CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200601629

# Intramolecular Reactions in Pseudo-Geminally Substituted [2.2]Paracyclophanes**

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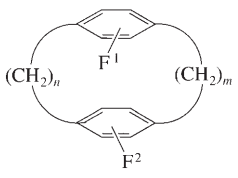
**Abstract:** A selection of pseudo-geminally substituted [2.2]paracyclophanes, the alkynes **6**, **7**, **10**, **11a**, and **11b** and the alkenes **8** and **9** were prepared for the study of intraannular reactions between functional groups in direct juxtaposition. Whereas **9** and **10** provide the corresponding cyclobutane and cyclobutene derivatives on irradiation (**12** and **13**, respectively), the bis-alkynes **7** and **11b** do not lead to a cyclobutadiene intermediate. In the latter case the "half-closed" butadiene derivative **17** was isolated. A Paterno–Büchi reaction took place on irradiation of **8** and **6**, although the oxetene intermediate **21** produced in the second example did not survive the reaction conditions (ring-opening to **22**). Bromine addition to **9**, **10**, and **7** occurred with high stereoselectivity (formation of the dibromides **27**, **30**, and **33**, respectively), and is rationalized by postulating the formation of the cationic intermediates **26**, **29**, and **32**, respectively. To study the interaction of a carbocation with a facing triple bond, the alcohol **34** was prepared from **6**. On acid treatment ring closure to the triply-bridged phane **38** took place, accompanied by the hydration of the triple bond to the ketoalcohol **37**. In an interesting intraannular [2+3]cycloaddition reaction the bisacetylene **11a**, on treatment with *n*-butyl lithium, provided the cyclopentadiene derivative **42**. That the two triple bonds of a pseudo-geminal diacetylene can engage in a cyclization reaction leading to the cyclopentadienone complex **44** was also shown by treating **11b** with iron pentacarbonyl.

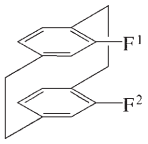
**Keywords:** cycloaddition · cyclophanes · dipolar reactions · intraannular reactions · iron

## Introduction

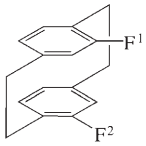
To study whether and how functional groups interact with each other, clearly one of the basic questions of organic chemistry, compounds in which these groups can be positioned at will in three-dimensional space are particularly attractive. One such system is the generalized phane molecule **1**. Here the distance between the benzene "decks" carrying the functional groups $F^1$ and $F^2$ can be adjusted both by the length of the two molecular bridges (variation of *m* and *n*), and by the relative orientation between these groups in terms of their substitution positions in the aromatic subsystems. Although there will never be a continuum of intrafunctional distances, numerous spatial arrangements of $F^1$ and $F^2$ are possible, keeping in mind that, for example, the molecular bridges of **1**—with the number of carbon atoms held constant—can be modified by introducing functionality in this part of the molecule, making the bridges more rigid,




**1**




**2**

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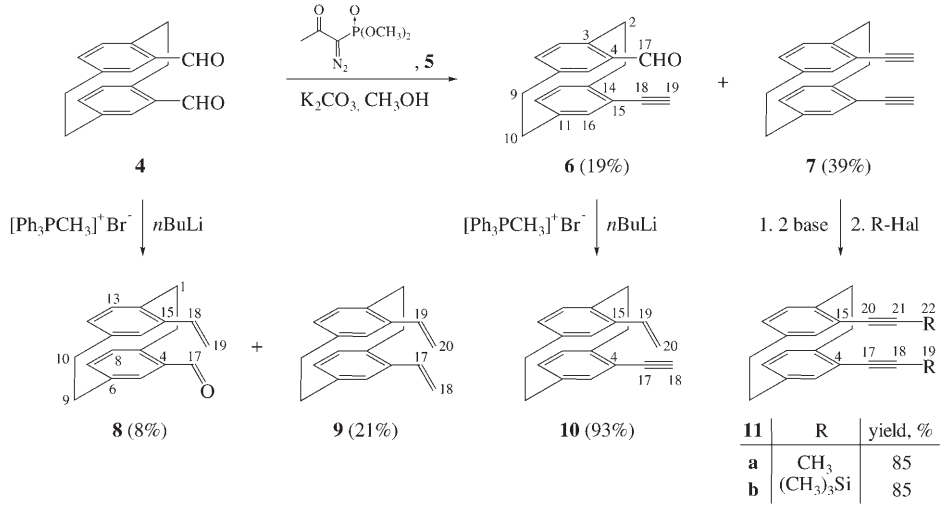
[**] Cyclophanes, LVII. For part LVI: see reference [1].

and/or by exchanging the benzene rings of **1** by other aromatic subsystems. The two bridges must not necessarily be of the same length nor the aromatic nuclei of the same type.

In this paper we concentrate on derivatives of [2.2]paracyclophane (**1**, $m=n=2$) with the two functional groups in pseudo-geminal positions, that is, directly above each other as shown in **2**. In a later contribution we will discuss the effects of shifting one of the groups by 60° into a pseudo-*ortho* orientation, **3**, while keeping the intraannular distance constant. This distance amounts to approximately 3.1 Å in [2.2]paracyclophane and hence is shorter than the separation of the layers in graphite (3.4 Å) or between the base pairs of DNA. In other words, the distance between the benzene rings of [2.2]paracyclophane and consequently of the two functional groups directly bonded to them is just slightly shorter than the length of a p orbital, an ideal prerequisite for an intraannular reaction to take place should other factors, such as excessive strain, not prevent it.

In principle cyclophanes such as **1** are thus excellent model compounds for "molecular workbenches"[2] and we have shown already that certain pseudo-geminally substituted derivatives can be used as proxies for the crystal lattice in various solid-state reactions.[3,4] For example, unsaturated ester functions bonded to the diamino derivative of **2** ($F^1=F^2=NH_2$) photodimerize in solution in the same way as cinnamic acids dimerize in the solid state on irradiation, allowing the stereospecific preparation of truxinic acid.[3] Another example of this concept is provided by the intramolecular formation of novel ladderanes on irradiation of a pseudo-geminally substituted triene ester **2** ($F^1=F^2=-(CH=CH)_3-COOCH_3$).[4,5]

In the present publication we describe additional examples of the interaction between functional groups in **2**, placing the above concept on a more general basis.




| 11 | R | yield, % |
|---|---|---|
| a | $CH_3$ | 85 |
| b | $(CH_3)_3Si$ | 85 |

Scheme 1. Preparation of various pseudo-geminally substituted [2.2]paracyclophanes.

## Results and Discussion

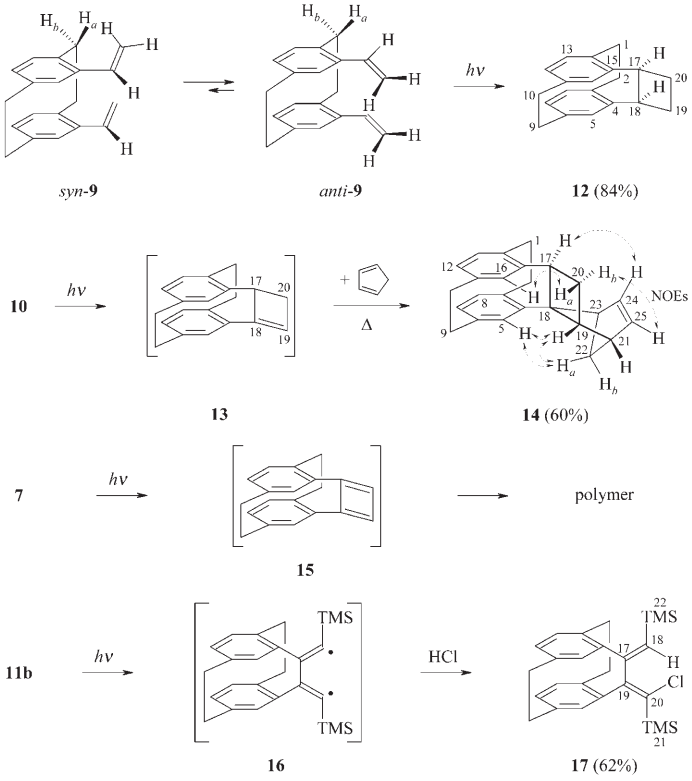
**Preparation of additional pseudo-geminally substituted [2.2]paracyclophanes 2**: In our previous studies we have described the syntheses and selected properties of several derivatives of **2** in which the functional groups $F^1$ and $F^2$ were identical: CHO, COOH, $COOCH_3$,[6] C≡N,[7] C≡CH,[8] $NH_2$,[3] SH,[9] halogen[10] and several others,[11] that is, of substrates possessing a mirror plane (*meso*-compounds). In this publication we return to the most elementary hydrocarbons as well as several unsymmetrical representatives, that is, $F^1\neq F^2$. These systems are chiral and could be of interest for example as chiral ligands with chelating groups in asymmetric synthesis.[12] The compounds prepared and studied in this publication are summarized in Scheme 1.

To obtain the monoaldehyde **8** and the diene **9** pseudo-*gem*-diformyl[2.2]paracyclophane (**4**) was treated with the ylide prepared from methyl triphenylphosphonium bromide with *n*-butyl lithium. The two compounds were obtained in 29% total yield and in about 1:3 ratio; column chromatography furnished the pure compounds, which were characterized by the usual spectroscopic and analytical methods (see Experimental Section). Since the ylide was employed in substoichiometric amounts, nearly half of the starting material **4** (42%) was isolated unchanged. Likewise, when **4** was treated with dimethyl 1-diazo-2-oxo-propylphosphonate (**5**, Bestmann–Ohira reagent)[13] a mixture of monoaldeyhde **6** (19%) and diyne **7** (39%) resulted; the reaction was accompanied by an intramolecular Cannizzaro process yielding 4-methyoxycarbonyl-15-hydroxymethyl[2.2]paracyclophane as a second major product (34%). Whereas **6** was methenylated to enyne **10** as described above for **8**/**9**, anionization of **7** with either *n*-butyl lithium or LDA in THF, followed by quenching of the resulting bis-acetylide with methyl iodide and trimethylsilyl chloride, yielded the derivatives **11a** and **11b** in 85% yield. The analytical data of these derivatives can also be found in the Experimental Section.

**Photochemical behavior of the new pseudo-geminal paracyclophane derivatives—[2+2]cycloadditions**: The first intramolecular photoaddition was carried out with the hydrocarbon **9**. In principle this diene can exist in two limiting conformations with the two vinyl substituents pointing towards the neighboring ethano bridge (*syn*-**9**) or oriented away from it (*anti*-**9**). Although the actual conformation of **9** is unknown, we prefer the latter possibility, since the steric interaction between the bridge hydrogen atom $H_a$ and an ole-

finic hydrogen atom should be smaller for the second alternative. When a solution of **9** in benzene is irradiated for 18 h either with a UV lamp used for spot detection in thin-layer chromatography or left unattended in diffuse daylight, it cyclizes quantitatively to the cyclobutane derivate **12**, which can be isolated in analytically pure form in 84% yield. Interestingly, **12** is also produced on refluxing a solution of **9** in toluene under daylight, although the yields are lower (32%). It should be noted that styrene does not undergo the corresponding [2+2]cycloaddition under the same conditions, thus demonstrating convincingly the effect of preorganization of the two reactive functional groups by the [2.2]paracyclophane spacer (Scheme 2).




Scheme 2. [2+2]Photoadditions of pseudo-geminally substituted [2.2]paracyclophanes.

A comparison of the $^{13}$C NMR spectrum of **12** with that of [2.2.2](1,2,4)cyclophane[14] is instructive. Considering the fact that C5 is a tertiary carbon in an aromatic hydrocarbon, it is rather strongly deshielded in the [2$_3$]cyclophane ($\delta =$ 139.2 ppm). The additional ethano bridge of the four-membered ring in **12** causes the chemical shift of C5 to move to $\delta = 133.7$ or 132.8 ppm, a relative shielding $\Delta\delta$ of approximately $-6$ ppm ($\gamma$-*cis* effect).[15] On the other hand, the $^{13}$C chemical shift of the *ortho*-ethano bridge (with respect to the cyclobutano moiety) in **12** ($\delta = 32.3$ ppm) is very similar to that of [2.2.2]-(1,2,4)cyclophane ($\delta = 32.9$ ppm). Both observations provide strong evidence for the configuration shown in formula **12**. As for the aromatic protons, H5 is considerably deshielded by 0.26 ppm in **12** relative to [2.2.2](1,2,4)cyclophane, whereas the chemical shifts of both H7 and H8 are affected by 0.05 ppm at the most.

We next turned our attention to the more rigid system of the enyne **10**. A solution of the hydrocarbon in dideuteriodichloromethane in a sealed NMR tube was left on a window sill for eight, mostly sunny days. After that period the starting material had been consumed completely as shown by $^1$H NMR spectra taken at regular intervals, which indicated that the *anti*-Bredt hydrocarbon intermediate **13** had been produced exclusively. Compound **13** was stable enough to allow all important 1D and 2D $^1$H and $^{13}$C NMR experiments to be performed (H,H-NOEDIF, H,H-COSY, H,C-HSQC, H,C-HMBC), and both the $^1$H and the $^{13}$C spectrum could be completely assigned and the $^1$H spectrum fully analyzed by iteration (see Experimental Section). The $^{13}$C NMR spectrum of **13** contains two remarkable chemical shifts: C18, the quaternary carbon of the cyclobutene double bond, is strongly deshielded to $\delta = 164.9$ ppm and the signal for C5, the tertiary carbon *ortho* with respect to the cyclobuteno bridge, is at $\delta = 144.5$ ppm, which means a deshielding of approximately 11 ppm compared to cyclobutano compound **12**, for which $\delta = 133.7$ or 132.8 ppm.

