as an orange-red solid, 111 mg (66%): mp 267−268 °C dec (sealed tube); ^{1}H NMR (250 MHz) δ 6.69 (s, 2, H-1,2), 5.06 (s, 2, H-5,13), ~3.18−3.06 (m, 2, H-9_{eq},10_{eq}), 2.23 (s, 6), ~2.22−2.11 (m, 2, H-9_{ax},10_{ax}), 2.13 (s, 6), 1.11 (s, 6); ^{13}C NMR (62.9 MHz) δ 233.8, 130.4, 115.7, 113.2, 108.4, 107.2, 98.0, 90.7, 32.5, 24.4, 19.01, 19.00; IR (KBr) 1840−90 (br), 1930−60 (br) cm^{-1}; CI MS *m*/*z* 563 (MH$^+$). Anal. Calcd for $C_{28}H_{26}Cr_2O_6$: C, 59.79; H, 4.66. Found: C, 59.57; H, 4.71.

The mother liquor was evaporated and the residue was chromatographed on SiGel under N_2 using PE/dichloromethane as eluant to give 20 mg (16%) of the monocomplex **29c** as a red solid: mp 196−198 °C; ^{1}H NMR (250 MHz) δ 6.95 (d, J = 11.3 Hz, 1), 6.72 (s, 1), 6.36 (d, J = 11.3 Hz, 1), 5.10 (s, 1), 3.20, 2.94, 2.43, 1.92 (see Table 2, H-9,10), 2.26, 2.24, 2.22, 2.10 (s, 3 each), 1.11 (s, 3), 0.49 (s, 3); ^{13}C NMR (62.9 MHz) δ 235.0, 138.9, 135.3, 134.3, 134.2, 133.2, 131.5, 130.4, 125.2, 116.8, 114.6, 107.3, 105.9, 100.5, 91.2, 33.2, 32.1, 21.1, 21.0, 19.11, 19.09, 18.90, 18.89; IR (KBr) 1860, 1870, 1945, 1955 cm^{-1}; CI MS *m*/*z* 427 (MH$^+$).

Tricarbonylchromium(0) Complexes 29a and 30a of the Monoene 7a. From monoene **7a** (70 mg, 0.3 mmol) and tricarbonylchromiumnaphthalene (130 mg, 0.8 mmol) exactly as described above for **7c** was obtained 87 mg (57%) of the orange-red bis-complex **30a**, mp >245 °C dec, and 42 mg (38%) of the red mono-complex **29a**, mp 178−179 °C. Bis-complex, **30a**: ^{1}H NMR (250 MHz) δ 6.65 (s, 2), 5.45−5.28 (m, 6), 3.03−2.92 (m, 2, H-9_{eq},10_{eq}), 2.57−2.47 (m, 2, H-9_{ax},10_{ax}), 1.20 (s, 6); ^{13}C NMR (90.6 MHz) δ 233.2, 131.8, 118.3, 97.2, 95.9, 93.0, 85.5, 37.7, 24.2; IR (KBr) 1855 (br), 1942, 1955 cm^{-1}; CI MS *m*/*z* 507 (MH$^+$). Anal. Calcd for $C_{24}H_{18}Cr_2O_6$: C, 56.92; H, 3.58. Found: C, 57.08; H, 3.53. Mono-complex, **29a**: ^{1}H NMR (360 MHz) δ 7.05−6.93 (m, 3), 6.88 (d, J = 11.1 Hz, 1), 6.35 (d, J = 11.1 Hz, 1), 5.44−5.20 (m, 3), 3.07, 2.77, 2.77, 2.19 (see Table 2, H-9,10), 1.31 (s, 3), 0.51 (s, 3); ^{13}C NMR (62.9 MHz) δ 234.4, 139.7, 137.3, 136.5, 134.6, 129.2, 126.6(×2), 125.0, 119.6, 118.0, 99.6, 94.9, 91.8, 86.5, 39.4, 37.1, 20.9, 20.5; IR (KBr) 1855 (br), 1936, 1953 cm^{-1}; CI MS *m*/*z* 371 (MH$^+$).

