Syntheses and Properties of Medium-Sized Metacyclophanediynes

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The syntheses of [11]metacyclophane-2,9-diyne (**3**), [4.4]metacyclophane-2,12-diyne (**4**), [4.4]orthometacyclophane-2,12-diyne (**5**), (*Z*)-[10]metacyclophane-5-ene-2,8-diyne (**6**), [10]metacyclophane-2,8-diyne (**7**), and 5-isopropylidene[9]metacyclophane-2,7-diyne (**8**) have been achieved. The systems could be stabilized by protecting the triple bonds in **3**−**8** with the $Co_2(CO)_6$ moiety. PE spectroscopic investigations of **3** and **6**−**8** gave no clear-cut evidence for homoconjugative interactions among the π fragments. The triple bonds in **3**−**8** could be transformed into the corresponding *cis* double bonds by applying 2−5 molar equiv of Schwartz's reagent (**28**). Treatment of **3**, **4**, and **7** with *t*-BuOK allows the transformation of the propargylic moieties into allenic moieties, whereas the same treatment of **5** and **6** transforms the 2-butynyl bridges into 1,3-butadiene bridges, giving rise to several isomers. The structural assignments of **3**−**8** and their reaction products are based on their spectroscopic properties.

[*n*]Metacyclophanes have been known for nearly 20 years.[1] The ones with short chains (n = 4−6) have attracted the attention of chemists as model compounds to test the limits of bending aromatic rings.[2] Another aspect arises from [*n*]metacyclophanes in which the chain contains heteroatoms such as oxygen and sulfur. These species enable the complexation of a metal atom such as magnesium or zinc at the 2-position of the aromatic ring.[3] Our interest in this field stems from investigations of cyclic diynes in which two double bonds were part of the ring systems.[4] Examples are (*Z*,*Z*)-4,10-cyclododecadiene-1,7-diyne (**1**) and 4,9-dimethylene-1,6-cyclodecadiyne (**2**). Both systems showed a considerable homoconjugation between the double and triple bonds, and their reactivity differed as compared to the parent systems.[4] These studies led us to conceive systems in which a benzene ring is part of the chain. In this paper we report the syntheses of [11]metacyclophane-2,9-diyne (**3**), [4.4]metacyclophane-2,12-diyne (**4**), [4.4]orthometacyclophane-2,12-diyne (**5**), (*Z*)-[10]metacyclophane-5-ene-2,8-diyne (**6**), [10]metacyclophane-2,8-diyne (**7**), and 5-isopropylidene[9]metacyclophane-2,7-diyne (**8**). Together with the preparation of these compounds we report their transformation into some hydrogenated species and into their bis(dicobalt hexacarbonyl) complexes as well as their reactions with strong bases.

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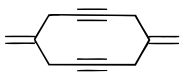

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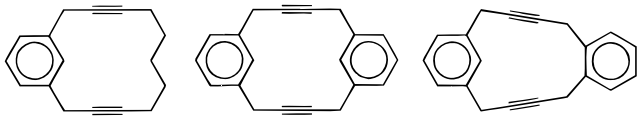
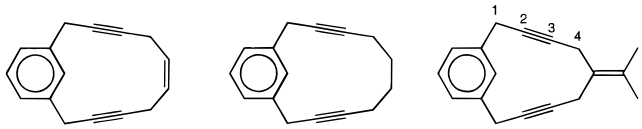


3 **4** **5**



6 **7** **8**

Syntheses of the Metacyclophanes 3−8

There are two paths in which the metacyclophanediynes **3**−**8** can be prepared by reacting a dihalogen compound with the dilithium salt of a dialkyne as shown in Scheme 1. With the exception of **10** all open-chain dialkynes needed for path A are described in the literature.[4−9] They can be prepared by reacting the corresponding α,ω-dihalogen compounds **15**−**20** with the lithium acetylide−ethylenediamine complex (**9**, **13**)[5,6] or acetylenemagnesium chloride (**21**)[4,10] (**11**,[7] **12**,[8,9] **14**[4]). With the exception of **11**, which can be isolated in only 30% yield, the yield of the other open-chain alkynes varies from 60% to 80%. The unknown compound **10** can be obtained in a similar manner from α,α′-dichloro-*m*-xylene (**16a**, Hal = Cl) and acetylenemagnesium chloride (**21**) in 24% yield. Also for path B the preparations of the halogen compounds, which could not be purchased, are described in the literature.[11,12] We preferred path A because the dialkynes **9**−**14** are available in good yields and α,α′-diiodo-*m*-

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(2) Bickelhaupt, F.; de Wolf, W. H. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press Ltd.: London, 1993; Vol. 3, p 185. Kane, V. V.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1994**, *50*, 4575.

(3) Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Angew. Chem.* **1988**, *100*, 1143. Markies, P. R.; Nomoto, T.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1991**, *10*, 3826. Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1991**, *10*, 3538.

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(9) Müller, P.; Rodriguez, D. *Helv. Chim. Acta* **1985**, *68*, 975.

(10) Jones, E. R. H.; Skatteböl, L.; Whiting, M. C. *J. Chem. Soc.* **1956**, 4765.

(11) Marshall, J. A.; Warne, T. M., Jr. *J. Org. Chem.* **1971**, *36*, 178.

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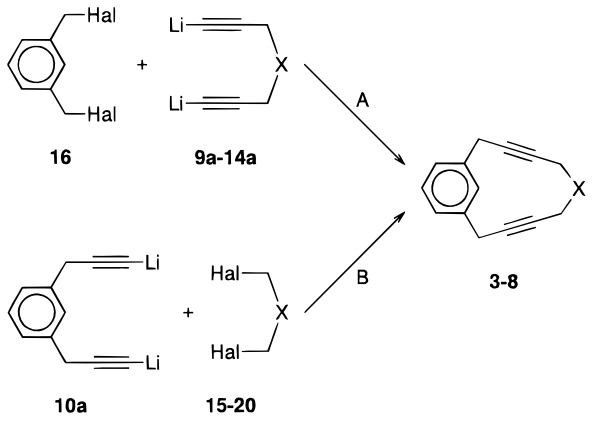
Scheme 1



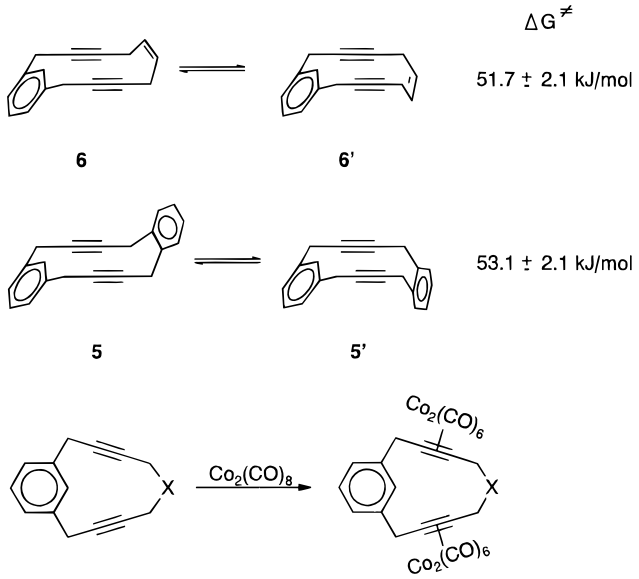
X = $-(CH_2)_3-$,  ,  ,  , $-(CH_2)_2-$, 

3	**4**	**5**	**6**	**7**	**8**
9	**10**	**11**	**12**	**13**	**14**
15	**16**	**17**	**18**	**19**	**20**

xylene (**16b**, Hal = I) can be prepared easily.[13] For path B, however, only the dibromo compounds of **18** and **20** are available. Former investigations have shown, however, that diiodo compounds achieve better yields during cyclization reactions. Furthermore 1,3-dipropargylbenzene (**10**), needed for path B in high amounts, can only be prepared in relatively low yields. In a high-dilution apparatus the α,ω-diynes are treated at −78 °C with *n*-butyllithium to form the dilithium salts **9a**−**14a** (Scheme 1). Subsequently α,α′-diiodo-*m*-xylene (**16b**) was added to yield **3**−**8**. The reaction time is 2−4 days with the exception of the preparation of **5** and **8**, which were 7 and 10 days, respectively. The yields obtained according to path A in Scheme 1 varied from 7% (**5**) to 24% (**3**, **7**). The reason for the low yields we ascribe to the high acidity of the benzylic/propargylic protons which rearrange to form an allenic system (see below) which polymerizes easily.