To estimate the strain in the *anti*-Bredt hydrocarbon **13**, we calculated its heat of hydrogenation and also that of the isomer incorporating the double bond within a C2 bridge. For comparison, the results for the two bicyclo[2.2.0]hex-1-ene isomers are also given (Table 1). These hydrocarbons may be regarded as models for **13** and its isomer with the whole [2.2]paracyclophane unit being replaced by an ethano bridge. All calculations were performed on the DFT (density functional theory) level of theory using a standard Pople basis (6–311G**) implemented in the Gaussian 03 program package.[16] The results are summarized in Table 1 and show that in the case of the more rigid bicyclo[2.2.0]hex-1-enes, the isomer with the *anti*-Bredt double bond in 1(2) position is 6.5 kcal mol$^{-1}$ less strained (lower heat of hydrogenation), than the 1(4) isomer. In the case of **13** and its isomer, both hydrocarbons show approximately the same double-bond strain. Due to its greater flexibility, the cyclophane moiety is

Table 1. Heat of hydrogenation ($H_{H2}$) and angle of olefin pyramidalization ($\Theta$) in **13** and various related hydrocarbons.

| | | | | |
|---|---|---|---|---|
| $H_{H2}$ [kcal mol$^{-1}$] | 41.81 | 41.83 | 58.84 | 65.34 |
| $\Theta$ [°] | 26.6 | 0.0 | 36.2 | 0.0 |

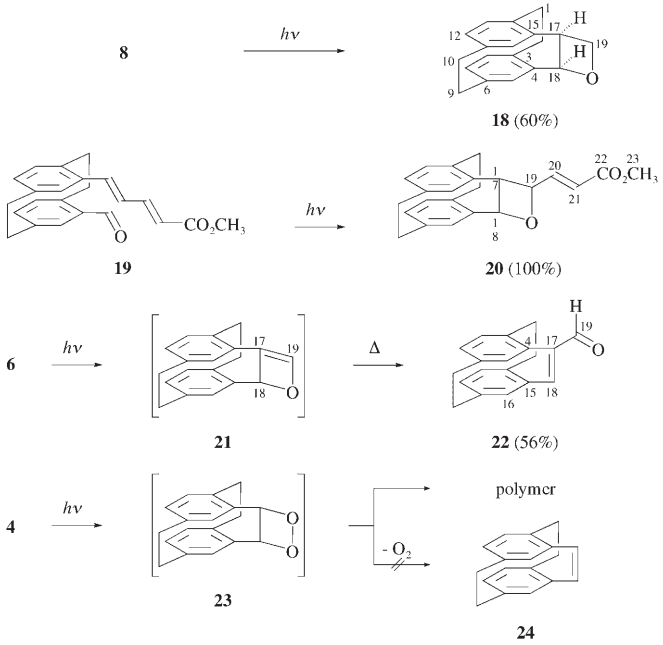
able to reduce the strain, which is also evident from the reduced degree of olefin pyramidalization.

To gain some knowledge about the chemical behavior of **13**, the NMR tube was opened and a freshly distilled sample of 1,3-cyclopentadiene was added immediately. Within a few minutes a 1:1 adduct had formed to which we assign structure **14** according to its spectral data (see Experimental Section). The regio- and stereochemistry of this Diels–Alder product followed from the complete assignment of its NMR spectra and, in particular, from the numerous nuclear Overhauser effects observed. The NOEs most relevant for the proof of structure and configuration of **14** are those within the proton pairs H5 and H19, H5 and $H22_a$, H19 and $H22_a$, H16 and $H20_a$, H17 and H24, and $H20_b$ and H25. Molecular modeling with MM2[17] indicated nonbonded distances between 2.05 and 3.07 Å within the proton pairs mentioned, the shortest ones being $d(H5\cdots H19)=2.05$ Å, which led to a very strong NOE, and $d(H16\cdots H20_a)=2.16$ Å.

If the remaining double bond in **10** is also replaced by an ethynyl function the diacetylene **7** results. When this is irradiated with light from a 150 W medium pressure mercury lamp in deuteriochloroform, solution decomposition starts within 30 min and is complete after 6 h. As revealed by NMR analysis no characteristic signals hinting to the formation of the bridged cyclobutadiene intermediate **15** can be detected. However, the basic feasibility of forming a structure related to **15** by intramolecular interaction between two parallel triple bonds is demonstrated by the bis-protected diacetylene **11b** (Scheme 2). Irradiation under the above conditions yields the stable $[2_3]$(1,2,4)paracyclophane derivative **17** in acceptable yield (61%). The structure assignment of this surprising product rests largely on extensive NMR measurements (see Experimental Section); the formation of a monochloride is revealed by the mass spectrum with a molecular ion peak at $m/z=436$ with the typical isotope pattern for $^{35}Cl/^{37}Cl$ of 75:25. We interpret this finding by postulating the initial generation of diradical **16** by formation of a single bond between two acetylenic carbon atoms. Subsequently this could stabilize itself by reaction with hydrogen chloride present in the solvent as a decomposition product or—more likely—by stepwise hydrogen abstraction from another cyclophane molecule and chlorine abstraction from the solvent. Another alternative would be the actual formation of a cyclobutadiene intermediate, followed by addition of the elements of hydrogen chloride to this reactive intermediate and subsequent electrocyclic ring-opening of the highly strained cyclobutene intermediate thus produced (see below).

Not only two unsaturated carbon–carbon bonds, but also a carbon–carbon double bond and a carbonyl group, can interact when held in proper orientation, as demonstrated by the monoaldehyde **8**, which readily undergoes a Paterno–Büchi addition when exposed to bright daylight for six days (Scheme 3).

Under these mild reaction conditions oxetane **18** is produced in 60% yield, with 20% of substrate **8** being re-isolated. The formation of the oxetane ring is reflected in the $^{13}C$ chemical shifts of the highly deshielded CH ($\delta=87.7$ ppm) and $CH_2$ ($\delta=69.6$ ppm) carbon nuclei next to the oxygen atom. The corresponding proton chemical shifts are $\delta=6.65$ ppm (H18) and $\delta=5.27$, 4.94 ppm (H19).




Scheme 3. Further [2+2]photoadditions of pseudo-geminally substituted [2.2]paracyclophanes.

Extended versions of **8**, such as the ester **19** (Scheme 3), react comparatively, providing the functionalized oxetane **20** in quantitative yield.[18]

An interesting transformation is observed when the acetylenic aldehyde **6** is irradiated for 29 h in deuteriochloroform with a medium pressure mercury lamp (150 W): the α,β-unsaturated aldehyde **22** is generated in 56% yield. Here it appears reasonable to propose the oxetene **21** as a precursor undergoing electrocyclic ring-opening. Formally this process transfers the aldehydic oxygen to the originally unsubstituted end of the triple bond. With its interesting functionality, compound **22** offers itself as a useful substrate for other cyclophane transformations.

In view of the success of the above three transformations, we had hoped to convert dialdeyde **4** into the unsaturated triply-bridged cyclophane **24**, via the bisoxetane **23**. Disappointingly, we only observed a slow decomposition of **4** to undefined material on extended irradiation with various light sources.

**Ionic additions to pseudo-geminally substituted cyclophanes**: Having shown that numerous functional groups interact with each other on photochemical (or thermal) activation when placed directly opposite each other at a distance of about 3 Å, we next investigated the behavior of pseudo-geminally substituted cyclophanes in ionic reactions, selecting bromine addition as a first test reaction.

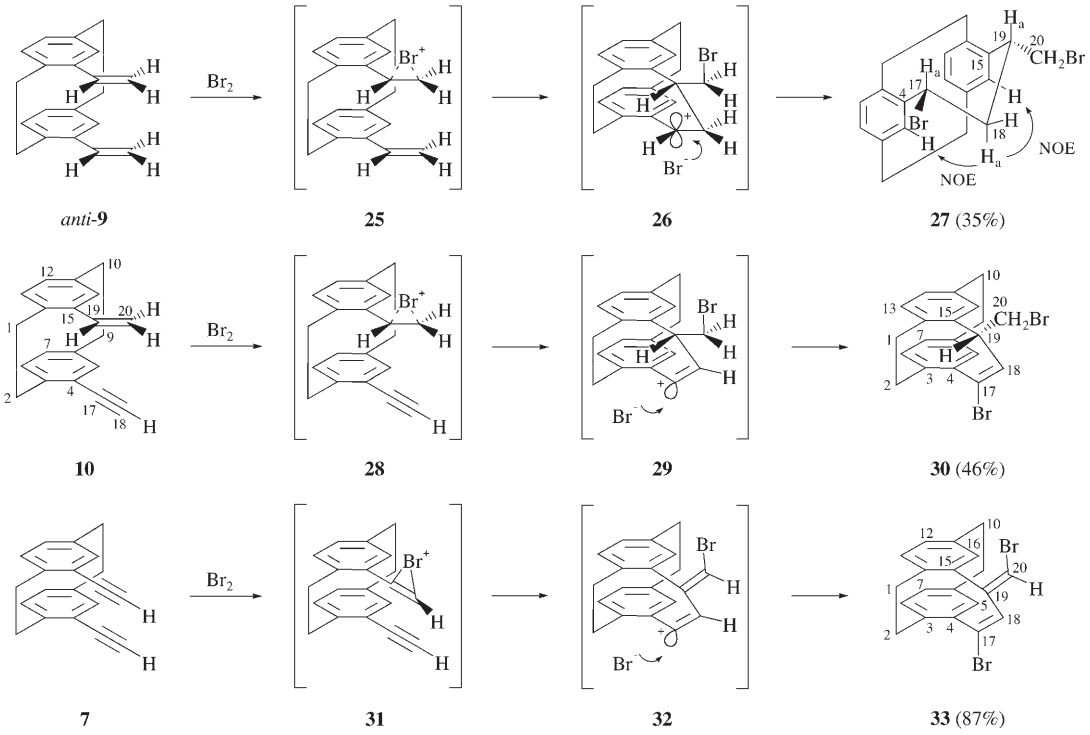
  

Addition of bromine to a dilute solution of **9** in dichloromethane at room temperature provides a single addition product in 35% yield to which we assign structure **27** on the basis of NMR studies that were carried out before the ready access to two-dimensional experiments (Scheme 4). In the reaction under discussion there are three possible modes of C–C bond formation between the two vinyl groups (α–α′, α–β′, or β–β′). That the α–β′ mode had been chosen by **9** followed from a $^{1}$H-coupled $^{13}$C NMR spectrum. For the four carbon atoms that had reacted, this spectrum showed two doublets with respective $^{1}J$(C,H) values of about 129 and 150 Hz and two triplets with $^{1}J$(C,H) ≈ 132 Hz and ≈ 154 Hz, respectively. Applying Malinowski's increment system for the prediction of $^{1}J$(C,H) in substituted methanes,[19] one estimates $^{1}J$(C,H) = 154 Hz for a CH or $CH_2$ group bound to Br and $^{1}J$(C,H) = 129 Hz for CH and $CH_2$ not bound to Br, in good agreement with the experimental values. Hence, the newly formed cyclophane bridge consists of one >CHBr, $>CH_2$, and >CH– unit each, and the >CH– unit carries a $-CH_2Br$ group as shown in structure **27**. Irradiation of one of the protons ($H_a$ in **27**; $\delta$ = 2.49 ppm) on the central methylene group induces NOEs at the *ortho*-proton of both aromatic rings. The same proton shows a quartet-like multiplicity ($J$(H,H) = 12.5 Hz) which is due to a geminal and two *anti*-vicinal couplings. These facts clearly prove that the Br and $CH_2Br$ substituents at the three-membered bridge are *cis* to each other and are pointing away from the *ortho*-ethano bridge. Furthermore the three-membered bridge prefers the chair conformation, as shown in structure **27**.

To rationalize the formation of **27** we propose that the bromonium ion **25** is produced first from the divinyl precursor, which again reacts from its *anti*-conformation (*anti*-**9**). Since one of the substituents of the bromonium ring—the benzene ring of the phane nucleus—can stabilize a positive charge better than the two hydrogen atoms at the other end, the cationic intermediate very likely will be distorted or even be "open" with the full positive charge residing on the benzylic carbon atom. In the next step, the opposing vinyl substituent compensates the positive charge by bridge formation thus generating the isomeric (benzylic) cation **26**. For steric reasons this can evidently only be attacked from the "outside" yielding the dibromide **27**.

The bromine additions to the still higher unsaturated cyclophanes **10** and **7** proceed similarly. In the enyne **10** the competition between the two unsaturated substituents is won by the vinyl group, and via **28** and **29**, the dibromide **30** is obtained as the main bromination product. It should be noted, though, that at least four isomeric dibromides are also produced from this precursor. Unfortunately, these were obtained in insufficient amounts and purity to allow full characterization.

Again, the structure elucidation of the dibromide **30** rests on a careful analysis of its 1D and 2D NMR spectra (see Experimental Section). The relative configuration of C19 followed from an H,H NOE difference experiment in which irradiation of the H19 resonance led to an enhancement of the $H1_{syn}$/$H2_{syn}$ multiplet at $\delta$ = 3.35 ppm, but not of the H16 signal at $\delta$ = 6.36 ppm. Hence, the $CH_2Br$ substituent is pointing away from the C1–C2 bridge.

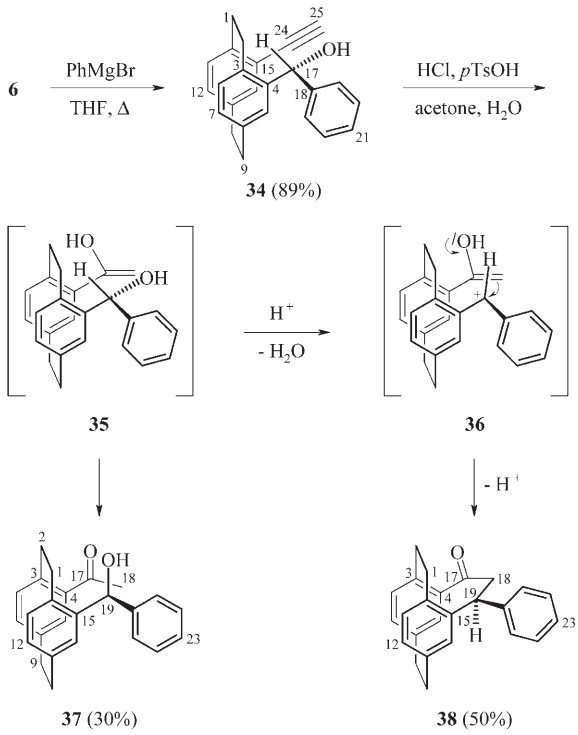



Scheme 4. Bromination of pseudo-geminally substituted [2.2]paracyclophanes.