The Cyclopentadienyl Iron Complexes 32a−c: General Procedure. A solution of the *p*-chlorotoluene iron complex[47] **33** (176 mg, 0.45 mmol) and the monoene (0.45 mmol) in N_2-purged dichloromethane (35 mL) was irradiated using a 150 W tungsten garden flood lamp for 1.5 h, when a further portion of iron complex **33** (176 mg, 0.45 mmol) was added and irradiation continued for a further 2 h. The solvent was then evaporated, and the residue was preabsorbed and chromatographed over alumina using dichloromethane/PE/methanol (55:40:5) as eluant to give the product.

Monoene **7a** (106 mg) yielded the brown complex **32a**: 176 mg (78%); mp >265 °C dec; ^{1}H NMR (360 MHz, CD_2Cl_2) δ 7.15−7.12 (m, 3), 7.13 (d, J = ~11 Hz, 1), 7.04 (t, J = 4.8 Hz, 1, H-13), 6.66 (t, J = 6.1 Hz, 1, H-5), 6.53 (d, J = 11.1 Hz, 1), 5.96 (d, J = 6.1 Hz, 1), 5.69 (d, J = 6.1 Hz, 1), 4.77 (s, 5), 3.11, 3.00, 2.58, 2.42 (see Table 2, H-9,10), 0.92 (s, 3), 0.67 (s, 3); ^{13}C NMR (62.9 MHz, CD_2Cl_2) δ 139.7, 137.6, 134.7, 130.2, 128.1, 125.4, 124.8, 117.7, 115.2, 89.3, 85.9, 81.6, 76.7, 38.4, 37.4, 22.3, 20.9. Anal. Calcd for $C_{23}H_{23}F_6FeP$: C, 55.22; H, 4.63. Found: C, 55.03; H, 4.64.

An X-ray structure was obtained on a crystal 0.94 × 0.42 × 0.36 mm in size, which was found to be monoclinic, space group $P2_1/c$, with a = 11.636 Å, b = 12.524 Å, c = 14.681 Å, and α = γ = 90° and β = 90.69°. The structure was refined to R = 0.0689. Full details of the X-ray determination can be found in the Supporting Information.

Monoene **7b** (118 mg) yielded the brown complex **32b**: 112 mg (47%); mp >220 °C dec; ^{1}H NMR (360 MHz, CD_2Cl_2) δ 7.08 (d, J = 11.1 Hz, 1), 6.95 (s, 1), 6.84 (s, 1), 6.49 (d, J = 11.1 Hz, 1), 5.89 (s, 1), 5.61 (s, 1), 4.66 (s, 5), 3.05, 2.95, 2.54, 2.42 (see Table 2, H-9,10), 2.64 (s, 3), 2.27 (s, 3), 0.90 (s, 3), 0.62 (s, 3); ^{13}C NMR (90.6 MHz, CD_2Cl_2) δ 139.8, 137.9, 137.4, 137.0, 134.5, 131.0, 125.8, 124.5, 116.5, 114.1, 96.8, 87.5, 86.5, 82.2, 77.0, 38.2, 37.0, 22.1, 20.7, 20.4, 20.2. Anal. Calcd for $C_{25}H_{27}F_6FeP$: C, 56.84; H, 5.15. Found: C, 56.52; H, 5.36.

Monoene **7c** (130 mg) yielded the red-brown complex **32c**: 205 mg (82%); mp >250 °C (decomp.); ^{1}H NMR (360 MHz, CD_2Cl_2) δ 7.24 (d, J = 11.3 Hz, 1), 6.82 (s, 1), 6.58 (d, J = 11.3 Hz, 1), 6.47 (s, 1), 4.62 (s, 5), 3.27−3.22 (m, 1), 3.19−3.15 (m, 1), 2.38, 2.29, 2.26, 2.25 (s, 3 each), 2.20−2.16 (m, 2), 0.86 (s, 3), 0.49 (s, 3); ^{13}C NMR (62.9 MHz, CD_2Cl_2) δ 139.0, 138.2, 136.9, 134.3, 133.9, 131.8, 131.5, 123.0, 115.5, 112.5, 97.2, 94.7, 88.5, 85.5, 76.8, 32.6, 32.4, 22.5, 21.1, 19.22, 19.20, 19.1, 18.9. Anal. Calcd for $C_{27}H_{31}F_6FeP$: C, 58.29; H, 5.62. Found: C, 58.18; H, 5.69.