Characteristic for all the metacyclophanes is the chemical shift of the inside-oriented proton at the benzene ring. Its signal is found at $\delta = 8.1-8.7$. Responsible for the downfield shift of the inner proton is the anisotropy of the triple bond. We encounter an especially strong downfield shift in the case of **5**, **6**, and **8**. The most significant signals of the ^{1}H NMR spectra are collected in Table 1. It is of interest that for the parent [10]metacyclophane no temperature dependence of the ^{1}H NMR spectrum was found even at low temperatures.[15] This is indicative for low barriers of rotation in the unsubstituted decamethylene bridge. In **5** and **6**, however, the incorporation of an aromatic ring or a double bond, respectively, leads to a restriction of the pseudorotation of the corresponding bridges at low temperatures (−10 °C for **5** and −20 °C for **6**). Therefore, for **5** and **6** we observe temperature dependent ^{1}H NMR spectra, which allow us to determine the activation parameters (see Scheme 2).[14] Both values for $\Delta G^{\ddagger}$ are in the same order of magnitude as reported for [7]metacyclophanes.[15] The ^{13}C NMR data obtained for the sp carbons in **3**, **4**, and **6** show no indication for a bending of the triple bonds, whereas the ^{13}C NMR signals of the acetylenic carbons in β-position to the aromatic ring of **5**, **7**, and **8** are slightly shifted downfield, indicating a deviation of the triple bond from linearity. Corresponding to this feature are the AM1 calculations,[16] which show angles of 174° (**5**), 176° (**7**), and 173° (**8**) for the angle C1−C2−C3 (see **8**). On the other hand the angle C2−C3−C4 is close to 180° in all metacyclophanediynes. This is also in agreement with the ^{13}C NMR data of **3**−**8**, which all show signals between $\delta = 78$ and 80 for the acetylenic carbon in γ-position to the aromatic ring. The UV data reported in the Experimental Section indicate that the benzene rings in **3**−**8** should be planar. In line with these findings are calculations using semiempirical methods (AM1,[16] MNDO[17]).

Scheme 2



X = $-(CH_2)_3-$,  ,  ,  , $-(CH_2)_2-$, 

3	**4**	**5**	**6**	**7**	**8**
22	**23**	**24**	**25**	**26**	**27**

To characterize the cyclic diynes further we reacted them with dicobalt octacarbonyl to obtain the bis(dicobalt hexacarbonyl) complexes **22**−**27** which are stable at room temperature and allow a characterization by elemental analysis (see Scheme 2). With the exception of **23** we were able to grow single crystals which allowed the X-ray investigation. The structures of the bis(dicobalt hexacarbonyl) complexes **22** and **24**−**27** show the anticipated characteristic features: the triple bonds are bend to 139−149° and the distances between the bond sp centers amount to 1.29−1.34 Å.

Photoelectron Spectroscopic Investigations

To elucidate a possible homoconjugation in **3**−**8** we recorded the He I photoelectron (PE) spectra of these

(13) For the preparation of α,α′-diiodo-*m*-xylene (**16b**) we used the method described by Finkelstein, H. *Chem. Ber.* **1910**, *43*, 1528, but using α,α′-dichloro-*m*-xylene (**16a**) instead of the corresponding dibromo compound as described in the original literature.

(14))Binsch, G. *Top. Stereochem.* **1968**, *3*, 97. Calder, I. C.; Garratt, P. J. *J. Chem. Soc. B* **1967**, 660.

(15) Hirano, S.; Hara, H.; Hiyama, T.; Fujita, S.; Nozaki, H. *Tetrahedron* **1975**, *31*, 2219.

(16) Dewar M. J. S.; Zoebisch, E. G.; Healy E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(17) Dewar M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

Table 1. ^{1}H NMR Data of the Metacyclophanediynes 3−8

	3	4	5	6	7	8
Ar-H_i[a]	8.11	8.24	8.49	8.43	8.36	8.69
Ar-H_r[b]	7.16−6.99	7.19−7.03	7.37−6.97	7.16−7.00	7.17−7.00	7.15−7.01
Ph−CH_2	3.65	3.72	3.58	3.58	3.60	3.56
≡−CH_2	2.35	3.72	3.71	3.07	2.27	3.05

[a] Ar-H_i: the inside orientated proton of the aromatic ring. [b] Ar-H_r: aromatic protons with the exception of H_i.

species. In the case of **4** and **5** we were not able to obtain any spectra due to decomposition upon heating of the sample. The recorded ionization energies of **3** and **6**−**8** are listed in Table 2. As an example we show in Figure 1 the PE spectra of **6** and **7**. All spectra have two peaks in common, one centered at 8.6 eV and a second more intensive one between 9.2 and 9.7 eV. From the areas below the envelopes of both peaks we assign the first peak to two and the second one to four (**3**, **7**) or five (**6**, **8**) transitions. The comparison between the ionization energies of *m*-xylene (8.5, 9.0 eV)[18] and cyclic diynes such as 1,7-cyclododecadiyne (9.1, 9.4 eV)[19] and 1,8-cyclotetradecadiyne (9.1, 9.3 eV)[19] allows us to assign the first peak in all PE spectra to the ionization events from the two highest π-MOs of the benzene fragment (π_{ar}) and the second peak to the four π-MOs of the triple bonds, arising from the in plane (π_i) and the out of plane (π_o) linear combinations π_i^-, π_i^+, π_o^-, and π_o^+ (see Table 2). In case of **6** we assign the shoulder at the low-energy part of the second peak to the ionization band from the double bond.

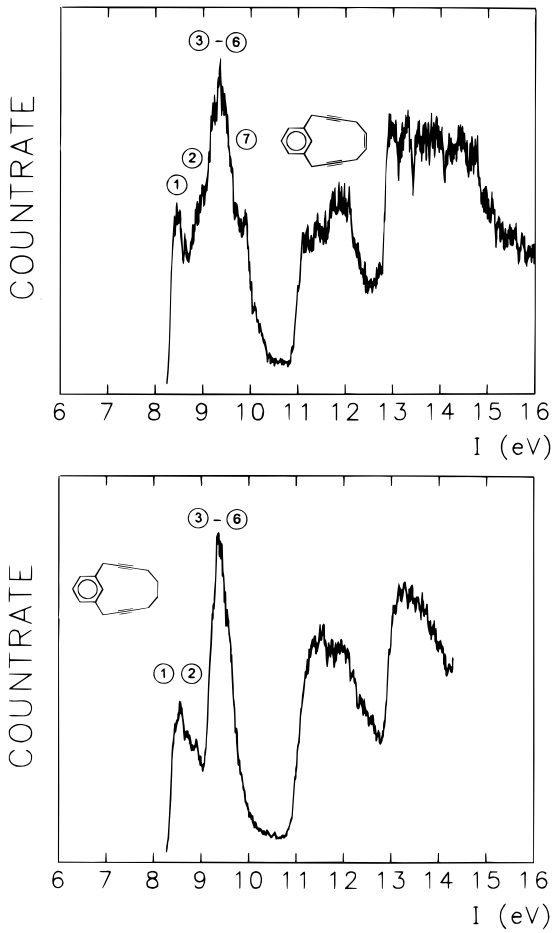


Figure 1. He I photoelectron spectra of **6** and **7**.

Our qualitative assignment is supported by MO results assuming the validity of Koopmans' theorem[20] which allows a direct correlation between the recorded vertical ionization energies, $I_{v,j}$, and the calculated orbital energies, ϵ_j. The latter were obtained by the AM1[16] procedure. Due to the strong overlap of the individual bands it is difficult to draw any conclusion concerning homoconjugation between the different π-units of the systems investigated. We observe in **6** and **8** a somewhat larger half-width of the second peak as compared to **3** and **7**; this might be indicative for a homoconjugation of the double bond and the triple bond in **6** and **8** similar to (*Z*,*Z*)-4,10-cyclododecadiene-1,7-diyne and 4,9-dimethylene-1,6-cyclodecadiyne.[4] Our PE spectroscopic investigations of **3** and **6**−**8** reveal no evidence for homoconjugation between the triple bonds and the aromatic ring system.