Finally the diacetylene **7** furnished the dibromide **33** as shown by NMR analysis. The two olefinic carbon atoms carrying the bromine substituents are characterized by being relatively highly shielded ($\delta = 124.3$ and 111.5 ppm for C17 and C20, respectively). Moreover, the one-bond C,H coupling constant $^{1}J(H20,C20) = 193$ Hz is very large due to the presence of bromine at C20, compare with the value of 196 Hz for C1 in bromoethene.[20] The *exo*-orientation of this substituent follows from the mutual NOEs between H18 and H20. In accordance with the mechanisms suggested for **9** and **10** we propose that the intermediates **31** and **32** are involved in the formation of **33**. The remainder of the product mixture contains at least one isomer of **33**, possibly the one with a *syn*-arrangement of the two bromine substituents.

To answer the question whether an unsaturated substituent can also trap a classical cation if the two are held directly opposite each other, the alcohol **34**, formally a benzhydrol derivative, was prepared by treating the acetylenic aldehyde **6** with phenyl magnesium bromide. The structure of **34** was determined by the usual spectroscopic methods but also by single-crystal X-ray diffraction (Scheme 5).




Scheme 5. Interception of a carbocation by a pseudo-geminal substituent.

The molecular structure of compound **34** is shown in Figure 1 (top). The molecule as pictured is a diastereomer, with *S* configuration both in the substituted cyclophane system (according to the Cahn–Ingold–Prelog convention for planar chirality; reference plane C3–C8, pilot atom C1) and at C17; the bulk sample is an (*RR*,*SS*) racemate. The cyclophane ring system shows the usual distortions, such as the

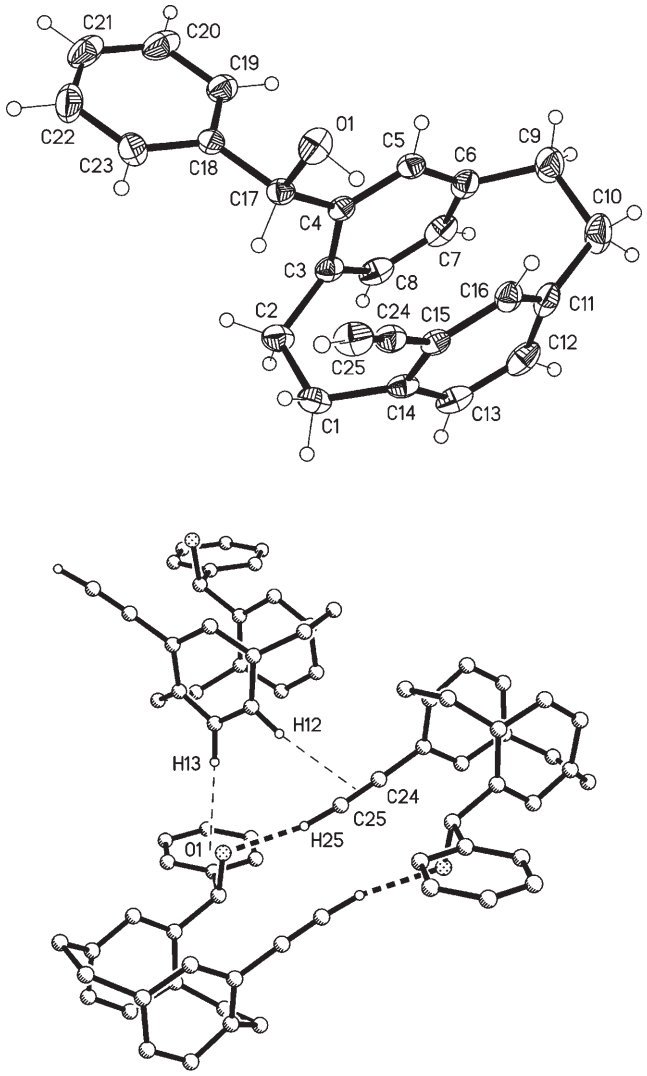



Figure 1. Top: Ellipsoid representation (50% level) of compound **34** in the crystal. Bottom: Packing diagram of compound **34** showing the weak hydrogen bonds (see text).

flattened boat shape of the rings (bridgehead atoms lie outside the planes of the other ring atoms by 0.16–0.18 Å) and the lengthened bridge bonds (details of the molecular dimensions for all structures in this paper can be consulted in the supplementary material deposited at the Cambridge Crystallographic Data Centre (see below)). The interplanar angle between the cyclophane decks is 2.4(1)°. The phenyl substituent is directed away from the phane system and the OH group points towards the triple-bond system; the hydroxy H atom is 2.65 Å from the center of the triple bond with a corresponding angle at H of 137°, so that this contact might be considered as a weak hydrogen bond (the OH group is, surprisingly, not otherwise involved in hydrogen bonding). The main feature of the molecular packing is the formation of inversion-symmetric dimers through the very short hydrogen bond from the acetylenic hydrogen H25 to the oxygen, with H···O 2.20 Å (C–H bond lengths are normalized to 1.08 Å throughout) and an angle of 169° at H25.

Additionally, the phenyl hydrogens H12 and H13 act as H bond donors in C–H···π interactions to the center of the triple bond and the centroid of the phenyl substituent respectively, with H···π 2.67, 2.71 Å and C-H···π angles 172, 171° (Figure 1, bottom). We have recently discussed the role of triple bonds as weak hydrogen-bond donors and acceptors in cyclohexanediols bearing C≡C substituents.[21]

Treatment of **34** with a mixture of hydrochloric acid and *p*-toluenesulfonic acid in aqueous acetone causes the formation of two ketones: the keto alcohol **37** and ketone **38**, in which a (functionalized) propane bridge has been generated between the two phane benzene rings. There are several ways to rationalize this result. As shown in Scheme 5, the first step could be acid-catalyzed addition of water to the triple bond of **6** and generation of the enol **35**, the tautomerization of which could lead to one of the isolated products, **37**. If, on the other hand, **35** loses the hydroxyl group of the benzhydrol moiety first, the cation **36** would result, which, after trapping by the neighboring double bond and proton loss, provides the main product **38**. This ketone would also result if **34** loses water first and the resulting benzhydryl cation is intercepted by the neighboring triple bond. The vinyl cation thus produced could react with water to furnish the ultimately isolated ketone **38**. The structure assignments for both **37** and **38** were derived again from X-ray investigations.

The molecular structure of compound **37** is shown in Figure 2 (top). The configuration shown is *R* at C19 and *S* at the cyclophane (reference plane and pilot atom as for **34**); again the material is a racemate of one diastereomer. The cyclophane geometry is essentially as expected, with an interplanar angle between decks of 2.6(1)°. The phenyl substituent is directed away from the phane ring, facilitating the formation of an intramolecular contact H19···O2 of 2.45 Å. The packing is largely determined by the classical hydrogen bond O1–H01···O2, forming pairs of molecules through the twofold axis at $0, y, 0.25$ (Figure 2, bottom). A long C8–H8···π contact to the centroid of C12,13,15,16 (2.87 Å, 148°; not shown in Figure 2) presumably plays a subordinate role.

The molecule of compound **38** is shown in Figure 3. The introduction of the third bridge between the cyclophane decks makes surprisingly little difference to the general cyclophane geometry, presumably because the bridge consists of three rather than two atoms and thus causes relatively little strain. This is confirmed by the distances between bridgehead atoms: C3···C14 2.731(2), C6···C11 2.776(2) but C4···C15 2.880(2) Å. The boat form of the rings is preserved, with the bridgehead atoms C3, C6, C11, C14 lying 0.15–0.16 Å out of the planes of the other four atoms. The angle between these planes is increased to 6.6(1)°. Again, the compound is a racemate and the molecule a diastereomer; in Figure 3, C19 is in an *S* configuration. The *R*/*S* definition for multi-bridged phane systems becomes complicated and in some cases ambiguous, and it is best simply to refer to Figure 3, but a plausible assignment would be: reference plane C3–C8, pilot atom C18, rotation C17→C4→C3 clockwise, hence *R*. The molecular packing is determined by the

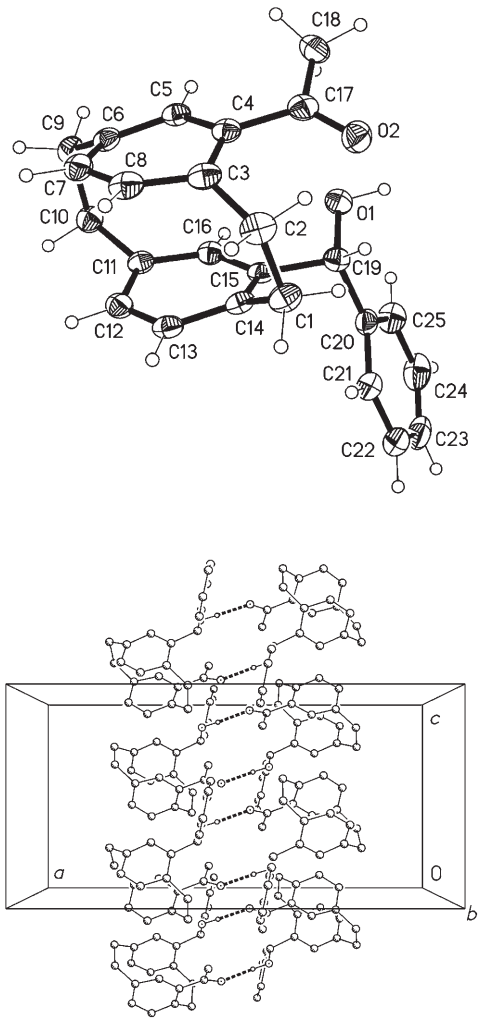



Figure 2. Top: Ellipsoid representation (50% level) of compound **37** in the crystal. Bottom: Packing diagram of compound **37** showing the classical hydrogen bonds.

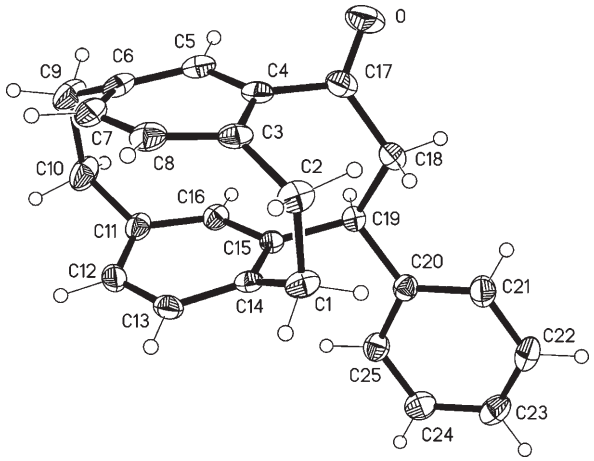



Figure 3. Ellipsoid representation (50% level) of compound **38** in the crystal.

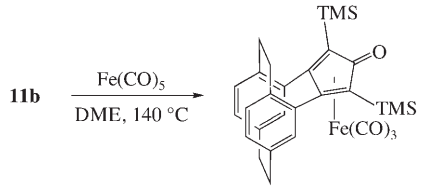
bifurcated contact to the oxygen from C12–H12 and C13–H13, by means of the *c* glide operator, forming chains of molecules parallel to the *z* axis. Relatively long C–H···π contacts from C24–H24 to C12,13,15,16 (2.82 Å, 155°) and C21–H21 to C4,5,7,8 (2.85 Å, 130°) are also observed.

After these successful experiments involving positively charged intermediates we next designed an experiment in which a carbanion is set up directly across an unsaturated substituent. The bis-propynyl derivative **11a** offered itself as a suitable precursor, since it should be deprotonated on treatment with base to provide a resonance-stabilized carbanion (Scheme 6). In fact, when **11a** is treated with *n*-butyl lithium in THF at −50 °C and the resulting dark brown solution quenched with water after 40 min, two hydrocarbon products are obtained: the cyclopentadiene **42**, formed in yield between 40 and 70%, and the allene **43**, produced as a minor side product. The rest of the product mixture is unrearranged starting material.

We believe that the initially produced carbanion **39** undergoes an intramolecular 1,3-dipolar-type cycloaddition involving the allenyl resonance structure **40** and the optimally positioned triple bond. The resulting cyclopentadiene carbanion **41** is then protonated to the main product **42**. To the best of our knowledge, cycloadditions of this type, reminiscent of an all-carbon 1,3-dipolar cycloaddition of the propargyl type, have not been reported. That the process occurs here clearly involves the special geometric arrangement of the two reaction partners. Hydrocarbon **43** is, of course, the expected isomer of a base-catalyzed propargyl rearrangement.