Reaction of Bromine with Complex 32b To Give Dibromide 34b. One drop of bromine was added to a solution of iron complex **32b** (5 mg) in CD_2Cl_2 in an NMR tube, and the spectrum was recorded after 10 min. The peaks for **32b** had then completely disappeared and were replaced by those of the dibromide **34b**: (360 MHz) δ 7.15 (s, 1), 7.04 (s, 1), 6.41 (s, 1), 6.10 (s, 1), 5.57 (d, J = 5 Hz, 1), 5.23 (d, J = 5 Hz, 1), 4.76 (s, 5), 3.14−2.64 (m, 4), 2.68 (s, 3), 2.26 (s, 3), 1.01 (s, 3), 0.92 (s, 3).

Reaction of Bromine with Complex 32c To Give Tribromide 35c. Bromine (~500 mg, 3 mmol) in dry dichloromethane (1 mL) was added to iron complex **32c** (167 mg, 0.3 mmol) in dry dichloromethane (2 mL), and the mixture was kept in the dark for 2 days. The product was collected by filtration and was dried under vacuum to yield 201 mg (94%) of **35c** as a red solid: mp >200 °C dec; ^{1}H NMR (360 MHz, CD_3CN) δ 6.45 (br s, 1), 6.39 (s, 1), 6.24 (br s, 1), 4.75 (s, 5), 3.50−3.40 (m, 1), 3.31−3.22 (m, 1), 2.65−2.54 (m, 2), 2.66, 2.64, 2.60, 2.43 (s, 3 each), 1.28 (s, 3), 0.74 (s, 3); ^{13}C NMR (90.6 MHz, CD_3NO_2) δ 143.3, 140.2, 137.2, 136.9, 130.4, 127.9, 115.1, 110.2, 101.8, 100.9, 93.1, 86.0, 79.4, 54.2, 51.1, 32.3, 30.3, 22.1, 21.9, 21.4, 21.3, 21.2, 19.8. Anal. Calcd for $C_{27}H_{30}Br_3F_6FeP$: C, 40.79; H, 3.80. Found: C, 40.84; H, 4.00.

Reaction of bromine with complex 32a was carried out in an NMR tube as for **32b** above.

The internal methyl proton and carbon signals for **32a** at δ 0.92, 0.67 and 22.3, 20.9 were replaced after 1 h by peaks at δ 1.18, 1.06, 1.00, 0.97 and 21.0, 20.9, 20.8, 20.7 corresponding to the two peaks for each of **34a** and **35a** in about equal amounts.

Reaction of the Tribromide 35c with Base. Sodium amide (100 mg, 2.6 mmol) was added to a suspension of tribromide **35c** (215 mg, 0.3 mmol) in dry THF (50 mL), and the mixture was refluxed for 30 min. After cooling, dichloromethane and water were added, and the organic layer was washed, dried, and evaporated. The residue was preabsorbed and filtered through a column of SiGel using PE/dichloromethane (4:1) as eluant and gave about 25 mg of white solid identified as the bromomonoene **36**: ^{1}H NMR (360 MHz) δ 6.69 (s, 1), 6.70 (*AB*, J = 13.9 Hz, 1), 6.67 (*AB*, 1), 3.19−3.05 (m, 2, H_{eq}), 2.48, 2.40, 2.27, 2.21 (s, 3 each), 2.31−2.12 (m, 2, H_{ax}), 0.83, 0.67 (s, 3 each); EI MS *m*/*z* 370, 368 (M$^+$, Br_1).

The same debromination occurred with NaOMe/MeOH, KOBu-*t*/HOBu-*t*/THF and DBU.