Table 2. First Vertical Ionization Energies, $I_{v,j}$, and Calculated Orbital Energies, ϵ_j, of 3 and 6−8 (All Values Are Given in eV)

compd	band	$I_{v,j}$	assignment	$-\epsilon$ (AM1[16])
3	1	8.5	19a″ (π_{ar})	9.30
	2	8.8	24a′ (π_{ar})	9.47
	3	9.2	23a′ (π_o^+)	10.18
	4	to	18a″ (π_i^-)	10.21
	5	9.5	17a″ (π_o^-)	10.33
	6		22a′ (π_i^+)	10.49
6	1	8.5	16a″ (π_{ar})	9.30
	2	8.7 (sh)	21a′ (π_{ar})	9.36
	3	9.2	20a′ (π_d)	10.10
	4	to	15a″ (π_o^-)	10.18
	5	9.7	19a′ (π_o^+)	10.33
	6		14a″ (π_i^-)	10.35
	7	9.9	18a′ (π_i^+)	10.50
7	1	8.6	(π_{ar})	9.24
	2	8.7	(π_{ar})	9.45
	3	9.4		10.24
	4	to	(π_i^-), (π_o^-)	10.27
	5	9.5	(π_o^+), (π_i^+)	10.38
	6			10.47
8	1	8.5	20a″ (π_{ar})	9.27
	2	8.6	25a′ (π_{ar})	9.33
	3	8.9	24a′ (π_d)	9.43
	4	9.2	19a″ (π_i^-)	10.10
	5	to	23a′ (π_o^+)	10.21
	6	9.5	18a″ (π_o^-)	10.32
	7	9.7	22a′ (π_i^+)	10.58

Hydrogenation Reactions

The result of a hydrogenation experiment with **5** using the Lindlar catalyst[21] was disappointing. Treating a solution of **5** in a petroleum ether/methanol mixture at 50 °C with 80 bar of hydrogen and Lindlar catalyst only gave very low yields (3−5%) of the dihydrogenated, the tetrahydrogenated, and the octahydrogenated products. This result was astonishing in so far as 1,8-cyclotetra-

(18) Klessinger, M. *Angew. Chem.* **1972**, *84*, 544; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 525.
(19) Gleiter, R.; Karcher, M.; Jahn, R.; Irngartinger, H. *Chem. Ber.* **1988**, *121*, 735. Gleiter, R.; Kratz, D.; Schäfer, W.; Schehlmann, V. *J. Am. Chem. Soc.* **1991**, *113*, 9258.
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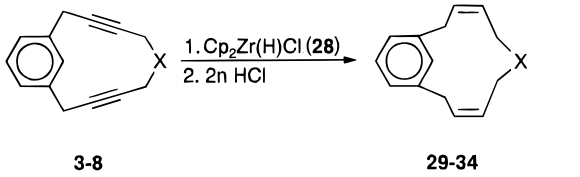
(21) Lindlar, H. *Helv. Chim. Acta* **1952**, *35*, 446. Dobson, N. A.; Eglinton, G.; Krishnamurti, M.; Raphael, R. A.; Willis, R. G. *Tetrahedron* **1961**, *16*, 16.

decadiyne could be hydrogenated to the diene in 77% yield at atmospheric pressure and room temperature.[22]

An alternative route to the partially hydrogenated products was found by applying $Cp_2Zr(H)Cl$, Schwartz's reagent (**28**),[23] in benzene at 0 °C as shown in Scheme 3. By using 2−5 equiv of **28** the yields of **29**−**34** varied between 30% and 65%. In the case of the 12- and 13-membered ring systems, 2−3 equiv of **28** was sufficient; for the less strained 14-membered ring systems **3** and **4**, 4−5 equiv had to be used. Larger amounts of **28** favor the products in which the triple bonds are reduced to the alkanes. On the basis of ^{1}H NMR investigations and the crystal structure of **30**, we found only the *cis* configuration of the newly prepared double bonds in **29**−**34**.

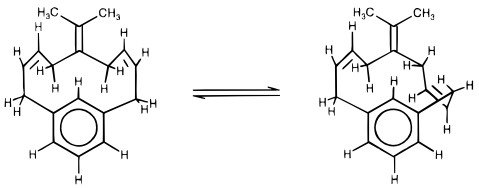
Scheme 3



3 **4** **5** **6** **7** **8**

29 **30** **31** **32** **33** **34**

Scheme 4



34a **34b**

With the exception of **34** we could not find any temperature dependence of the signals of the allylic protons down to −60 °C. In the ^{1}H NMR spectrum of **34** we found at 0 °C a coalescence of the allylic protons neighbored to the isopropylidene group and at −30 °C the coalescence of the benzylic protons was found. This is due to a restricted rotation of the C3 bridge between the double bonds and the olefinic group itself. In Scheme 4 we show two conformations for **34** which were predicted close in energy by AM1[16] and MNDO[17] calculations.

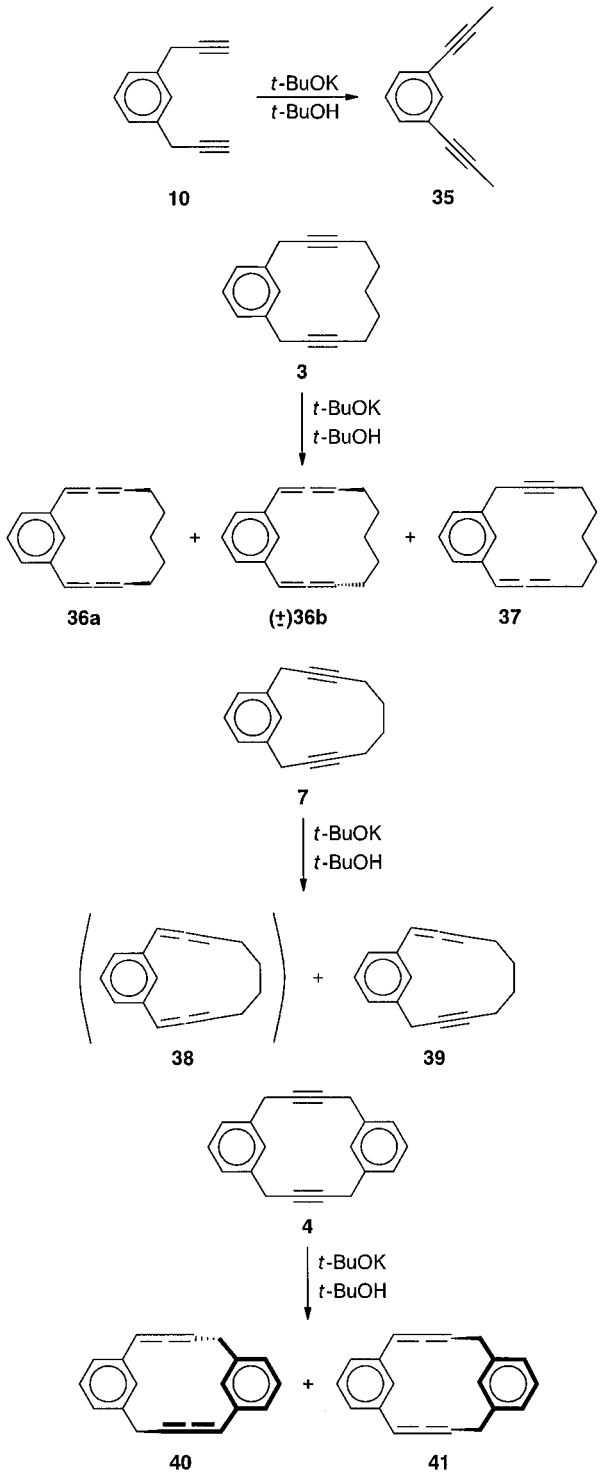
Base-Catalyzed Isomerizations of 3−8

In the preceding sections we mentioned the high reactivity of the benzylic/propargylic hydrogens of **3**−**8** toward bases. This reactivity was made responsible for their decomposition in solution. The ease of the isomerization was demonstrated by treating 1,3-dipropargylbenzene (**10**) with *t*-BuOK in *t*-BuOH. At 50 °C the conversion to 1,3-bis(1-propynyl)benzene (**35**)[24] was completed (Scheme 5) quantitatively after 12 h.

Treatment of **3** with *t*-BuOK at room temperature yields the mixture of the bisallenes **36a** and **36b** as the main product (42%) and **37** (10%) as a side product. All species have been identified by their spectroscopic properties. In the ^{13}C NMR spectrum of the first-mentioned mixture, two sets of ten signals close together, which differ in intensity, prove the availability of the two diastereomers **36a** and **36b**. On the basis of AM1 calculations[16] which predict the *meso* compound **36a** to be more stable than the racemate **36b** by 2 kcal/mol, we assume that the main product has the *meso* configuration. Our structural assignment of **37** is based both on the ^{1}H and ^{13}C NMR data. The latter shows two signals at δ = 83.4 and 78.6 for the alkyne carbons and three signals at δ = 206.2, 94.9, and 94.0 for the allene system.