As the methylene protons of the cyclopentadiene moiety in **42** are anisochronic, the geminal coupling constant between them is directly visible, $^{2}J(H,H) = (-)23.15 \pm 0.02$ Hz. Its magnitude is larger than that of the corresponding coupling constant in fluorene, (−)22.5 Hz,[22] which is usually quoted in textbooks as the largest $^{1}H,^{1}H$ geminal coupling constant at an $sp^3$-hybridized carbon. However, an even larger value of (−)23.5 Hz (but not its error) was reported for 8-oxabicyclo[5.2.0]nona-1(9),3,5-triene.[23]

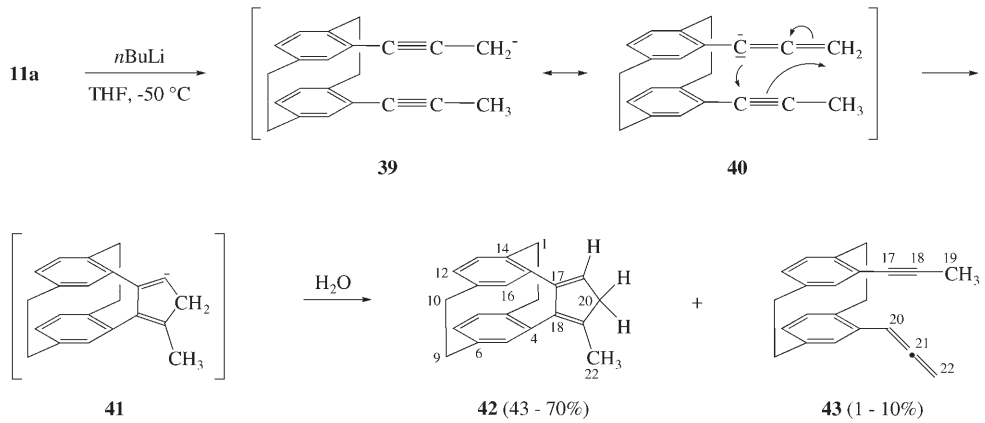
**Preparation of metal complexes from pseudo-geminally substituted [2.2]paracyclophanes**: The photochemical behavior of **11b** had already indicated that two pseudo-geminally positioned triple bonds can react with each other (see above, Scheme 2), although there is no tendency to close the second single bond and produce a cyclobutadiene derivative. Since these highly reactive intermediates have often been stabilized by metal complexation, we reasoned that a cycloaddition experiment in the presence of a metal carbonyl could yield the desired cyclobutadiene–metal complex. We therefore heated a sample of **11b** together with iron pentacarbonyl in DME at 140 °C. After 21 h intense yellow crystals were obtained in 74% yield, shown by spectroscopic (see Experimental Section) and X-ray analysis to possess the cyclopentadienone structure **44** (Scheme 7).




**44** (74%)

Scheme 7. Preparation of a metal carbonyl complex from **11b**.

The molecular structure of compound **44** is shown in Figure 4. Of the four structures presented here, molecule **44** is the only one that is achiral (it contains an approximate mirror plane); ironically, it is the only one to crystallize in a chiral space group. The "extra" bridge in the phane system consists of two atoms (rather than the three in compound **38**) and the effect on the geometry is thus more marked. The distances between bridgehead atoms are: C3···C14 2.754(2), C4···C15 2.720(2), and C6···C11 2.782(2) Å. The boat form of the parent cyclophane is, however, retained to a surprising extent, the main distortion being a much larger angle of 12.2(2)° between the planes C4,5,7,8 and C12,13,15,16.




Scheme 6. Interception of a carbanion by a pseudo-geminal substituent.

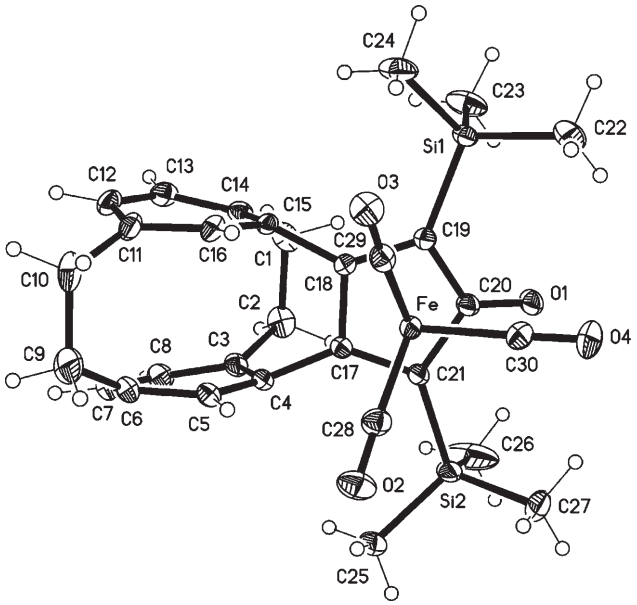



Figure 4. Ellipsoid representation (30% level) of compound **44** in the crystal.

The cyclopentadienone ring displays an envelope conformation, with the carbonyl carbon C20 lying 0.3 Å out of the plane of the other four atoms. The iron atom is coordinated principally to these four atoms, with Fe–C distances of 2.077(2), 2.070(2), 2.128(2), 2.393(2), and 2.130(2) Å to C17–C21, respectively. A search of the Cambridge Database[24] revealed 18 structures with iron bonded to cyclopentadienone; the mean Fe–C(=O) bond length was 2.38 Å and the mean distance of the carbonyl oxygen out of the plane was 0.26 Å.

There are no short contacts involving the oxygen atom. One short C–H···π contact is observed, from C23–H23C to the centroid of C12,13,15,16, with an H···π distance of 2.78 Å and an angle of 163°.

## Experimental Section

**General**: $^1$H and $^{13}$C NMR: Bruker AC-200 (200.1 and 50.3 MHz), Bruker WM-250 (250.1 and 62.9 MHz), Bruker DRX-400 (400.1 and 100.6 MHz), respectively. $CDCl_3$ was generally used as the solvent. Chemical shifts ($\delta$) are expressed in ppm to high frequency of internal tetramethylsilane. The $^{13}$C chemical shifts were referenced to the solvent peak as a secondary standard: $\delta(CDCl_3) = 77.0$ ppm). Coupling constants are given in Hz; the degree of substitution of the carbon atoms was determined by employing the DEPT-135 technique; signal assignment by 1D and 2D techniques as indicated for the individual compounds. Iterative analyses on the complete line shape were carried out by the use of the program Win-DAISY 4.05.[25] The NMR spectra of some compounds from the earlier phases of this work were not completely assigned due to the lack of appropriate facilities at the time. IR: Nicolet 320 FT-IR and Bruker Tensor 27. UV/Vis: Beckman UV 8452 A Diode Array Spectrophotometer. MS: Finnigan MAT 90 spectrometer (EI, 70 eV). Melting points: Büchi 510 melting point apparatus, uncorrected. Anhydrous THF, dichloromethane and $Et_2O$ were distilled from $CaH_2$ under nitrogen prior to use. Chromatography: TLC: Polygram Sil G/UV$_{254}$ (Macherey–Nagel): column chromatography: Silica gel 60 (70–230 mesh, Merck); preparative TLC: PLC plates Silica gel 60 $F_{254+366}$, 2 mm (Merck).

**4-Formyl-15-ethynyl[2.2]paracyclophane (6) and 4,15-diethynyl-[2.2]paracyclophane (7)**: A suspension of **4** (0.264 g, 1.0 mmol) and potassium carbonate (0.622 g, 4.5 mmol) in methanol (35 mL) was prepared and homogenized by stirring for 30 min. Compound **5** (0.5 g, 2.6 mmol) was added dropwise to this mixture, and the resulting reaction mixture was stirred for 60 h at RT. For the workup, diethyl ether (50 mL) was added and the solution washed with 5% aqueous bicarbonate solution. The aqueous phase was extracted several times with dichloromethane and the combined organic layers were dried with $MgSO_4$. The solvent was removed in vacuo and the remainder subjected to flash chromatography with dichloromethane. Fraction 1: Compound **7** (100 mg, 39%); fraction 2: Compound **6** (50 mg, 19%); fraction 3: 4-methoxycarbonyl-15-hydroxymethyl[2.2]paracyclophane (100 mg, 34%); the spectroscopic data of these products have already been reported.[8a]

**4-Formyl-15-ethenyl[2.2]paracyclophane (8) and 4,15-diethenyl-[2.2]paracyclophane (9)**: *n*-Butyl lithium in hexane (1.9 M, 1.2 mL, 2.27 mmol) was added with stirring to a mixture of methyltriphenylphosphonium bromide (1.1 g, 3.08 mmol) and anhydrous tetrahydrofuran (30 mL). The color changed to yellow-orange, and the ylide was stirred for 2 h at RT, before a solution of **4** (0.6 g, 2.27 mmol) in tetrahydrofuran (30 mL) was added with stirring. After 16 h at RT the reaction mixture was hydrolyzed at 0 °C, the organic phase was separated and the aqueous phase thoroughly extracted with dichloromethane. The combined organic phases were washed twice with water and dried with $MgSO_4$. The solvent was removed in vacuo and the remaining solid crude product separated by plate chromatography on silica gel with dichloromethane.

*Fraction 1*: Compound **9** (123 mg, 21%) was obtained as colorless needles (ethanol). M.p. 165 °C (decomp); for $^1$H- and $^{13}$C NMR data, see reference [26]; IR (KBr): $\tilde{\nu} = 3080$ (s), 3000 (s), 2920 (vs), 2890 (s), 2850 (s), 1620 (m), 1450 (w), 985 (m), 900 (vs), 720 cm$^{-1}$ (m); UV (ethanol): $\lambda_{max}$ ($\log\varepsilon$) = 223 (4.39), 253 (4.35), 287 (3.45), 322 nm (2.95); MS (70 eV): *m*/*z* (%): 260 (55) [$M^+$], 129 (100), 115 (65); HRMS: *m*/*z* calcd for $C_{20}H_{20}$: 260.1565; found 260.1565.

*Fraction 2*: Compound **8** (45 mg, 8%) was obtained as colorless microneedles (ethanol). M.p. 162 °C; $^1$H NMR (400 MHz): $\delta = 2.80$–3.19 (m, 6H; 1-, 2-, 9-, 10-H), 3.54 (m, 1H; 1-H$_s$), 4.08 (m, 1H; 2-H$_s$), 5.26 (dd, $J = 10.9$, 1.0 Hz, 1H; 19-H$_E$), 5.45 (dd, $J = 17.5$, 1.0 Hz, 1H; 19-H$_Z$), 6.51–6.58 (m, 4H; 8-, 12-, 13-, 16-H), 6.64 (dd, $J = 17.5$, 10.9 Hz, 1H; 18-H), 6.73 (dd, $J = 7.7$, 1.7 Hz, 1H; 7-H), 6.97 (d, $J = 1.9$ Hz, 1H; 5-H), 9.93 ppm (s, 1H; 17-H); $^{13}$C NMR (101 MHz): $\delta = 31.4$, 32.8 ($CH_2$, C1,2), 34.8, 34.9 ($CH_2$, C9,10), 116.0 ($CH_2$, C19), 129.1 (CH, C16), 131.8 (CH, C12), 134.3, 134.8, 135.1, 136.0, 137.9 (CH, C5,7,8,13,18), 136.1, 137.7, 138.4, 139.6, 140.1, 142.9 ($C_q$, C3,4,6,11,14,15), 191.5 ppm (CH, C17): IR (KBr): $\tilde{\nu} = 2940$ (s), 2860 (s), 2740 (m), 2720 (m), 1690 (vs), 1600 (m), 1555 (m), 1490 (w), 1240 (m), 995 (m), 910 cm$^{-1}$ (m); UV (ethanol): $\lambda_{max}$ ($\log\varepsilon$) = 218 (4.39), 259 (4.12), 300 (3.30), 333 nm (sh, 3.04); MS (70 eV): *m*/*z* (%): 262 (8) [$M^+$], 130 (36), 129 (100), 116 (31), 104 (15); HRMS: *m*/*z* calcd for $C_{19}H_{18}O$: 262.1357; found 262.1357.

*Fraction 3*: Starting material **4** (252 mg, 42%).

**4-Ethenyl-15-ethynyl[2.2]paracyclophane (10)**: *n*-Butyl lithium (1.6 M in hexane, 2.5 mL, 4.0 mmol) was added to a suspension of methyltriphenylphosphonium bromide (1.43 g, 4 mmol) in THF (20 mL) at 0 °C. The reaction mixture was stirred at RT for 2 h, cooled again to 0 °C, and a solution of **6** (260 mg, 1.0 mmol) in THF (5 mL) was added. After stirring at RT for 18 h, ice and water were added, and the product mixture was extracted several times with dichloromethane. The combined organic phases were washed with brine, dried with $MgSO_4$, the solvent was evaporated and the remainder purified by silica gel chromatography. Compound **10** (240 mg, 93%) was obtained as colorless needles. M.p. 148 °C; $^1$H NMR (200 MHz): $\delta = 2.94$–3.03 (m, 2H; $CH_2$), 3.04 (br s, 4H; $CH_2$), 3.12 (s, 1H; 18-H), 3.60–3.78 (m, 2H; $CH_2$), 5.10 (dd, $J = 10.9$, 1.5 Hz, 1H; 20-H$_E$), 5.42 (dd, $J = 17.4$, 1.5 Hz, 1H; 20-H$_Z$), 6.45–6.68 (m, 6H; 5-, 7-, 8-, 12-, 13-, 16-H), 7.15 ppm (dd, $J = 17.4$, 10.9 Hz, 1H; 19-H); $^{13}$C NMR (50 MHz): $\delta = 32.6$ ($CH_2$, C1), 33.2 ($CH_2$, C2), 34.9, 35.0 ($CH_2$, C9,10), 80.9 (CH, C18), 83.7 ($C_q$, C17), 114.6 ($CH_2$, C20), 122.4 ($C_q$, C4), 128–135 (CH, C7,8,12,13,16,19), 136.2 (CH, C5), 137.2, 139.0, 139.3, 139.4

($C_q$, C6,11,14,15), 142.3 ppm ($C_q$, C3); IR (KBr): $\tilde{\nu}$ = 3305 (s), 2955 (m), 2931 (m), 2095 (w), 1621 (m), 1587 (m), 1479 (m), 1434 (m), 896 (s), 642 $cm^{-1}$ (s); UV (EtOH): $\lambda_{max}$ ($\log\varepsilon$) = 218 (4.61), 252 (4.36), 280 nm (3.33); MS (EI): *m*/*z* (%): 258 (18) [$M^+$], 243 (21) [$M^+-CH_3$], 129 (100) [0.5 $M^+$]; HRMS (EI): *m*/*z* calcd for $C_{20}H_{18}$ : 258.1409; found 258.1400.