Attempted Formylation of Complex 32a. $TiCl_4$ (0.05 mL, 0.45 mmol) was added to a solution of complex **32a** (100 mg, 0.2 mmol) and Cl_2CHOCH_3 (35 mg, 0.3 mmol) in dry dichloromethane (10 mL) at 0 °C and was stirred for 3 h without further cooling. The mixture was poured on to ice−water, and more dichloromethane was added. The organic layer was washed, dried, and evaporated, and the residue was chromatographed over SiGel using PE/CH_2Cl_2/MeOH (4:5:1) as eluant and gave first unchanged starting material, 32 mg, and then 2 mg of aldehyde **37**: ^{1}H NMR (360 MHz, CD_3CN), δ 9.88 (s, 1), 7.69 (s, 1), 7.59 (s, 1), 7.19 (d, J = 11.0 Hz, 1), 6.69 (d, J = 11.0 Hz, 1), 6.64 (t, J = 6.2 Hz, 1), 6.00 (d, J = 6.2 Hz, 1), 5.75

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(d, J = 6.2 Hz, 1), 4.80 (s, 5), 3.27−3.20 (m, 1, H-10$_{eq}$) 3.05−2.98 (m, 1, H-9$_{eq}$), 2.68−2.60 (m, 1, H-10$_{ax}$), 2.48−2.40 (m, 1, H-9$_{ax}$), 0.87, 0.75 (s, 3 each).

Deuteration of Complex 29a. *n*-BuLi (0.30 mmol in hexane (0.2 mL)) was added to a solution of complex **29a** (78 mg, 0.21 mmol) in dry THF (10 mL) at −78 °C and was stirred for 1 h. D_2O (1 mL) was then added cautiously, and then the mixture was allowed to warm to 20 °C. The solvent was evaporated, and the residue was preabsorbed on neutral alumina and chromatographed under N_2 using PE/dichloromethane (3:1) as eluant to yield 68 mg (87%) of **38a**−**c** with an almost identical ^{1}H NMR spectrum to **29a**, but ^{2}D NMR (55.3 MHz) δ 6.37, 5.43, 5.24 (broad singlets, ∼0.5:4:4); in the ^{13}C NMR spectrum, the peaks at δ 118, 95, 92 and 86.5 now appeared as assymmetric doublets: CI MS m/z 372, MH$^+$ with D_1.

***tert*-Butylated cyclophane 40.** *t*-BuLi (0.11 mmol in hexane (0.1 mL)) was added to a solution of the complex **29a** (37 mg, 0.1 mmol) in dry THF (5 mL) at −78 °C. After the mixture was stirred for 1 h, $FeCl_3$/DMF (195 mg) was added, followed by ether (50 mL). The organic layer was washed, dried, and evaporated, and the residue was chromatographed on SiGel using PE as eluant to give the monoene **40**, 18 mg (62%), as an oil: ^{1}H NMR (360 MHz) δ 7.17−6.88 (m, 5), 6.61 (s, 2), 2.95−2.87 (m, 2), 2.53−2.39 (m, 2), 1.36 (s, 9), 0.76 and 0.61 (s, 3 each); CI MS m/z 291 (MH$^+$).

X-ray Structure of *anti*-9,18-Dimethyl-2,11-dithia[3,3]-metacyclophane (41). An X-ray structure was obtained on a crystal[4] 0.74 × 0.18 × 0.17 mm in size, which was found to be orthorhombic, space group *Pccn*, with a = 13.045 Å, b = 14.952 Å, c = 7.687 Å, and $\alpha = \beta = \gamma = 90°$. The structure was refined to R = 0.0657. Full details of the X-ray determination can be found in the Supporting Information.

Photoisomerization of the Monoenes 7a−c to 42a−c and Their Thermal Return. A solution of the monoene (1.2 × 10^{-4} M) in acetonitrile was degassed thoroughly with argon for 15 min and then placed in a closed UV cell. The cell was equilibrated at the desired temperature in a thermostated cell holder in the UV spectrometer and then was irradiated at 254 nm for 1−2 min. The rate of the disappearance of the dihydrophenanthrene **42a**−**c** (the thermal return reaction) was measured by continuously monitoring the absorption at ∼324−328 nm. In each case the rates were measured at five temperatures. The graphed data can be found in the Supporting Information. A summary of the rate constants obtained and thermodynamic parameters is in Table 4.

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Supporting Information Available: Full X-ray structural data for compounds **41**, **8a**, and **32a** and photoisomerization data (UV) of **7a**−**c** to **42a**−**c** and kinetic data for the thermal return reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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