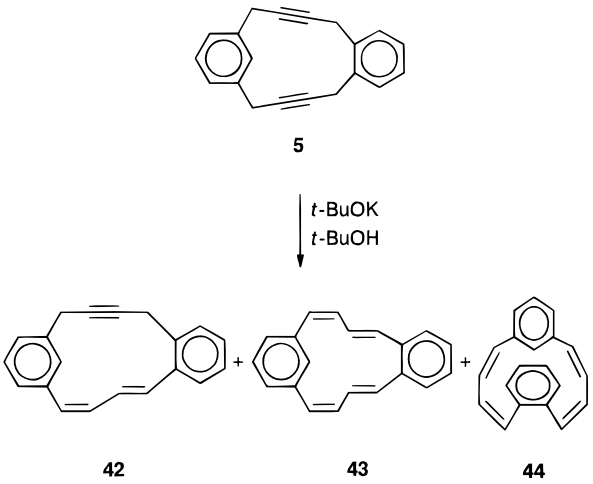
The treatment of **7** with a surplus of *t*-BuOK shows two products from which the minor one (9%) was too

Scheme 5

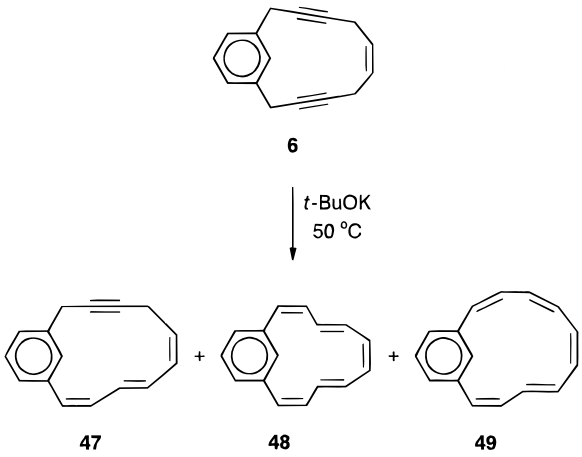


(22) Dale, J.; Hubert, A. J.; King, G. S. D. *J. Chem. Soc.* **1963**, 73.
(23) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679.
(24) Tanaka, Y.; Yamashita, H.; Tanaka, M. *Organometallics* **1995**, *14*, 530.

Scheme 6



Scheme 7



unstable to be characterized fully by spectroscopic means. We assigned its structure to **38**. The main product **39** could be isolated and fully characterized. Common to the monoalkynes **37** and **39** is a restricted ring inversion of the aromatic ring at room temperature which leads to doublets of the benzylic protons in both cases in the ^{1}H NMR spectra.

We notice that the base-induced rearrangement of **3** leads mainly to the bisallene products **36a** and **36b** while **7** leads only to the monoallenic metacyclophane. We ascribe this to the higher strain energy of **38** as compared to **39**. In **36a** and **36b** the longer chain should favor the bisallene compounds over **37**. In line with these arguments are the results of AM1[16] calculations of **36**−**39**, predicting the *meso* compound **36a** to be more stable than **37** by 2 kcal/mol. In the case of **38** and **39**, the latter is predicted by 4 kcal/mol to be more stable than **38**.

The treatment of **4** with *t*-BuOK yields a mixture of two products which could not be separated by column chromatography or by HPLC. The ^{13}C and ^{1}H NMR spectra of the mixture could be recorded in CS_2. The analysis of the NMR spectra shows the existence of two compounds with two allenic moieties in each (δ = 206.3, 96.4, 95.3 and 206.4, 95.6 and 94.5, respectively). The data obtained are compatible with **40** (C_i) and **41** (C_s) in the ratio of 2:3. This assignment is further supported by the observation of three singlets in the downfield region of the ^{1}H NMR spectrum. The most deshielded signal at δ = 7.94 can be assigned to the inner proton of the C_i-symmetrical isomer **40**, the two signals at δ = 7.77 and 7.52 to the C_s-symmetrical bisallene **41**.

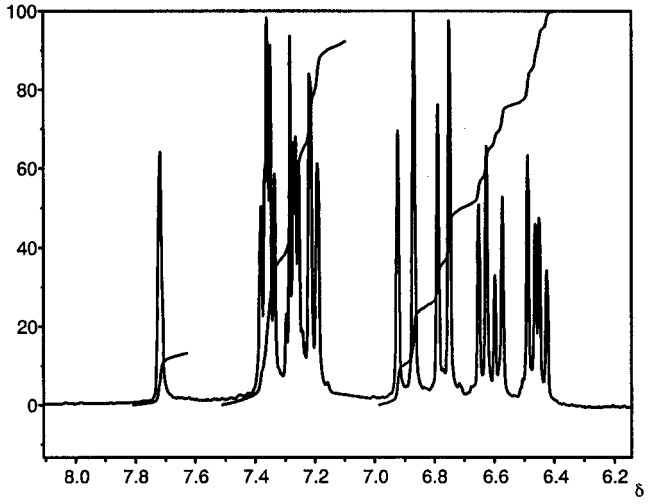


Figure 2. ^{1}H NMR spectrum of **43** in $CDCl_3$.

The base-induced isomerization of **5** and **6** takes a different course (Schemes 6 and 7). Treatment of **5** with *t*-BuOK at room temperature yields three new compounds. The main product with the lowest R_f value is assigned to structure **42**. This assignment is based on the observation of two sp carbon signals (δ = 94.2 and 83.5) and four additional signals in the sp^2 region. Remarkable in the ^{1}H NMR spectrum is a doublet of doublets at δ = 8.12. This is due to an "inner" proton of the butadiene moiety. With the help of a H,H COSY spectrum we are able to assign the further three protons of the butadiene moiety at δ = 6.79, 6.73, and 6.53. The ^3J coupling constants of 16.1 and 10.9 Hz, respectively, support a *Z*,*E* configuration of the butadiene fragment. On the basis of the spectroscopic properties we are left with two possibilities, **42** and **45**. The AM1[16] calculations predict **42** by 15 kcal/mol more stable than **45**.

The isomer with the next higher R_f value is formed in only 11% yield. The ^{1}H NMR spectrum of this species (**43**) is shown in Figure 2. In this spectrum the signals of the four protons at the butadiene moiety are seen between δ = 6.4 and 6.9 as two doublets and two doublets of doublets. The ^3J coupling constants support a *Z*,*E* configuration of the butadiene moiety. As in the case of **42** there is another isomer (**46**) possible. AM1[16] calculations predict that **43** should be more stable than **46** by 35 kcal/mol.

The structure of the isomer with the highest R_f value, which is formed in only 1% yield, can be assigned to structure **44**. As in the case of **43** we expect in the ^{1}H NMR spectrum of **44** two doublets for the protons in the neighborhood of the aromatic rings and two doublets of doublets for the protons at the 2,3 positions of the butadiene moieties. One of the doublets is recognized at δ = 6.53 (Figure 3). From the H,H COSY spectrum we were able to assign the other butadiene protons at δ = 6.19, 6.17, and 5.95. The ^3J coupling constants were found to be 12.8 Hz as well as 13.6 Hz, respectively. These values favor a *Z* more than an *E* configuration. The *all-cis* configuration is further supported by the failure to detect an out of plane C−H vibration between

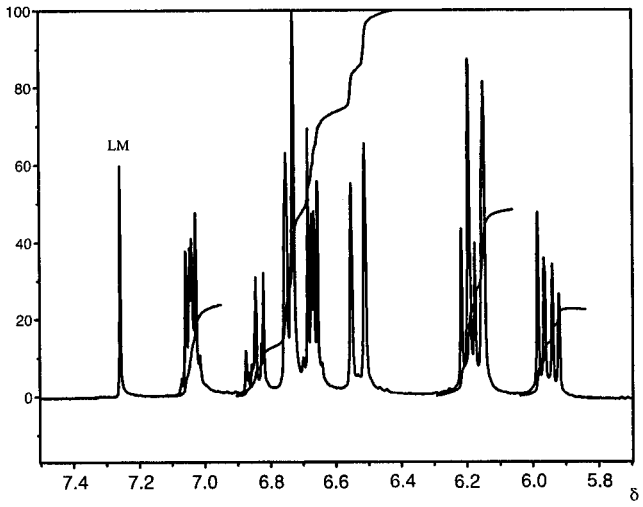


Figure 3. ^{1}H NMR spectrum of **44** in $CDCl_3$ (LM stands for $CHCl_3$).

900 and 1000 cm^{-1}. Such a vibration was detectable in all butadienes with an *E* configuration (e.g., **42**, **43**). The singlet of the *meta*-substituted benzene ring, which is part of the doublet at $\delta = 6.74$, is shifted toward high field ($\delta = 6.73$) as compared to **42** and **43**. This is in line by assuming that the proton is shielded by the *ortho*-substituted aromatic ring. This would be the case if the configuration and conformation of **44** is close to that shown. Furthermore, this result is supported by AM1 calculations.[16]

UV data of the isomerization products indicate that in both bis(butadiene) compounds **43** and **44** the butadiene moieties are not coplanar, whereas in the dieneyne **42** the butadiene moiety is close to planarity.