**Preparation of 4,15-bis(1-propynyl)[2.2]paracyclophane (11a)**: A solution of **7** (150 mg, 0.69 mmol) in THF (10 mL) was cooled to 0 °C, and *n*-butyl lithium (1 mL, 1.6 M in hexane) was added dropwise. The reaction mixture was left for 1 h at RT, $CH_3I$ (1 mL) was added and the mixture heated at 40–45 °C for 6 h. The reaction was performed under nitrogen passed through solutions of KOH/pyrogallol and $H_2SO_4$. After cooling, water and dilute HCl were added, and the mixture extracted three times with dichloromethane. The combined organic solutions were washed with $NaHCO_3$ and brine, and dried over $MgSO_4$. The solvent was removed and the residue filtered through 15 g $SiO_2$ with pentane/dichloromethane 8:2, and later 7:3, to give **11a** (142 mg, 85 %) as colorless amorphous crystals. $^1$H NMR (400 MHz): $\delta$ = 2.10 (s, 6H; $CH_3$), 2.93–3.03 (m, 6H; $CH_2$), 3.78 (m, 2H; *AA′*XX′, 1-$H_s$, 2-$H_s$), 6.42 (dd, *J* = 7.8, 1.9 Hz, 2H; 7-, 12-H), 6.47 (d, *J* = 7.8 Hz, 2H; 8-, 13-H), 6.59 ppm (d, *J* = 1.9 Hz, 2H; 5-, 16-H); $^{13}$C NMR (101 MHz): $\delta$ = 4.8 ($CH_3$, C19,22), 33.4 ($CH_2$, C1,2), 34.8 ($CH_2$, C9,10), 79.7 ($C_q$, C18,21), 88.5 ($C_q$, C17,20), 124.2 ($C_q$, C4,15), 132.2, 133.7 (CH, C7,8,12,13), 135.6 (CH, C5,16), 138.9 ($C_q$, C6,11), 141.5 ppm ($C_q$, C3,14); IR (diamond-ATR): $\tilde{\nu}$ = 3285 (w), 2919 (m), 2847 (m), 2225 (w), 1900 (w), 1587 (w), 1479 (m), 1448 (m), 1431 (m), 1406 (m), 906 (m), 876 (m), 836 (m), 725 $cm^{-1}$ (s); UV (ethanol): $\lambda_{max}$ ($\log\varepsilon$) = 228 (4.25), 252 nm (4.38); MS (EI): *m*/*z* (%): 284 (18) [$M^+$], 269 (65), 255 (24), 142 (100); HRMS (EI): *m*/*z* calcd for $C_{22}H_{20}$: 284.1565; found: 284.1563.

**4,15-Bis(trimethylsilylethynyl)[2.2]paracyclophane (11b)**: *n*-Butyl lithium (0.77 mL, 1.2 mmol, 1.6 M in hexane) was added in one portion to a solution of diisopropylamine (141 mg, 1.38 mmol, 0.2 mL) in anhydrous THF (6 mL) at −30 °C. The reaction mixture was stirred for 30 min at −30 °C and subsequently for 1 h at RT. After re-cooling to −40 °C **7** (130 mg, 0.40 mmol) in THF (6 mL) was slowly added at this temperature. After warming to 0 °C trimethylsilyl chloride (129 mg, 1.2 mmol, 0.15 mL) in THF (0.5 mL) was added, and the mixture stirred overnight while the reaction temperature increased to RT. After hydrolysis and careful extraction of the aqueous phase with dichloromethane, the organic phases were combined and dried ($MgSO_4$), and the solvent was removed in vacuo. The raw product was purified by flash chromatography on silica gel with pentane, yielding **11b** (136 mg, 85 %) as a colorless microcrystalline solid. M.p. 136 °C; $^1$H NMR (400 MHz): $\delta$ = 0.24 (s, 18H; 19-, 22-H), 2.96–3.04 (m, 6H; 1-$H_a$, 2-$H_a$, 9-, 10-H), 3.76–3.80 (m, 1-$H_s$; 2-$H_s$), 6.48 (dd, *J* = 7.8, 1.7 Hz, 2H; 7-, 12-H), 6.51 (d, *J* = 7.8 Hz, 2H; 8-, 13-H), 6.64 ppm (d, *J* = 1.7 Hz, 2H; 5-, 16-H); $^{13}$C NMR (101 MHz): $\delta$ = 0.2 (q, C19,22), 33.5 (t, C1,2), 34.7 (t, C9,10), 97.4 (s, C18,21), 105.1 (s, C17,20), 123.4 (s, C4,15), 133.0 (d, C7,12), 133.8 (d, C8,13), 135.3 (d, C5,16), 138.8 (s, C6,11), 141.9 ppm (s, C3,14); IR (KBr): $\tilde{\nu}$ = 2957 (m), 2140 (m), 1477 (w), 1403 (w), 1247 (m), 899 (m), 869 (s), 840 $cm^{-1}$ (vs); UV (acetonitrile): $\lambda_{max}$ ($\log\varepsilon$) = 220 (4.70), 256 (4.42), 264 nm (4.44); MS (70 eV): *m*/*z* (%): 400 (31) [$M^+$], 385 (10), 327 (12), 312 (20), 297 (18), 200 (100), 185 (80); elemental analysis calcd (%) for $C_{26}H_{32}Si_2$ (400.71): C 77.93, H 8.05; found: C 77.99, H 8.06.

**Photoaddition to 4,15-diethenyl[2.2]paracyclophane (9)**: A solution of **9** (25 mg, 0.096 mmol) in perdeuteriobenzene (0.3 mL) was irradiated for 18 h with a UV-lamp used for spot detection in plate chromatography (wavelengths 254 and 366 nm). The solvent was removed in vacuo and the remaining solid sublimed at 165 °C at $10^{-3}$ torr. Compound **12** (21 mg, 84 %) was obtained as colorless plates. M.p. 219 °C; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 2.42–2.61, 2.95–3.20 (m, 6H each; 1-, 2-, 9-, 10-, 19-, 20-H), 4.50 (m, 2H; 17-, 18-H), 6.19 (d, *J* = 8 Hz, 2H; 8-, 13-H), 6.36 (d, *J* = 1.5 Hz, 2H; 5-, 16-H), 6.46 ppm (dd, *J* = 8, 1.5 Hz, 2H; 7-, 12-H); $^{13}$C NMR (63 MHz): $\delta$ = 19.0 ($CH_2$, C19,20), 32.3 ($CH_2$, C1,2), 36.2 ($CH_2$, C9,10), 45.7 (CH, C17,18), 128.2 (CH, C7,12), 132.8, 133.7 (CH, C5,16, C8,13), 139.0, 139.7, 140.6 ppm ($C_q$, C3,14, C4,15, C6,11); assignments by comparison with the assigned spectra of [2.2.2](1,2,4)cyclophane;[14] IR (KBr): $\tilde{\nu}$ = (m), 2970 (s), 2930 (vs), 2860 (s), 1485 (m), 1410 (m), 915 (m), 800 (w), 730 $cm^{-1}$ (m); UV (EtOH): $\lambda_{max}$ ($\log\varepsilon$) = 209 (4.20), 226 (4.16), 290 nm (2.85); MS (70 eV): *m*/*z* (%): 260 (61) [$M^+$], 129 (100), 115 (62); elemental analysis calcd (%) for $C_{20}H_{20}$ (260.36): C 92.26, H 7.74; found: C 92.13, H 7.87.

When the intramolecular cycloaddition was carried out by heating a solution of **9** in toluene (reflux, 72 h) the cyclobutane derivative **12** was produced in 32 % yield.[27]

**Photochemical reaction of 4-ethenyl-15-ethynyl[2.2]paracyclophane (10)**: A solution of **10** (15 mg, 0.058 mmol) in $CD_2Cl_2$ (0.75 mL) was placed in an NMR tube, which was sealed after several freeze–pump–thaw cycles. The reaction solution was left on a window sill (South side) and the progress of the photoaddition monitored by NMR spectroscopy. After eight days the cyclobutene product **13** was formed exclusively. $^1$H NMR (400 MHz): $\delta$ = 2.49 (ddd, *J*(1a,1s) = −13.8 Hz, *J*(1a,2a) = 10.5 Hz, *J*(1a,2s) = 7.4 Hz, 1H; 1-$H_a$), 2.61 (ddd, *J*(9a,9s) = −13.6 Hz, *J*(9a,10a) = 9.9 Hz, *J*(9a,10s) = 7.5 Hz, 1H; 9-$H_a$), 2.69 (m, *J*(2a,2s) = −13.2 Hz, 1H; 2-$H_a$), 2.72 (m, *J*(9s,10s) = 10.2, *J*(10a,10s) = −13.2 Hz, 1H; 10-$H_s$), 2.87 (dt, *J*(17,20n) = 1.6 Hz, *J*(19,20n) ≈ 2 Hz, *J*(20n,20x) = −14.1 Hz, 1H; 20-$H_n$), 3.04 (dd, *J*(17,20x) = 4.4, *J*(20n,20x) = −14.1 Hz, 1H; 20-$H_x$), 3.13 (m, *J*(9s,10a) ≈ 0 Hz, 1H; 9-$H_s$), 3.14 (m, 1H; 2-$H_s$), 3.17 (m, 1H; 10-$H_a$), 3.35 (br ddd, *J*(1a,1s) = −13.8 Hz, *J*(1s,2a) ≈ 0 Hz, *J*(1s,2s) = 9.9 Hz, 1H; 1-$H_s$), 4.60 (m, 1H; 17-H), 5.94 (d, *J*(5,7) = 2.0 Hz, 1H; 5-H), 6.02 (d, *J*(12,16) = 1.9 Hz, 1H; 16-H), ≈6.02 (hidden, 1H; 19-H), 6.28 ppm (d, *J*(7,8) = 7.9 Hz; 1H; 8-H), 6.28 (d, *J*(12,13) = 8.0 Hz, 1H; 13-H), 6.43 (dd, *J*(12,13) = 8.0 Hz, 1H; *J*(12,16) = 1.9 Hz, 1H; 12-H), 6.51 ppm (dd, *J*(5,7) = 2.0 Hz, *J*(7,8) = 7.9 Hz, 1H; 7-H); $^{13}$C NMR (101 MHz): $\delta$ = 31.3 ($CH_2$, C20), 32.5 ($CH_2$, C2), 35.6 ($CH_2$, C9), 36.0 ($CH_2$, C1), 36.3 ($CH_2$, C10), 54.4 (CH, C17), 122.8 (CH, C19), 127.6 (CH, C12), 131.8 (CH, C7), 132.4 (CH, C8), 132.8 (CH, C16), 134.9 (CH, C13), 136.1 ($C_q$, C4), 140.0 ($C_q$, C14), 140.1 ($C_q$, C3), 140.4 ($C_q$, C6), 140.9 ($C_q$, C11), 141.1 ($C_q$, C15), 144.5 (CH, C5), 164.9 ppm ($C_q$, C18); assignment techniques used: iterative analysis, DEPT-135, H,H-COSY, H,C-HSQC, H,C-HMBC, H,H-NOEDIF (17-H → 1-$H_s$, 2-$H_s$, 20-$H_x$; 7-H → 9-$H_a$).

**Interception of 13 by cyclopentadiene**: The sealed NMR tube was opened and immediately a few drops of freshly distilled cyclopentadiene were added. After several min the mixture was subjected to chromatography on silica gel (20 g). Elution with pentane/$CH_2Cl_2$ (94:6) gave cyclopentadiene adduct **14** (10 mg, 60 %) as colorless crystals. M.p. 132–133 °C; $^1$H NMR (400 MHz): $\delta$ = 1.22 (dt, *J*(22a,22b) = −8.5, *J*(21,22a) ≈ 1.6, *J*(22a,23) ≈ 1.6 Hz, 1H; 22-$H_a$), 1.62 (ddd, *J*(20a,20b) = −13.5, *J*(17,20b) = 9.4, *J*(19,20b) = 5.7 Hz, 1H; 20-$H_b$), 1.68 (dt, *J*(22a,22b) = −8.5, *J*(21,22b) ≈ 1.7, *J*(22b,23) ≈ 1.7 Hz, 1H; 22-$H_b$), 2.17 (ddd, *J*(20a,20b) = −13.4, *J*(19,20a) = 9.5, *J*(17,20a) = 5.1 Hz, 1H; 20-$H_a$), 2.58, 2.65 (m, 1H each; 1-, 2-H), 2.94–3.05 (m, 3H; 9-, 10-, 21-H), 3.05–3.20 (m, 3H; 1-, 9-, 10-H), 3.27 (ddd, *J*(19,20a) = 9.5, *J*(19,20b) = 5.7, *J*(19,21) = 4.7 Hz, 1H; 19-H), 3.52 (m, 1H; 17-H), 3.54 (m, 1H; 23-H), 3.56 (m, 1H; 2-H), 6.21 (d, *J*(7,8) = 8.3 Hz, 1H; 8-H), 6.25 (d, *J*(12,13) = 8.2 Hz, 1H; 13-H), 6.394 (dd, *J*(5,7) = 2.0, *J*(7,8) = 8.3 Hz, 1H; 7-H), 6.397 (d, *J*(5,7) = 2.0 Hz, 1H; 5-H), 6.429 (dd, *J*(12,13) = 8.2, *J*(12,16) = 1.9 Hz, 1H; 12-H), 6.431 (d, *J*(12,16) = 1.9 Hz, 1H; 16-H), 6.66 (br dd, *J*(24,25) = 5.7, *J*(21,25) = 3.0 Hz, 1H; 25-H), 6.89 ppm (br dd, *J*(24,25) = 5.7, *J*(23,24) = 3.2 Hz, 1H; 24-H); $^{13}$C NMR (101 MHz): $\delta$ = 22.0 ($CH_2$, C20), 32.4 ($CH_2$, C1), 33.4 ($CH_2$, C2), 36.17 ($CH_2$, C9), 36.21 ($CH_2$, C10), 40.7 (CH, C19), 45.6 (CH, C21), 46.0 (CH, C17), 51.5 ($CH_2$, C22), 52.5 (CH, C23), 65.6 (Cq, C18), 128.4 (CH, C12), 128.7 (CH, C7), 132.0 (CH, C13), 135.3 (CH, C8), 135.59 (CH, C16), 135.63 (CH, C24), 137.2 (CH, C5), 138.4 (CH, C25), 139.0 ($C_q$, C3), 139.5 ($C_q$, C11), 140.2 ($C_q$, C6), 140.3 ($C_q$, C14), 143.0 ($C_q$, C15), 143.8 ppm ($C_q$, C4); assignment methods used: DEPT-135, H,H-DQF-COSY, NOEDIF, homodecoupling, H,C-HSQC, H,C-HMBC; IR (KBr): $\tilde{\nu}$ = 2967 (s), 2967 (s), 1589 (w), 1486 (m), 1463 (m), 1445 (m), 1410 (m), 745 (s), 730 $cm^{-1}$ (s); MS (EI): *m*/*z* (%): 324 (50) [$M^+$], 258 (75) [$M^+-C_5H_6$], 193 (100); HRMS (EI): *m*/*z* calcd for $C_{25}H_{24}$: 324.1878; found: 324.1865.

**Irradiation of 4,15-diethynyl[2.2]paracyclophane (7)**: A solution of **7** (15.0 mg, 0.06 mmol) in deuteriochloroform (0.8 mL) was irradiated in a quartz NMR tube for 1.5 h with a medium pressure mercury lamp (Original Hanau, TQ 150). As shown by TLC and NMR analysis, the starting material was by then consumed completely. However, only polymeric de-

composition products were formed, and no defined photoadduct(s) could be isolated.

**Irradiation of 4,15-bis(trimethylsilyl-ethynyl)[2.2]paracyclophane (11b)**: In a quartz NMR tube a solution of **11b** (12.0 mg, 0.03 mmol) in deuteriochloroform (0.8 mL) was irradiated for 2.5 h with a medium pressure mercury lamp, the photoaddition being monitored by TLC and NMR control. The solvent was removed and the solid residue purified by plate chromatography (silica gel, pentane). Compound **17** (8.0 mg, 62%) was obtained as colorless crystals. M.p. 104–106°C; $^1$H NMR (400 MHz): $\delta = -0.32$, 0.06 (s, 9H each; 21-, 22-H), 2.76–2.90 (m, 2H; $CH_2$), 2.98–3.21 (m, 6H; $CH_2$), 6.12 (d, $J = 1.7$ Hz, 1H; 5- or 16-H), 6.28 (dd, $J = 7.8$, 1.9 Hz, 1H; 7- or 12-H), 6.34 (dd, $J = 7.5$, 1.8 Hz, 1H; 12- or 7-H), 6.36 (d, $J = 7.8$ Hz, 1H; 8- or 13-H), 6.41 (m, 2H; 13- or 8-H, 16- or 5-H), 6.71 ppm (s, 1H; 18-H); $^{13}$C NMR (101 MHz): $\delta = -0.5$, 0.0 ($CH_3$, C21,22), 32.6, 34.4, 34.9, 35.3 ($CH_2$, C1,2,9,10), 130.4, 132.8, 133.1, 133.6, 133.9, 135.2, 137.6 (CH, C5,7,8,12,13,16,18), 135.5, 139.1, 139.5, 139.7, 141.0, 143.4, 147.3 (2 C), 151.9 ppm ($C_q$, C3,4,6,11,14,15,17,19,20); IR (KBr): $\tilde{\nu} = 2953$ (m), 1533 (w), 1248 (s), 858 (vs), 848 (vs), 839 cm$^{-1}$ (vs); UV (acetonitrile): $\lambda_{max}$ ($\log\varepsilon$) = 228 (4.25), 266 nm (4.16); MS (70 eV): *m/z* (%): 436 (52) [$M^+$], 421 (17), 401 (4), 328 (60), 313 (37), 255 (40), 73 (100); HRMS: *m/z* calcd for $C_{26}H_{33}Si_2Cl$: 436.1803; found:436.1806.

**Irradiation of 4-formyl-15-ethenyl[2.2]paracyclophane (8)**: In a 25 mL round-bottom flask a solution of **8** (25 mg, 0.095 mmol) in anhydrous dichloromethane (10 mL) was subjected to sunlight for six days at RT (window sill). The solvent was removed in vacuo and the remaining photolysate purified by plate chromatography on silica gel with dichloromethane. Fraction 1: starting material **8** (5 mg, 20%). Fraction 2: Oxetane **18** (15 mg, 60%), colorless microcrystalline needles (dichloromethane), m.p. 172°C; $^1$H NMR (400 MHz): $\delta = 2.54$–2.67 (m, 2H), 2.84–3.30 (m, 6H; 1-, 2-, 9-, 10-H), 4.70 (td, $J = 7.5$, 7.5, 4 Hz, 1H; 17-H), 4.94 (dd, $J = 7.5$, 4 Hz, 1H; 19-H), 5.27 (t, $J = 7.5$ Hz, 1H; 19-H′), 6.19 (d, $J = 7.8$ Hz, 1H; 13-H), 6.25 (d, $J = 7.8$ Hz, 1H; 8-H), 6.50 (dd, $J = 7.8$, 1.9 Hz, 1H; 12-H), 6.54 (dd, $J = 7.8$, 1.7 Hz, 1H; 7-H), 6.62 (d, $J = 1.7$ Hz, 1H; 5-H), 6.65 (d, $J = 7.5$ Hz, 1H; 18-H), 6.75 ppm (d, $J = 1.9$ Hz, 1H; 16-H); $^{13}$C NMR (101 MHz): 30.5, 32.5 ($CH_2$, C1,2), 36.2, 36.4 ($CH_2$, C9,10), 46.2 (CH, C17), 69.6 ($CH_2$, C19), 87.7 (CH, C18), 129.4, 129.8 (CH, C7,12), 132.7, 133.6, 133.95, 134.04 (CH, C5,8,13,16), 135.8, 137.1, 139.54, 139.62, 140.3, 140.6 ppm ($C_q$, C3,4,6,11,14,15); assignments by DEPT-135, H,H-COSY and by comparison with **12**; IR (KBr): $\tilde{\nu} = 2960$ (s), 2920 (s), 2890 (s), 2850 (s), 1490 (w), 1445 (w), 1415 (w), 990 (m), 970 (m), 955 cm$^{-1}$ (w); UV (ethanol): $\lambda_{max}$ ($\log\varepsilon$) = 215 (sh, 4.10), 226 (4.14), 292 nm (2.70); HRMS: *m/z* calcd for $C_{19}H_{18}O$: 262.1357; found: 262.1357.

**Irradiation of 4-formyl-15-(4-methoxycarbonylbuta-1(*E*),3(*E*)-dienyl)-[2.2]paracylophane (19)**: A solution of **19** (50 mg, 0.14 mmol; prepared from **4** by a Wittig–Horner reaction with methyl dimethylphosphonocrotonate in THF with sodium hydride as base) in ethanol (150 mL) was irradiated with a 150 W mercury high pressure lamp in a Pyrex immersion well photoreactor for 30 min under nitrogen. The solvent was removed in vacuo leaving the oxetane **20** in quantitative yield (50 mg). Colorless plates (dichloromethane); m.p. 163°C; $^1$H NMR (400 MHz): $\delta = 2.52$–2.65 (m, 2H; $CH_2$), 2.78–2.89 (m, 1H; $CH_2$), 2.96–3.28 (m, 5H; $CH_2$), 3.83 (s, 3H; 23-H), 4.39 (dd, $J = 7.4$, 4.7 Hz, 1H; 17-H), 5.58 (m, 1H; 19-H), 6.18 (d, $J = 7.8$ Hz, 1H; 8- or 13-H), 6.25 (d, $J = 7.7$ Hz, 1H; 13- or 8-H), 6.49–6.56 (m, 5H; 5- or 16-, 7-, 12-, 18-, 21-H), 6.77 (d, $J = 1.7$ Hz, 1H; 16- or 5-H), 7.37 ppm (dd, $J(20,21) = 15.6$, $J(19,20) = 3.9$ Hz, 1H; 20-H); $^{13}$C NMR (101 MHz): $\delta = 30.4$, 32.3 ($CH_2$, C1,2), 36.1, 36.3 ($CH_2$, C9,10), 51.6 ($CH_3$, C23), 51.8 (CH, C17), 77.7 (CH, C19), 84.6 (CH, C18), 120.4, 129.7, 130.0, 132.9, 133.6, 134.4, (CH, C5,7,8,12,13,16), 135.95, 135.97, 139.0, 139.5, 140.4, 140.6 ($C_q$, C3,4,6,11,14,15), 147.6 (CH, C20), 166.86 ppm ($C_q$, C22); IR (FT-IR, KBr): $\tilde{\nu} = 3005$ (w), 2954 (m), 2929 (s), 2851 (w), 1714 (vs), 1648 (w), 1311 (m), 1269 (vs), 1170 (s), 1041 (m), 986 cm$^{-1}$ (s); UV (acetonitrile): $\lambda_{max}$ ($\log\varepsilon$) = 200 (4.73), 224 nm (sh, 4.36); MS (70 eV): *m/z* (%) = 346 (10) [$M^+$], 314 (40), 286 (36), 213 (65), 181 (100); elemental analysis calcd (%) for $C_{23}H_{22}O_3$ (346.45): C 79.73, H 6.41; found: C 79.86, H 6.65.

**Irradiation of 4-formyl-15-ethynyl[2.2]paracyclophane (6)**: In a quartz NMR tube a solution of **6** (16.0 mg 0.06 mmol) in deuteriochloroform (0.8 mL) was irradiated with a medium pressure mercury lamp (Original Hanau TQ 150). The progress of the reaction was monitored by TLC and NMR analysis and after 29 h the solvent was removed and the raw product purified by column chromatography on silica gel with dichloromethane/pentane = 4:1 (v/v) to give **22** (9.0 mg, 56%) as a colorless solid. M.p. 183°C; $^1$H NMR (400 MHz): $\delta = 2.62$–2.70 (m, 2H; $CH_2$), 2.84–3.09 (m, 6H; $CH_2$), 6.18, 6.19 (s, 1H each; 5-, 16-H), 6.36–6.39 (m, 2H; 8-, 13-H), 6.45–6.47 (m, 2H; 7-, 12-H), 8.14 (s, 1H; 18-H), 9.98 ppm (s, 1H; 19-H); $^{13}$C NMR (101 MHz): $\delta = 33.3$, 33.6 ($CH_2$, C1,2), 35.0 ($CH_2$, 2 C, C9,10), 131.3, 131.6, 133.4 (2 C), 135.9, 136.2, 139.2 (CH, C5,7,8,12,13,16,18), 137.5, 139.3, 139.4, 139.9, 140.2, 140.8, 154.0 ($C_q$, C3,4,6,11,14,15,17), 189.9 ppm (CH, C19); IR (KBr): $\tilde{\nu} = 3037$ (w), 2923 (m), 1683 (vs), 1669 (s), 1553 (m), 1400 (m), 844 cm$^{-1}$ (m); UV (acetonitrile): $\lambda_{max}$ ($\log\varepsilon$) = 194 (4.62), 222 (sh, 4.34), 246 nm (sh, 3.88); MS (70 eV): *m/z* (%): 260 (100) [$M^+$], 245 (18), 232 (38), 217 (39), 202 (33); elemental analysis calcd (%) for $C_{19}H_{16}O$: C 87.66, H 6.19; found: C 87.56, H 6.12.

**Irradiation of 4,15-diformy[2.2]paracyclophane (4)**: A solution of (20.0 mg, 0.086 mmol) of **4** in toluene (10.0 mL) was irradiated in a quartz photoreactor for 1 h with a medium pressure mercury lamp (Original Hanau, TQ 150). As shown by TLC and NMR analysis the starting material was by then consumed completely. However, only oligo- or polymeric decomposition products were formed; no defined photoadduct(s) could be isolated.

**Bromination of 4,15-diethenyl[2.2]paracyclophane (9)**: To a solution of **9** (50 mg, 0.19 mmol) in anhydrous dichloromethane (40 mL) was added under vigorous stirring a 0.04 M solution of bromine in dichloromethane until the brown color persisted. After stirring for 16 h at RT, the solvent was removed in vacuo and the remaining solid was purified by silica gel thick-layer chromatography with dichloromethane to give **27** (30 mg, 35%) as colorless needles (ethanol/dichloromethane). M.p. 162°C; $^1$H NMR (400 MHz): $\delta = 2.49$ (q, $J(18a,18e) = J(17,18a) = J(18a,19) = 12.5$ Hz, 1H; 18-$H_a$), 2.88–3.34 (m, 11H; 1-, 2-, 9-, 10-H, 18-$H_e$, 19-H, 20-H′), 3.41 (dd, $J(20',20'') = 10.0$ Hz, $J(19,20'') = 8.5$ Hz, 1H; 20-H″), 5.30 (dd, $J(17,18a) = 12.5$ Hz, $J(17,18e) = 3.8$ Hz, 1H; 17-H), 6.31 (d, $J(5,7) = 1.8$ Hz, 1H; 16-H), 6.35 (m, 2H; 7-, 8-H), 6.39 (dd, $J(12,13) = 7.9$ Hz, $J(12,16) = 1.8$ Hz, 1H; 12-H), 6.44 (d, $J(12,13) = 7.9$ Hz, 1H; 13-H), 6.79 ppm (brs, 1H; 5-H); $^{13}$C NMR (101 MHz): $\delta = 32.1$, 32.8 ($CH_2$, C1,2), 35.5, 35.6 ($CH_2$, C9,10), 36.8 ($CH_2$, C20), 43.0 (CH, C19), 44.4 ($CH_2$, C18), 48.3 (CH, C17), 131.5, 131.7, 132.9, 133.8, 134.1, 134.8 (CH, C5,7,8,12,13,16), 136.4, 138.4, 138.8, 139.7, 141.0, 141.2 ppm ($C_q$, C3,4,6,11,14,15); IR (KBr): $\tilde{\nu} = 2960$ (s), 2925 (vs), 2875 (s), 2855 (s), 1450 (m), 1230 (m), 100 (w), 990 (w), 905 cm$^{-1}$ (w); UV (EtOH): $\lambda_{max}$ ($\log\varepsilon$) = 212 (4.21), 220 (4.24), 227 (sh, 4.18), 275 (3.11), 305 nm (sh, 2.60); MS (70 eV): *m/z* (%): 422 (9) [$M^+$], 420 (19) [$M^+$], 418 (11) [$M^+$], 341 (13), 339 (15), 259 (33), 143 (21), 129 (100), 115 (53); HRMS: *m/z* calcd for $C_{20}H_{20}Br_2$: 417.9931; found: 417.9802.