The base-induced isomerization of **6** depends on the reaction temperature. The treatment of **6** with 2.6 equiv of *t*-BuOK at room temperature yields only one product which could be isolated in 45% yield. The four signals at $\delta = 98.1$ and 82.8 as well as $\delta = 32.7$ and 23.4 in the ^{13}C NMR spectrum suggest one triple bond and a hexatriene unit as present in (*Z*,*E*,*Z*)-[10]metacyclophane-1,3,5-trien-8-yne (**47**). The structural assignment is further confirmed by the analysis of the ^{1}H NMR and H,H COSY spectrum of **47**. As in the case of **42**, the signal of the proton at C3 is shifted downfield ($\delta = 7.98$). Remarkable are furthermore the strong highfield shift of the ^{13}C signal of C6 ($\delta = 108.0$) and the downfield shift of the sp carbon atom ($\delta = 98.1$). This latter points to a strong bending of the triple bond.

If the base treatment is carried out at 50 °C with 5 equiv of *t*-BuOK two further substances, (*Z*,*E*,*Z*,*E*,*Z*)-[10]metacyclophane-1,3,5,7,9-pentaene (**48**) and (*Z*,*Z*,*Z*,*E*,*Z*)-[10]metacyclophane-1,3,5,7,9-pentaene (**49**), could be isolated in low yields in addition to **47** which was the main product (40%) also under these conditions. In the case of **48** and **49** the NMR data clearly point to the presence of decapentaene units. The ^{1}H NMR spectra of **48** and **49** could be assigned on the basis of double-resonance experiments (**48**) and the H,H COSY spectrum (**49**), respectively. Higher yields of **48** (54%) can be achieved, if 10 equiv of base is used at 50 °C, whereas the yield of **49** (6%) stays almost constant under these conditions.

As in the case of the isomerization products of **5**, the UV data of the pentaenes **48** and **49** indicate that the decapentaene units are not coplanar. For the trieneyne **47**, however, we pressume an almost planar arrangement of the hexatriene moiety, based on UV data.

The different isomerization behavior of the metacyclophanes **5** and **6** as compared to **3** and **7** can be rationalized by assuming that in all four cases the first step is the formation of two allenic systems in conjugation to the benzene nucleus. In case of **5** and **6** the additional π-system allows the abstraction of an additional proton in its α-position. This leads to an irreversible rearrangement, and the thermodynamic more stable butadiene system(s)[25] results. In the case of **4** kinetic reasons might be responsible for the fact that no butadiene moiety was found.

Treatment of the isopropylidene compound **8** with *t*-BuOK results exclusively in the formation of polymers, according to the high strain of the allenic intermediate.

Conclusion

The incorporation of one or two benzene rings in the skeleton of a cyclic diyne changes the properties considerably. The hydrogen atoms which share the benzylic and propargylic positions have a high tendency to tautomerize. Thus allenic and olefinic isomers of the starting diynes can be generated easily in the presence of a strong base. The presence of one or two aromatic rings hampers the catalytic hydrogenation by Pd/C. This can be circumvented by using Schwartz's reagent.

Experimental Section

General. Moisture sensitive reactions were conducted in oven-dried (150 °C) glassware in a positive argon atmosphere. Solvents were distilled and dried under argon before use: THF, benzene, toluene, and *tert*-butyl alcohol from sodium, CH_2Cl_2 from P_4O_{10}. *n*-BuLi was purchased from Merck, α,α'-dichloro-*m*-xylene (**16a**) from Fluka. *t*-BuOK from Aldrich was used for the isomerization reactions of the metacyclophanediynes and sublimated before use. The acyclic diynes **9**,[5,6] **11**,[7] **12**,[8,9] **13**,[5,6] and **14**[4] as well as Schwartz's reagent (**28**)[26] were prepared according to the literature. Reactions were monitored either by GC or TLC. Column chromatography was carried out on Merck Kieselgel 60 (230−400 mesh) and alumina (Aldrich). TLC analyses were performed on precoated plates SIL G/UV_{254} and ALOX N/UV_{254}, purchased from Macherey-Nagel. ^{1}H NMR spectra were determined at 300 MHz and ^{13}C NMR spectra at 75.47 MHz if not otherwise mentioned by using the solvent as an internal standard. Assignments were based on COSY and double-resonance experiments.

***m*-Dipropargylbenzene (10).** To a cooled solution of 276 g (3.25 mol) of acetylenemagnesium chloride (**21**)[4,10] in 3 L of dry THF were added 6.0 g (60.6 mmol) of CuCl, 4.0 g (26.7 mmol) of NaI, and 70.0 g (0.40 mol) of α,α'-dichloro-*m*-xylene (**16a**), and the mixture was heated to 60 °C for 7 d with stirring. For workup it was hydrolyzed at 0 °C by slow addition to a stirred mixture of 600 mL of concentrated HCl, 2.4 kg of ice, and 600 mL of petroleum ether. The organic layer was separated, and the aqueous layer was extracted three times with 300 mL of petroleum ether. The combined organic layers were washed with 200 mL of diluted HCl and then treated with 100 mL portions of a solution of *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetate (HEDTA) (400 g of HEDTA and 80 mL of concentrated HCl in 2 L of water) until the aqueous layer no longer turned blue. After the solution was washed with brine twice and dried over $MgSO_4$, the solvent was evaporated and the residue subjected to fractionated distillation under reduced pressure to afford **10** as a colorless oil (14.8 g, 24%): bp 60 °C (0.11 mbar); UV (CH_2Cl_2) 232 nm (lg ϵ 2.47), 256 (2.56), 262 (2.36), 272 (2.19), 290 (2.19);

(25) Hubert, A. J.; Dale, J. *J. Chem. Soc.* **1965**, 3118.
(26) Buchwald, S. L.; LaMaire S. J.; Nielsen R. B.; Watson B. T.; King S. M. *Tetrahedron Lett.* **1987**, 3895.

^{1}H NMR ($CDCl_3$) δ 7.35 (s, 1H), 7.33−7.25 (m, 3H), 3.62 (d, ^4J = 2.7 Hz, 4H), 2.21 (t, ^4J = 2.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 136.5, 128.8, 127.5, 126.3, 81.9, 70.5, 24.7; HRMS *m*/*z* calcd for $C_{12}H_{10}$ (M^+) 154.0783, found 154.0729.

General Procedure for the Cyclization Reactions. In a typical run 30.0 mmol of the acyclic diyne was dissolved in 500 mL of dry THF and cooled to −78 °C whereupon 60.0 mmol of 1.6 N *n*-BuLi in *n*-hexane was added slowly with vigorous stirring. After 30 min of additional stirring, 33.0 mmol of α,α′-diiodo-*m*-xylene (**16b**)[13] was added. After warming up, the mixture was stirred at rt, until one of the educts could not be detected any more by GC. For workup the mixture was poured into concentrated NH_4Cl solution. The layers were separated, and the aqueous layer was extracted several times with CH_2Cl_2. After the combined organic layers were washed with water twice, they were dried over Na_2SO_4 and the solvent was evaporated. Column chromatography (SiO_2, CCl_4) of the residue gave the crude metacyclophanediyne which was subjected to further purification by Kugelrohr distillation.

[11]Metacyclophane-2,9-diyne (3) was synthesized from 3.6 g (30.0 mmol) of 1,8-nonadiyne (**9**)[5,6] and 11.8 g (33.0 mmol) of α,α′-diiodo-*m*-xylene (**16b**). **3**: reaction time 2 d; yield 1.60 g (24%); bp 140 °C (0.11 mbar), yellow oil; UV (CH_2Cl_2) 222 nm (lg ϵ 3.73), 254 (3.26), 292 (3.00); ^{1}H NMR ($CDCl_3$) δ 8.11 (s, 1H), 7.16 (t, ^3J = 7.5 Hz, 1H), 6.99 (d, ^3J = 7.5 Hz, 2H), 3.65 (s, 4H), 2.35 (m, 4H), 1.93 (m, 2H), 1.58 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 137.8, 127.7, 126.7, 125.8, 82.9, 78.1, 27.8, 27.0, 25.0, 18.6; HRMS *m*/*z* calcd for $C_{17}H_{18}$ (M^+) 222.1408, found 222.1385.