**Bromination of 4-ethenyl-15-ethynyl[2.2]paracyclophane (10)**: A solution of $Br_2$ in anhydrous dichloromethane (0.04 M, ca. 4.2 mL) was added to a solution of enyne **10** (58 mg, 0.22 mmol) in dry dichloromethane (50 mL) until the bromine color persisted. The mixture was left at RT for about 15 h, the solvent was evaporated, and the remainder was subjected to chromatography over silica gel (20 g) with pentane/dichloromethane 92:8 and later 91:9 to give dibromide **30** (44 mg, 47%). M.p. 149°C; $^1$H NMR (400 MHz): $\delta = 2.88$ (m, 2H; 1-$H_a$, 2-$H_a$), 2.95 (m, 1H; 9-H), 3.01 (m, 1H; 10-H), 3.14 (m, 1H; 10-H), 3.15 (m, 1H; 9-H), 3.35 (m, 2H; 1-$H_s$, 2-$H_s$), 3.62 (dd, $J = 6.8$, 9.9 Hz, 1H; 20-H′), 3.76 (dd, $J = 8.4$, 9.9, 1H; 20-H″), 4.04 (ddd, $J = 3.5$, 6.8, 8.4 Hz, 1H; 19-H), 6.29 (d, $J = 2.0$ Hz, 1H; 5-H), 6.36 (d, $J = 2.0$ Hz, 1H; 16-H), 6.39 (dd, $J = 2.0$, 7.9 Hz, 1H; 12-H), 6.41 (d, $J = 7.9$ Hz, 1H; 13-H), 6.46 (dd, $J = 2.0$, 8.0 Hz, 1H; 7-H), 6.48 (dd, $J = 0.6$, 8.0 Hz, 1H; 8-H), 6.71 ppm (d, $J = 3.5$ Hz, 1H; 18-H); irradiation of the 19-H resonance generated NOEs at the signal of 1-$H_s$/2-$H_s$ but not at the signal of 16-H; $^{13}$C NMR (101 MHz): $\delta = 32.69$ ($CH_2$, C1), 32.72 ($CH_2$, C2), 34.5 ($CH_2$, $^1J_{CH}$(av.) = 153 Hz, C20), 35.0 ($CH_2$, C9), 35.6 ($CH_2$, C10), 46.6 (CH, $^1J_{CH} = 130$ Hz, C19), 123.3 ($C_q$, C17), 131.3 (CH, C18), 131.9 (CH, C12), 132.7 (CH, C16), 133.3 (CH, C7), 133.8 (CH, C8), 134.8 (CH, C13), 135.3 (CH, C5), 135.4 ($C_q$, C15), 136.1 ($C_q$, C3), 138.5 ($C_q$, C4), 139.8 ($C_q$, C14), 140.5 ($C_q$, C11), 140.7 ppm ($C_q$, C6); assignment of the NMR spectra was achieved by DEPT-135, H,H-COSY, H,C-

HSQC, H,C-HMBC, and H,H-NOEDIF experiments and by recording a $^1$H-coupled $^{13}$C spectrum; IR (KBr): $\tilde{\nu}$ = 2957 (m), 2929 (s), 2916 (s), 2901 (m), 2850 (m), 1902 (w), 1644 (m), 1434 (m), 1319 (m), 1214 (s), 900 (s), 884 (m), 841 (s), 807 (s), 749 cm$^{-1}$ (s); UV (ethanol): $\lambda_{max}$ (log $\varepsilon$) = 206 (4.50), 224 (4.26), 228 (4.24), 234 (4.20), 248 (3.73), 254 (3.55), 264 nm (3.30); MS (EI): *m*/*z* (%): 418 (32) [$M^+$], 337 (17), 257 (15), 129 (100); HRMS: *m*/*z* calcd for $C_{20}H_{18}Br_2$ 415.9775; found: 415. 9751.

**Bromination of 4,15-diethynyl[2.2]paracyclophane (7)**: A solution of $Br_2$ in dichloromethane (0.04 M, ≈3.5 mL) was added to a solution of diyne **7** (60 mg, 0.23 mmol) in anhydrous dichloromethane (50 mL) until the bromine color persisted. The mixture was left at RT for 5 h, the solvent was evaporated, and the residue was subjected to chromatography on $SiO_2$ (20 g). Elution with pentane/dichloromethane 92:8 and later 90:10 afforded dibromide **33** (85 mg, 87%). M.p. 148 °C; $^1$H NMR (400 MHz): $\delta$ = 2.85 (m, 1H; 2-H$_a$), 2.87 (m, 1H; 1-H$_a$), 3.00 (m, 1H; 9-H), 3.05–3.13 (m, 4H; 1-H$_s$, 9-H, both 10-H), 3.30 (m, 1H; 2-H$_s$), 6.25 (d, *J* = 1.7 Hz, 1H; 16-H), 6.31 (brs, 1H; 5-H), 6.45 (dd, *J* = 1.7, 8.0 Hz, 1H; 12-H), 6.47 (d, partly hidden, 1H; 13-H), 6.49 (brs, 2H; 7-, 8-H), 6.62 (s, 1H; 20-H), 7.01 ppm (s, 1H; 18-H); saturation of the 18-H resonance produced an NOE of the 20-H signal and vice versa; $^{13}$C NMR (101 MHz): $\delta$ = 32.5 (CH$_2$, C1), 33.3 (CH$_2$, C2), 34.8 (CH$_2$, C9), 35.2 (CH$_2$, C10), 111.5 (CH, $^1J$(C,H) = 193 Hz, C20), 124.3 (C$_q$, C17), 132.0 (CH, C18), 133.2 (CH, C12), 133.5 (CH, C7), 134.2 (CH, C8), 134.5 (CH, C13), 135.0 (CH, C16), 135.3 (CH, C5), 135.9 (C$_q$, C15), 137.4 (C$_q$, C3), 138.2 (C$_q$, C14), 138.8 (C$_q$, C4), 140.3 (C$_q$, C6), 140.4 (C$_q$, C11), 144.5 ppm (C$_q$, C19): assignments by DEPT-135, H,C-HSQC and -HMBC; IR (KBr): $\tilde{\nu}$ = 2958 (m), 2927 (s), 2892 (m), 2852 (m), 1481 (m), 1434 (m), 1334 (s), 876 (s), 829 (s), 780 (s), 618 (s), 518 cm$^{-1}$ (s); UV (ethanol): $\lambda_{max}$ (log $\varepsilon$) = 206 (4.45), 208 (4.44), 212 (4.42), 226 (4.33), 232 (4.36), 254 (4.31), 278 (3.91), 290 (3.63), 296 (3.49), 302 nm (3.34); MS (EI): *m*/*z* (%): 416 (45) [$M^+$], 335 (20), 255 (100), 239 (70), 128 48); HRMS (EI): *m*/*z* calcd for $C_{20}H_{16}Br_2$ 413.9619; found: 413.9612.

**Grignard reaction of aldehyde 6**: Phenyl magnesium bromide (2 mL, 1.0 M in THF, 2 mmol), protected under $N_2$ that had been passed through solutions of pyrogallol/KOH and $H_2SO_4$, was added to a solution of aldehyde **6** (260 mg, 1.0 mmol) in dry THF (20 mL). The reaction mixture was stirred for 1 h at RT and then refluxed for 2 h. Ice was added to the cooled solution, followed by dilute HCl, and threefold extraction with dichloromethane. The combined organic phases were washed with bicarbonate solution and brine, and finally dried with $MgSO_4$. The solvent was removed in vacuo and the crude product was subjected to chromatography on silica gel (25 g). Elution with pentane/dichloromethane 2:8 (v/v) afforded the alcohol **34** (308 mg, 89%) as colorless crystals. M.p. 152–153 °C; $^1$H NMR (400 MHz): $\delta$ = 2.90 (ddd, *J* = 13.6, 10.8, 5.3 Hz, 1H; 1- or 2-H$_a$), 3.00–3.15 (m, 5H; 9-, 10-H, 2- or 1-H$_a$), 3.35 (d, *J* = 3.8 Hz, OH), 3.44 (s, 1H; 25-H), 3.57 (ddd, *J* = 13.6, 10.2, 2.4 Hz, 1H; 2- or 1-H$_s$), 3.74 (ddd, *J* = 13.3, 10.2, 5.4 Hz, 1H; 1- or 2-H$_s$), 6.28 (d, *J* = 3.8 Hz, 17-H), 6.44 (d, *J* = 7.7 Hz, 1H; 8-H), 6.48 (dd, *J* = 7.7, 1.9 Hz, 1H; 7-H), 6.57 (d, *J* = 7.9 Hz, 1H; 13-H), 6.59 (dd, *J* = 7.9, 1.7 Hz, 1H; 12-H), 6.73 (d, *J* = 1.7 Hz, 1H; 16-H), 6.97 (d, *J* = 1.9 Hz, 1H; 5-H), 7.09–7.21 ppm (m, 5H; Ph); $^{13}$C NMR (101 MHz): $\delta$ = 32.8 (CH$_2$, C1,2), 34.9, 35.1 (CH$_2$, C9,10), 72.3 (CH, C17), 80.6 (CH, C25), 84.2 (C$_q$, C24), 120.9 (C$_q$, C15), 126.6 (CH, Ph-*o*), 127.0 (CH, Ph-*p*), 128.3 (Ph-*m*), 131.9 (CH, C7), 133.9 (CH, C13), 134.8 (CH, C12), 135.4 (CH, C8), 136.8 (CH, C16), 135.2, 139.6, 139.9 (C$_q$, C3,6,11), 142.8, 143.4, 143.5 ppm (C$_q$, C4,14, Ph-*i*); IR (diamond-ATR): $\tilde{\nu}$ = 3540 (m), 3517 (m), 3231 (s), 2930 (m), 2893 (w), 2853 (w), 1589 (m), 1491 (m), 1451 (m), 1367 (m), 1170 (m), 1016 (s), 725 (s), 698 (s), 641 cm$^{-1}$ (s); UV (EtOH): $\lambda_{max}$ (log $\varepsilon$) = 205 (4.69), 280 nm (3.46); MS(EI): *m*/*z* (%): 338 (45) [$M^+$], 207 (50), 191 (100), 129 (35), 104 (30).

**Treatment of alcohol 34 with acid; formation of 37/38**: *p*-TsOH (≈20 mg) was added to the solution of alcohol **34** (105 mg, 0.31 mmol) in acetone (15 mL) and water (1 mL), and the reaction mixture was stirred at RT for 12 h. Dilute HCl (1 mL) was added, the mixture stirred at RT for 3 h, and then under reflux for 8 h. The cooled solution was diluted with water and extracted threefold with dichloromethane. The combined organic phases were washed with $NaHCO_3$ and NaCl solution, dried over $MgSO_4$, and the solvent evaporated to dryness. The mixture of products was subjected to chromatography on $SiO_2$ (20 g) with dichloromethane to afford the ketone **38** (50 mg, 50%). M.p. 199 °C; $^1$H NMR (400 MHz): $\delta$ = 2.83 (ddd, *J* = 13.3, 11.3, 3.0 Hz, 1H; 1-H$_a$), 2.93–3.23 (m, 6H; 1-H$_s$, 2-H$_a$, 9-H, 10-H), 3.34 (ddd, *J* = 13.5, 11.0, 3.0 Hz, 1H; 2-H$_s$), 3.50 (dd, *J* = 13.7, 6.5 Hz, 1H; 18-H′), 3.73 (dd, *J* = 13.7, 11.8 Hz, 1H; 18-H″), 4.23 (dd, *J* = 11.8, 6.5 Hz, 1H; 19-H), 6.33 (d, *J* = 1.9 Hz, 1H; 16-H), 6.38 (d, *J* = 7.8 Hz, 1H; 13-H), 6.41 (d, *J* = 7.9 Hz, 1H; 8-H), 6.44 (dd, *J* ≈ 8, 1.8 Hz, 1H; 12-H), 6.45 (d, *J* = 2.0 Hz, 1H; 5-H), 6.61 (dd, *J* = 7.9, 2.0 Hz, 1H; 7-H), 7.15–7.29 ppm (m, 5H; Ph); $^{13}$C NMR (101 MHz): $\delta$ = 33.8 (CH$_2$, C1), 34.7 (CH$_2$, C2), 34.9 (CH$_2$, C10), 35.1 (CH$_2$, C9), 47.7 (CH$_2$, C18), 48.6 (CH, C19), 126.3 (CH, Ph-*p*), 127.2 (CH, Ph-*o*), 128.3 (CH, Ph-*m*), 132.2 (CH, C12), 134.4 (CH, C8), 134.7 (CH, C5), 135.2 (CH, C7), 136.1 (CH, C13), 137.4 (C$_q$, C3), 138.4 (CH, C16), 138.7 (C$_q$, C14), 139.9 (C$_q$, C15), 140.8 (C$_q$, C11), 141.1 (C$_q$, C6), 142.3 (C$_q$, Ph-*i*), 143.0 (C$_q$, C4), 207.7 ppm (C$_q$, C17); assignment techniques used: DEPT-135, H,H-COSY, H,C-HSQC, H,C-HMBC; IR (diamond-ATR): $\tilde{\nu}$ = 3552 (w), 3310 (w), 2949 (m), 2922 (m), 2888 (m), 2868 (m), 2850 (m), 1679 (s), 1589 (m), 1491 (m), 1424 (m), 1257 (m), 1029 (m), 947 (m), 906 cm$^{-1}$ (m); UV (EtOH): $\lambda_{max}$ (log $\varepsilon$) = 202 (4.58), 285 nm (3.25); MS(EI): *m*/*z* (%): 338 (60) [$M^+$], 260 (40) [$M^+$−C$_6$H$_6$], 191 (100), 128 (80); elemental analysis calcd (%) for $C_{25}H_{22}O$ (338.43): C 88.72, H 6.55; found: C 88.75, H 6.54.

Elution with dichloromethane/diethyl ether 9:1 (v/v) afforded ketoalcohol **37** (30 mg, 28%). M.p. 145 °C; $^1$H NMR (400 MHz): $\delta$ = 2.55 (s, 3H; 18-H), 2.86 (ddd, *J* = 13.7, 10.6, 4.1 Hz, 1H; 1-H$_a$), 3.03–3.21 (m, 5H; 2-H$_a$, 9-, 10-H), 3.32 (brs, 1H; OH), 3.37 (ddd, *J* = 13.7, 10.0, 3.9 Hz, 1H; 1-H$_s$), 3.87 (ddd, *J* = 13.1, 10.0, 4.1 Hz, 1H; 2-H$_s$), 5.63 (brs, 1H; 19-H), 6.45 (d, *J* = 7.7 Hz, 1H; 13-H), 6.50 (dd, *J* = 7.7, 1.9 Hz, 1H; 12-H), 6.57 (d, *J* = 7.7 Hz, 1H; 8-H), 6.68 (dd, *J* = 7.7, 1.9 Hz, 1H; 7-H), 6.94 (d, *J* = 1.9 Hz, 1H; 16-H), 6.96 (d, *J* = 1.9 Hz, 1H; 5-H), 7.07–7.19 ppm (m, 5H; Ph); $^{13}$C NMR (101 MHz): $\delta$ = 30.3 (CH$_3$, C18), 32.7 (CH$_2$, C1), 34.1 (CH$_2$, C2), 34.9 (CH$_2$, C9), 35.0 (CH$_2$, C10), 72.4 (CH, C19), 127.0 (CH, C21,25), 127.2 (CH, C23), 128.0 (CH, C16), 128.3 (CH, C22,24), 131.6 (CH, C12), 132.8 (CH, C5), 134.9 (CH, C13), 135.4 (C$_q$, C14), 136.0 (CH, C8), 136.7 (CH, C7), 138.0 (C$_q$, C4), 139.6 (C$_q$, C11), 139.8 (C$_q$, C6), 140.3 (C$_q$, C3), 143.2 (C$_q$, C15), 143.8 (C$_q$, C20), 203.7 ppm (C$_q$, C17); assignment techniques used: DEPT-135, H,H-COSY, H,C-HSQC, H,C-HMBC; IR (diamond-ATR): $\tilde{\nu}$ = 3438 (m), 2852 (m), 1655 (s), 1590 (m), 1552 (m), 1486 (m), 1348 (m), 1265 (s), 889 (m), 852 (m), 726 (s), 696 (s), 631 cm$^{-1}$ (s); UV (EtOH): $\lambda_{max}$ (log $\varepsilon$) = 214 (4.57), 290 nm (3.50); MS(EI): *m*/*z* (%): 356 (30) [$M^+$], 338 (40), 191 (100); HRMS (EI): *m*/*z* calcd for $C_{25}H_{24}O_2$: 356.1776; found: 356.1782.

**Treatment of 4,15-bis(1-propynyl)[2.2]paracyclophane (11a) with *n*-BuLi**: A solution of **11a** (145 mg, 0.5 mmol) in THF (10 mL) was cooled to −50 °C and *n*-BuLi (1 mL, 1.6 M in hexane) was added. The red-brown solution was stirred for 40 min, quenched with ice water, and left to warm up to RT. The mixture was extracted threefold with dichloromethane, and the combined organic phases were washed with brine and dried with $MgSO_4$. The solvent was removed and the residue was subjected to chromatography on silica gel (20 g). Elution with pentane/dichloromethane 95:5 (v/v) provided the methylcyclopentadiene **42** in 66% yield (95 mg). M.p. 159–160 °C; $^1$H NMR (400 MHz): $\delta$ = 2.09 (s, 3H; 22-H), 2.49 (m, *AA′*XX′-like, *N* = 9.4 Hz, 2H; 1-H$_a$, 2-H$_a$), 2.93–3.11 (m, 6H; 1-H$_s$, 2-H$_s$, 9-, 10-H), 3.21 (dd, *J* = 23.2, 1.7 Hz, 1H; 20-H′), 3.35 (dd, *J* = 23.2, 1.6 Hz, 1H; 20-H″), 6.10–6.12 (m, 3H; 5-, 16-, 21-H), 6.32 (d, *J* = 7.9 Hz, 1H; 8- or 13-H), 6.34 (d, *J* = 7.9 Hz, 1H; 13- or 8-H), 6.50 (dd, *J* = 7.9, 2.0 Hz, 1H; 7- or 12-H), 6.52 ppm (dd, *J* = 7.9, 2.0 Hz, 1H; 12- or 7-H); $^{13}$C NMR (101 MHz): $\delta$ = 15.0 (CH$_3$, C22), 32.8, 33.0 (CH$_2$, C1,2), 35.5, 35.6 (CH$_2$, C9,10), 45.7 (CH$_2$, C20), 118.3 (CH, C21), 130.17, 130.24 (CH, C7,12), 132.0 (C$_q$, C19), 132.83, 132.87 (CH, C8,13), 138.4, 139.06 (CH, C5,16), 139.02, 139.43, 139.45, 140.2, 140.9, 141.6 (C$_q$, C3,4,6,11,14,15), 147.2, 153.3 ppm (C$_q$, C17,18); assignments by DEPT-135, H,H-COSY, H,C-HSQC; IR (KBr): $\tilde{\nu}$ = 2928 (s), 2851 (m), 1663 (w), 1480 (m), 1434 (m), 1401 (m), 1376 (m), 918 (m), 743 cm$^{-1}$ (s); UV (ethanol): $\lambda_{max}$ (log $\varepsilon$) = 204 (4.51), 216 (4.22), 226 (4.17), 234 (4.10), 240 (3.95), 248 (3.78), 262 (3.58), 274 nm (3.35); MS (EI): *m*/*z* (%): 284 (100) [$M^+$], 269 (35) [$M^+$−CH$_3$].

Further elution with pentane/dichloromethane gave the unstable monoallene **43** (ca. 7 mg, 5%). $^1$H NMR (400 MHz): $\delta$ = 2.03 (s, 3H; 19-H),

Table 2. Details of X-ray structure analyses.

| | **34** | **37** | **38** | **44** |
|---|---|---|---|---|
| formula | $C_{25}H_{22}O$ | $C_{25}H_{24}O_2$ | $C_{25}H_{22}O$ | $C_{30}H_{32}FeO_4Si_2$ |
| $M_r$ | 338.43 | 356.44 | 338.43 | 568.59 |
| habit | colorless prism | colorless tablet | colorless prism | yellow prism |
| crystal size [mm] | $0.45\times0.25\times0.2$ | $0.45\times0.25\times0.08$ | $0.5\times0.2\times0.2$ | $0.36\times0.33\times0.24$ |
| crystal system | monoclinic | orthorhombic | monoclinic | orthorhombic |
| space group | $P2_1/n$ | $Pbcn$ | $P2_1/c$ | $P2_12_12_1$ |
| $a$ [Å] | 7.6288(8) | 22.316(2) | 7.5665(6) | 11.4196(16) |
| $b$ [Å] | 13.1704(14) | 15.0230(12) | 13.0093(11) | 12.784(2) |
| $c$ [Å] | 18.120(2) | 10.9436(9) | 17.8659(14) | 19.724(3) |
| $\alpha$ [°] | 90 | 90 | 90 | 90 |
| $\beta$ [°] | 98.289(4) | 90 | 102.074(4) | 90 |
| $\gamma$ [°] | 90 | 90 | 90 | 90 |
| $V$ [Å$^3$] | 1801.6 | 3669.0 | 1719.7 | 2.8796 |
| $Z$ | 4 | 8 | 4 | 4 |
| $\rho_{calcd}$ [Mg m$^{-3}$] | 1.248 | 1.291 | 1.307 | 1.312 |
| $\mu$ [mm$^{-1}$] | 0.07 | 0.08 | 0.08 | 0.64 |
| $F$(000) | 720 | 1520 | 720 | 1192 |
| $T$ [°C] | −140 | −140 | −140 | −130 |
| $2\theta_{max}$ | 60 | 56.6 | 60 | 56.6 |
| reflns measured | 23823 | 34485 | 19572 | 44088 |
| independent reflns | 5282 | 4559 | 5031 | 7136 |
| $R_{int}$ | 0.042 | 0.072 | 0.032 | 0.027 |
| parameters | 243 | 249 | 235 | 340 |
| $wR$ ($F^2$ all data) | 0.129 | 0.131 | 0.135 | 0.076 |
| $R$ [$F>4\sigma(F)$] | 0.045 | 0.047 | 0.047 | 0.028 |
| $S$ | 1.03 | 1.02 | 1.05 | 1.03 |
| max $\Delta\rho$ [e Å$^{-3}$] | 0.36 | 0.25 | 0.39 | 0.39 |

2.87–3.07 (m, 6H; 1-H$_a$, 2-H$_a$, 9-, 10-H), 3.59–3.69 (m, 2H; 1-H$_s$, 2-H$_s$), 5.04 (dd, $J$=11.8, 6.8 Hz, 1H; 22-H′), 5.12 (dd, $J$=11.8, 6.9 Hz, 1H; 22-H″), 6.39 (t, $J$=6.8 Hz, 1H; 20-H), 6.40 (dd, $J$=7.8, 1.9 Hz, 1H; 7-H), 6.446 (dd, $J$=7.8, 1.8 Hz, 1H; 12-H), 6.454 (dd, $J$=7.8 Hz, 1H; 8-H), 6.48 (d, $J$=7.8 Hz, 1H; 13-H), 6.52 (d, $J$=1.9 Hz, 1H; 5-H), 6.55 ppm (d, $J$=1.8 Hz, 1H; 16-H); $^{13}$C NMR (101 MHz): $\delta$=4.6 ($CH_3$, C19), 32.9, 33.1 ($CH_2$, C1,2), 34.9 ($CH_2$, C9,10), 77.5 ($CH_2$, C22), 80.0 ($C_q$, C18), 88.5 ($C_q$, C17), 93.1 (CH, C20), 124.1 ($C_q$, C15), 131.4 (CH, C7), 131.6 (CH, C5), 132.5 (CH, C8), 133.5 (CH, C13), 133.8 ($C_q$, C4 or C3), 134.9 (CH, C12), 135.7 (CH, C16), 137.1 ($C_q$, C3 or C4), 139.0, 139.4 ($C_q$, C6,11), 141.3 ($C_q$, C14), 210.4 ppm ($C_q$, C21); GS/MS: $m/z$ (%): 284 (100) [$M^+$], 155 (58), 141 (50), 129 (40).

**Preparation of the iron complex 44**: A solution of **11b** (140 mg, 0.35 mmol) in DME (1.5 mL) and iron pentacarbonyl (0.1 mL, 0.76 mmol) was placed in a heavy-walled tube, which was deoxygenated by several freeze–pump–thaw cycles and sealed. After heating the mixture at 140 °C for 21 h, it was filtered through Celite, the solvent was evaporated, and the remainder was subjected to chromatography on silica gel (20 g). Elution with dichloromethane/diethyl ether 95:5 (v/v) gave **44** as yellow needles (140 mg, 74%). M.p. 200–215 °C (decomp); $^1$H NMR (200 MHz): $\delta$=0.03 (brs, 18H; $(CH_3)_3Si$), 2.43–2.52 (m, 2H), 2.77–2.99 (m, 6H), 6.09 (d, $J$=1.6 Hz, 2H; 5-, 16-H), 6.18 (d, $J$=7.9 Hz, 2H; 8-, 13-H), 6.38 ppm (dd, $J$=7.9, 1.7 Hz, 2H; 7-, 12-H); $^{13}$C NMR (50 MHz): $\delta$=0.8 ($CH_3$, 22-, 25-H), 32.8, 35.4 ($CH_2$, C1,2,9,10), 72.1 ($C_q$), 123.8 ($C_q$), 131.7 (CH), 133.4 ($C_q$), 133.7 (CH), 138.9 (CH), 140.3 ($C_q$), 140.9 ($C_q$), 181.2 ($C_q$), 208.8 ppm ($C_q$); IR (diamond-ATR): $\tilde{\nu}$=2936 (w), 2901 (w), 2859 (w), 2054 (s), 1985 (s), 1617 (s), 1458 (w), 1421 (w), 1360 (w), 1244 (s), 907 (m), 864 cm$^{-1}$ (s); UV ($CH_2Cl_2$): $\lambda_{max}$ (log $\varepsilon$)=229 (4.46), 295 (3.71), 310 nm (3.70); MS (EI): $m/z$ (%): 568 (3) [$M^+$−FeCO], 540 (8) [$M^+$−Fe(CO)$_2$], 512 (28) [$M^+$−Fe(CO)$_3$], 484 (100); elemental analysis calcd (%) for $C_{36}H_{44}FeO_4Si_2$ (652.21): C 66.24, H 6.80; found: C 63.13, H 5.67.

**X-ray structure determinations**: Numerical details are presented in Table 2. Data collection: crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (Bruker SMART 1000 CCDC). Measurements were performed with monochromated Mo$_{K\alpha}$ radiation. For **44**, an absorption correction based on multiple scans was performed. Structure refinement: The structures were refined anisotropically against $F^2$ (program SHELXL-97[28]). Acetylenic and hydroxy hydrogen atoms were refined freely; methyl groups as rigid groups; other H atoms were included using a riding model. Special features: Compound **44** crystallizes by chance in a chiral space group; the Flack parameter refined to −0.005(9). The bulk material was, however, a racemate.

CCDC-606672 (**38**), CCDC-606673 (**37**), CCDC-606674 (**34**), and CCDC-606675 (**44**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## Acknowledgement

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for their continued support of our work.

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Received: November 14, 2006
Published online: March 20, 2007

  