[4.4]Metacyclophane-2,12-diyne (4) was synthesized from 3.0 g (19.5 mmol) of *m*-dipropargylbenzene (**10**) and 7.7 g (21.5 mmol) of α,α′-diiodo-*m*-xylene (**16b**). **4**: reaction time 3 d; yield 510 mg (10%); point of decomposition 184 °C, white solid; UV (CH_2Cl_2) 230 nm (lg ϵ 2.94), 256 (2.64), 262 (2.62), 286 (1.81); ^{1}H NMR (CD_2Cl_2) δ 8.24 (s, 2H), 7.19 (t, ^3J = 7.8 Hz, 2H), 7.03 (d, ^3J = 7.8 Hz, 4H), 3.72 (s, 8H); ^{13}C NMR (50.33 MHz, CD_2Cl_2) δ 138.2, 128.3, 127.1, 126.3, 80.4, 25.3; HRMS *m*/*z* calcd for $C_{20}H_{16}$ (M^+) 256.1252, found 256.1219.

[4.4]Orthometacyclophane-2,12-diyne (5) was synthesized from 3.0 g (19.5 mmol) of *o*-dipropargylbenzene (**11**)[7] and 7.7 g (21.5 mmol) of α,α′-diiodo-*m*-xylene (**16b**). **5**: reaction time 7 d; yield 350 mg (7%); mp 157 °C, white solid; UV (CH_2Cl_2) 230 nm (lg ϵ 2.99), 246 (2.82), 256 (2.85), 260 (2.86), 268 (2.76); ^{1}H NMR ($CDCl_3$) δ 8.49 (s, 1H), 7.37−7.33 (m, 2H), 7.28−7.24 (m, 2H), 7.14 (t, ^3J = 7.5 Hz, 1H), 6.97 (d, ^3J = 7.5 Hz, 2H), 3.71 (s, 4H), 3.58 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 136.3, 135.6, 131.1, 128.6, 127.6, 127.3, 125.2, 84.3, 79.8, 24.8, 22.8; HRMS *m*/*z* calcd for $C_{20}H_{16}$ (M^+) 256.1252, found 256.1217.

(*Z*)-[10]Metacyclophane-5-ene-2,8-diyne (6) was synthesized from 10.4 g (0.10 mol) of (*Z*)-4-octene-1,7-diyne (**12**)[8,9] and 43.0 g (0.12 mol) of α,α′-diiodo-*m*-xylene (**16b**). **6**: reaction time 3 d; yield 2.70 g (13%); mp 101 °C, white solid; UV (CH_2Cl_2) 232 nm (lg ϵ 3.25), 244 (3.17); ^{1}H NMR ($CDCl_3$) δ 8.43 (s, 1H), 7.16 (t, ^3J = 7.4 Hz, 1H), 7.00 (d, ^3J = 7.4 Hz, 2H), 5.73 (m, 2H), 3.58 (s, 4H), 3.07 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 136.7, 127.6, 127.4, 126.0, 125.3, 83.2, 78.8, 24.5, 16.7; HRMS *m*/*z* calcd for $C_{16}H_{14}$ (M^+) 206.1096, found 206.1051.

[10]Metacyclophane-2,8-diyne (7) was synthesized from 3.0 g (28.3 mmol) of 1,7-octadiyne (**13**)[5,6] and 11.3 g (31.6 mmol) of α,α′-diiodo-*m*-xylene (**16b**). **7**: reaction time 3 d; yield 1.39 g (24%); mp 76 °C, white solid; UV (CH_2Cl_2) 230 nm (lg ϵ 3.22), 254 (3.12); ^{1}H NMR ($CDCl_3$) δ 8.36 (s, 1H), 7.17 (t, ^3J = 7.6 Hz, 1H), 7.00 (d, ^3J = 7.6 Hz, 2H), 3.60 (s, 4H), 2.27 (s, 4H), 1.90 (t, ^3J = 2.7 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 137.4, 127.6, 127.3, 125.6, 85.4, 77.9, 28.6, 24.6, 19.0; HRMS *m*/*z* calcd for $C_{16}H_{16}$ (M^+) 208.1252, found 208.1271.

5-Isopropylidene[9]metacyclophane-2,7-diyne (8) was synthesized from 7.5 g (56.7 mmol) of 4-isopropylidene-1,6-heptadiyne (**14**)[4] and 22.4 g (62.6 mmol) of α,α′-diiodo-*m*-xylene (**16b**). **8**: reaction time 10 d; yield 1.36 g (10%); mp 85 °C, white solid; UV (CH_2Cl_2) 218 nm (lg ϵ 2.97), 230 (3.26), 242 (3.18), 246 (3.16); ^{1}H NMR ($CDCl_3$) δ 8.69 (s, 1H), 7.15 (t, ^3J = 7.4 Hz, 1H), 7.01 (d, ^3J = 7.4 Hz, 2H), 3.56 (s, 4H), 3.05 (s, 4H), 1.78 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 136.7, 132.1, 129.7, 127.1, 125.1, 124.6, 85.0, 79.2, 24.8, 21.5 (one signal missing); HRMS *m*/*z* calcd for $C_{18}H_{18}$ (M^+) 234.1409, found 234.1403.

General Procedure for the Preparation of the Bis(dicobalt hexacarbonyl) Complexes 22−27. To a solution of the metacyclophanediyne in dry CH_2Cl_2 was added 2.2 equiv of $Co_2(CO)_8$. After the solution was stirred overnight at rt, the solvent was removed and the residue was purified by column chromatography on neutral alumina containing 6% water. The complexes were eluted with petroleum ether and isolated quantitatively. For elemental analysis it was necessary to subject them to further column chromatography on silica gel using petroleum ether as eluent; considerable amounts of the complexes decomposed during this purification. The reported yields refer to the amount of bis(dicobalt hexacarbonyl) complexes isolated after the second column chromatography. Crystallization of the complexes **22** and **24**−**27** in petroleum ether/ether mixtures yielded dark red single crystals.

Bis(dicobalt hexacarbonyl)[11]metacyclophane-2,9-diyne (22) was synthesized from 130 mg (0.58 mmol) of [11]metacyclophane-2,9-diyne (**3**) and 448 mg (1.31 mmol) of $Co_2(CO)_8$ in 30 mL of CH_2Cl_2. **22**: yield 312 mg (67%); point of decomposition 156 °C, red crystals; ^{1}H NMR ($CDCl_3$) δ 7.26−7.23 (m, 2H), 7.14 (d, ^3J = 7.8 Hz, 2H), 4.20 (s, 4H), 3.01 (t, ^3J = 8.0 Hz, 4H), 1.87 (m, 4H), 1.65 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 199.9, 140.7, 129.1, 128.3, 127.5, 98.3, 96.9, 41.9, 33.8, 29.4, 26.7. Anal. Calcd for $C_{29}H_{18}Co_4O_{12}$: C, 43.86; H, 2.28. Found: C, 43.98; H, 2.38.

Bis(dicobalt hexacarbonyl)[4.4]metacyclophane-2,12-diyne (23) was synthesized from 40 mg (0.16 mmol) of [4.4]metacyclophane-2,12-diyne (**4**) and 118 mg (0.35 mmol) of $Co_2(CO)_8$ in 10 mL of CH_2Cl_2. **4**: yield 95 mg (73%); point of decomposition 169 °C, red crystals; ^{1}H NMR ($CDCl_3$) δ 7.20 (m, 2H), 7.06 (m, 4H), 6.94 (s, 2H), 4.07 (s, 8H); ^{13}C NMR ($CDCl_3$) δ 199.7, 140.0, 129.9, 128.9, 127.7, 96.3, 41.6. Anal. Calcd for $C_{32}H_{16}Co_4O_{12}$: C, 46.41; H, 1.95. Found: C, 46.66; H, 2.22.

Bis(dicobalt hexacarbonyl)[4.4]orthometacyclophane-2,12-diyne (24) was synthesized from 100 mg (0.39 mmol) of [4.4]orthometacyclophane-2,12-diyne (**5**) and 300 mg (0.88 mmol) of $Co_2(CO)_8$ in 20 mL of CH_2Cl_2. **5**: yield 205 mg (64%); point of decomposition 98 °C, red crystals; ^{1}H NMR ($CDCl_3$) δ 7.44 (s, 1H), 7.36−7.16 (m, 7H), 4.28 (s, 4H), 3.69 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 199.7, 139.4, 138.1, 130.5, 130.2, 129.8, 127.6, 127.3, 97.9, 94.3, 42.2, 36.7. Anal. Calcd for $C_{32}H_{16}Co_4O_{12}$: C, 46.41; H, 1.95. Found: C, 46.71; H, 2.24.

Bis(dicobalt hexacarbonyl)-(*Z*)-[10]metacyclophane-5-ene-2,8-diyne (25) was synthesized from 150 mg (0.73 mmol) of (*Z*)-[10]metacyclophane-5-ene-2,8-diyne (**6**) and 616 mg (1.80 mmol) of $Co_2(CO)_8$ in 20 mL of CH_2Cl_2. **25**: yield 193 mg (34%); point of decomposition 135 °C, red crystals; ^{1}H NMR ($CDCl_3$) δ 7.29−7.20 (m, 2H), 7.09 (d, ^3J = 6.8 Hz, 2H), 5.64 (s, 2H), 4.15 (s, 4H), 3.72 (d, ^3J = 3.1 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 199.7, 139.8, 129.4, 128.6, 127.6, 127.1, 96.7, 95.6, 41.6, 33.8. Anal. Calcd for $C_{28}H_{14}Co_4O_{12}$: C, 43.22; H, 1.81. Found: C, 43.05; H, 1.84.

Bis(dicobalt hexacarbonyl)[10]metacyclophane-2,8-diyne (26) was synthesized from 40 mg (0.19 mmol) of [10]metacyclophane-2,8-diyne (**7**) and 150 mg (0.44 mmol) of $Co_2(CO)_8$ in 10 mL of CH_2Cl_2. **26**: yield 91 mg (61%); point of decomposition 125 °C, red crystals; ^{1}H NMR ($CDCl_3$) δ 7.35 (s, 1H), 7.26 (t, ^3J = 7.2 Hz, 1H), 7.15 (d, ^3J = 7.2 Hz, 2H), 4.21 (s, 4H), 2.93 (t, ^3J = 6.4 Hz, 4H), 1.38 (t, ^3J = 6.4 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 199.9, 139.9, 130.7, 129.0, 127.8, 98.2, 97.0, 42.5, 34.2, 31.1. Anal. Calcd for $C_{28}H_{16}Co_4O_{12}$: C, 43.11; H, 2.07. Found: C, 43.17; H, 2.24.

Bis(dicobalt hexacarbonyl)-5-isopropylidene[9]metacyclophane-2,7-diyne (27) was synthesized from 100 mg (0.43 mmol) of 5-isopropylidene[9]metacyclophane-2,7-diyne (**8**) and 335 mg (0.98 mmol) of $Co_2(CO)_8$ in 25 mL of CH_2Cl_2. **8**: yield 103 mg (30%); point of decomposition 131 °C, red crystals; ^{1}H NMR ($CDCl_3$) δ 7.53 (s, 1H), 7.28 (t, ^3J = 6.9 Hz, 1H), 7.12 (d, ^3J = 6.9 Hz, 2H), 4.29 (s, 4H), 3.26 (br s, 4H), 1.77 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 199.8, 139.2, 131.8, 131.1, 130.5, 129.4, 126.5, 98.3, 95.3, 42.7, 34.8, 20.9. Anal. Calcd for $C_{30}H_{18}Co_4O_{12}$: C, 44.70; H, 2.25. Found: C, 44.61; H, 2.42.

(*Z*,*Z*)-[11]Metacyclophane-2,9-diene (29). To a solution of 222 mg (1.0 mmol) of [11]metacyclophane-2,9-diyne (**3**) in 25 mL of dry toluene was added 1.30 g (5.0 mmol) of Schwartz's

reagent (**28**) at once. The reaction was monitored by TLC. After 4 d **3** could not be detected any more and the solution was cooled to 0 °C. Subsequently 3.0 mL (6.0 mmol) of 2 N HCl was added at once and the mixture was stirred for additional 10 min. The suspension was filtered, and the residue was washed several times with CH_2Cl_2. The filtrate was dried over Na_2SO_4 and the solvent evaporated in vacuo. Crude **29** could be isolated by column chromatography (SiO_2, petroleum ether). Further purification by Kugelrohr distillation yielded pure **29** as a colorless oil: yield 76 mg (34%); bp 115 °C (0.02 mbar); ^{1}H NMR ($CDCl_3$) δ 7.24 (t, ^3J = 7.5 Hz, 1H), 7.21 (s, 1H), 7.08 (d, ^3J = 7.5 Hz, 2H), 5.70−5.50 (m, 4H), 3.41 (d, ^3J = 7.8 Hz, 4H), 2.25 (q, ^3J = 6.4 Hz, 4H), 1.51 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 140.8, 131.5, 128.5, 128.2, 127.9, 125.9, 33.2, 29.0, 27.9, 26.4; HRMS *m*/*z* calcd for $C_{17}H_{22}$ (M^+) 226.1722, found 226.1713.

(*Z*,*Z*)-[4.4]Metacyclophane-2,12-diene (30). The reaction procedure was the same as that described for **29**, using 200 mg (0.78 mmol) of [4.4]metacyclophane-2,12-diyne (**4**) in 10 mL of dry benzene and 800 mg (3.1 mmol) of Schwartz's reagent (**28**). Reaction time was 12 h. The mixture was quenched by 1.6 mL (3.2 mmol) of HCl. Crude **30** could be isolated by column chromatography (SiO_2, CCl_4). Further purification by Kugelrohr distillation yielded **30** as a white solid at 145 °C (0.04 mbar). After crystallization in petroleum ether/ether at 0 °C a colorless single crystal could be isolated: yield 88 mg (43%); mp 148 °C; ^{1}H NMR ($CDCl_3$) δ 7.43 (s, 2H), 7.23 (t, ^3J = 7.4 Hz, 2H), 7.08 (d, ^3J = 7.4 Hz, 4H), 5.67 (t, ^3J = 6.0 Hz, 4H), 3.47 (d, ^3J = 6.0 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 140.4, 129.3, 129.1, 128.5, 126.2, 33.2; HRMS *m*/*z* calcd for $C_{20}H_{20}$ (M^+) 260.1565, found 260.1566.

(*Z*,*Z*)-[4.4]Orthometacyclophane-2,12-diene (31). The reaction procedure was the same as that described for **29**, using 200 mg (0.78 mmol) of [4.4]orthometacyclophane-2,12-diyne (**5**) in 10 mL of dry benzene and 460 mg (1.8 mmol) of Schwartz's reagent (**28**). Reaction time was 7 h. The mixture was quenched by 1.4 mL (2.8 mmol) of HCl. Crude **31** could be isolated by column chromatography (SiO_2, CCl_4). Further purification by Kugelrohr distillation yielded **31** as a white, waxy solid at 115 °C (0.04 mbar): yield 134 mg (66%); mp 39 °C; ^{1}H NMR ($CDCl_3$) δ 7.61 (s, 1H), 7.25 (t, ^3J = 7.6 Hz, 1H), 7.18 (s, 4H), 7.07 (d, ^3J = 7.6 Hz, 2H), 5.74 (dtt, ^3J = 10.8, 7.5 Hz, ^4J = 2.4 Hz, 2H), 5.53 (dt, ^3J = 10.8, 5.5 Hz, 2H), 3.46 (d, ^3J = 7.5 Hz, 4H), 3.24 (dd, ^3J = 5.5 Hz, ^4J = 2.4 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 139.9, 138.9, 133.3, 130.3, 128.8, 128.6, 126.8, 126.6, 125.8, 33.6, 31.8; HRMS *m*/*z* calcd for $C_{20}H_{20}$ (M^+) 260.1565, found 260.1536.

(*Z*,*Z*,*Z*)-[10]Metacyclophane-2,5,8-triene (32). The reaction procedure was the same as that described for **29**, using 160 mg (0.78 mmol) of (*Z*)-[10]metacyclophane-5-ene-2,8-diyne (**6**) in 25 mL of dry toluene and 680 mg (2.6 mmol) of Schwartz's reagent (**28**). Reaction time was 4 d. The mixture was quenched by 1.5 mL (3.0 mmol) of HCl. Pure **32** could be isolated by column chromatography (SiO_2, petroleum ether) as a colorless oil: yield 55 mg (33%); ^{1}H NMR ($CDCl_3$) δ 7.40 (s, 1H, C16-H_{aromat}), 7.23 (t, ^3J = 7.4 Hz, 1H, C13-H_{aromat}), 7.04 (d, ^3J = 7.4 Hz, 2H, C12-H_{aromat}, C14-H_{aromat}), 5.73 (dtt, ^3J = 11.0, 7.2 Hz, ^4J = 1.8 Hz, 2H, C2-H_{olefin}, C9-H_{olefin}), 5.50 (dtt, ^3J = 11.0, 7.0 Hz, ^4J = 1.0 Hz, 2H, C3-H_{olefin}, C8-H_{olefin}), 5.37 (tt, ^3J = 4.9 Hz, ^4J = 1.1 Hz, 2H, C5-H_{olefin}, C6-H_{olefin}), 3.40 (d, ^3J = 7.2 Hz, 4H, Ph-CH_2), 2.70 (t, ^3J = 6.0 Hz, 4H, ═C−CH_2); ^{13}C NMR ($CDCl_3$) δ 140.1, 131.1, 128.9, 128.7, 127.2, 126.1, 126.0, 33.8, 26.5; HRMS *m*/*z* calcd for $C_{16}H_{18}$ (M^+) 210.1409, found 210.1392.

(*Z*,*Z*)-[10]Metacyclophane-2,8-diene (33). The reaction procedure was the same as that described for **29**, using 200 mg (0.96 mmol) of [10]metacyclophane-2,8-diyne (**7**) in 25 mL of dry benzene and 785 mg (3.0 mmol) of Schwartz's reagent (**28**). Reaction time was 44 h. The mixture was quenched by 2.0 mL (4.0 mmol) of HCl. Crude **33** could be isolated by column chromatography (SiO_2, petroleum ether). Further purification by Kugelrohr distillation yielded **33** as a colorless oil at 115 °C (0.04 mbar), which solidified when cooled: yield 118 mg (57%); mp 23 °C; ^{1}H NMR ($CDCl_3$) δ 7.34 (s, 1H), 7.21 (t, ^3J = 7.5 Hz, 1H), 7.00 (d, ^3J = 7.5 Hz, 2H), 5.74 (q, ^3J = 8.9 Hz, 2H), 5.35 (dt, ^3J = 10.7, 7.7 Hz, 2H), 3.35 (d, ^3J = 8.0 Hz, 4H), 2.18 (q, ^3J = 6.2 Hz, 4H), 1.30 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 141.8, 132.5, 129.5, 128.7, 127.6, 125.4, 33.8, 26.8, 26.5; HRMS *m*/*z* calcd for $C_{16}H_{20}$ (M^+) 212.1565, found 212.1550.

5-Isopropylidene-(*Z*,*Z*)-[9]metacyclophane-2,7-diene (34). The reaction procedure was the same as that described for **29**, using 222 mg (0.95 mmol) of 5-isopropylidene[9]-metacyclophane-2,7-diyne (**8**) in 25 mL of dry toluene and 540 mg (2.1 mmol) of Schwartz's reagent (**28**). Reaction time was 20 h. The mixture was quenched by 1.5 mL (3.0 mmol) of HCl. Pure **34** could be isolated by column chromatography (SiO_2, CCl_4) as a colorless oil: yield 126 mg (56%); ^{1}H NMR ($CDCl_3$) δ 7.72 (s, 1H), 7.23 (t, ^3J = 7.5 Hz, 1H), 7.03 (d, ^3J = 7.5 Hz, 2H), 5.72 (dtt, ^3J = 10.8, 7.3 Hz, ^4J = 1.7 Hz, 2H), 5.47 (dt, ^3J = 10.8, 6.9 Hz, 2H), 3.42 (d, ^3J = 7.3 Hz, 4H), 2.71 (d, ^3J = 6.9 Hz, 4H), 1.75 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 139.3, 132.9, 129.5, 128.5, 127.7, 126.5, 125.3, 32.8, 31.7, 20.5 (one signal missing); HRMS *m*/*z* calcd for $C_{18}H_{22}$ (M^+) 238.1722, found 238.1686.

General Procedure for the Isomerization of the Metacyclophanediynes 3−8 and 1,3-Dipropargylbenzene (10) with *t*-BuOK. The solution of the diyne in dry THF was cooled to −78 °C. After addition of *t*-BuOH and *t*-BuOK the mixture was stirred for 1 h at the same temperature and was then allowed to warm up to rt or was heated to 50 °C (see below). When the educt could not be detected by TLC any more, water and CH_2Cl_2 was added successively. The layers were separated, and the aqueous layer was extracted several times with CH_2Cl_2. After the combined organic layers were dried over Na_2SO_4, the solvent was evaporated and the residue was subjected to column chromatography on SiO_2 with petroleum ether as eluent.

Isomerization of [11]Metacyclophane-2,9-diyne (3). A solution of 100 mg (0.45 mmol) of **3** in 25 mL of THF was treated with 135 mg (1.2 mmol) of *t*-BuOK and 165 mg of *t*-BuOH. Reaction time 12 h at rt. For workup 20 mL of H_2O was used. After column chromatography two fractions could be isolated. The first contained a mixture of the two stereoisomeric bisallenes **36a** and (±)-**36b**, the second consisted of the alleneyne **37**. **36a,b**: yield 42 mg (42%); mp 87 °C, yellowish solid; R_f (SiO_2, petroleum ether) 0.25; IR (KBr) 1941 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.96 (s, 1H), 7.23 (t, ^3J = 7.5 Hz, 1H), 6.98 (d, ^3J = 7.5 Hz, 2H), 6.08 (m, 2H), 5.45 (m, 2H), 2.52−1.08 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 206.4, 135.3, 128.9, 125.6, 123.6, 95.2, 93.7, 30.4, 29.8, 28.6 (**36a**); 206.6, 135.8, 128.7, 125.6, 124.6, 94.5, 93.6, 31.7, 30.5, 28.1 ((±)-**36b**); HRMS *m*/*z* calcd for $C_{17}H_{18}$ (M^+) 222.1409, found 222.1419. **37**: yield 10 mg (10%); viscous, yellow oil; R_f (SiO_2, petroleum ether) 0.11; IR (neat) 2196, 1952 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.02 (s, 1H), 7.18 (t, ^3J = 7.5 Hz, 1H), 6.99 (d, ^3J = 7.5 Hz, 1H), 6.94 (d, ^3J = 7.5 Hz, 1H), 6.11 (m, 1H), 5.46 (m, 1H), 3.67 (d, ^2J = 19.4 Hz, 1H), 3.48 (d, ^2J = 19.4 Hz, 1H), 2.31−0.83 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 206.2, 137.9, 135.4, 128.2, 126.1, 125.5, 125.3, 94.9, 94.0, 83.4, 78.6, 29.7, 28.9, 28.3, 27.6, 24.9, 19.0; HRMS *m*/*z* calcd for $C_{17}H_{18}$ (M^+) 222.1409, found 222.1406.

Isomerization of [4.4]Metacyclophane-2,12-diyne (4). A solution of 100 mg (0.39 mmol) of **4** in 20 mL of THF was treated with 105 mg (0.94 mmol) of *t*-BuOK and 105 mg of *t*-BuOH. Reaction time was 12 h at rt. For workup 20 mL of H_2O was used. After column chromatography a mixture of two isomeres **40** and **41** could be isolated which could neither be separated by HPLC nor by further column chromatography. **40**, **41**: yield 50 mg (50%); point of decomposition 135 °C, white solid; R_f (SiO_2, petroleum ether) 0.12; IR (KBr) 1943 cm^{-1}; ^{1}H NMR (200 MHz, CS_2/CD_2Cl_2) δ 7.94 (s, 2H, C10-*H*, C20-*H*), 7.77, 7.52 (s, 1 H each, C10′-*H*, C20′-*H*), 7.25−7.16 (m, 2H each, C7-*H*, C17-*H*, C7′-*H*, C17′-*H*), 7.08−6.95 (m, 4H each, C6-*H*, C8-*H*, C16-*H*, C18-*H*, C6′-*H*, C8′-*H*, C16′-*H*, C18′-*H*), 6.23−6.15 (m, 2H each, Ph*H*C═C═CH), 5.67−5.55 (m, 2H each, PhHC═C═C*H*), 3.52 (t, ^3J = 12.2 Hz, 4H, C4′-*H*, C11′-*H*), 3.37−3.26 (m, 4H, C4-*H*, C14-*H*); ^{13}C NMR (50.33 MHz, CS_2/CD_2Cl_2) δ 206.4, 206.3, 140.7, 140.6, 135.6, 131.6, 129.6, 129.2, 129.0, 128.0, 127.4, 127.0, 126.7, 126.4, 124.1, 96.4, 95.6, 95.3, 94.5, 37.9, 37.7 (one signal missing); HRMS *m*/*z* calcd for $C_{20}H_{16}$ (M^+) 256.1252, found 256.1262. The reaction was repeated with a 5-fold excess of *t*-BuOK at 50 °C, but only polymers were found.

Isomerization of [4.4]Orthometacyclophane (5). A solution of 100 mg (0.39 mmol) of **5** in 20 mL of THF was treated with 105 mg (0.94 mmol) of *t*-BuOK and 105 mg of

Table 3. Reaction Conditions and Yields for the Isomerization of 6

			yield, %		
temp, °C	time, h	*t*-BuOK/*t*-BuOH	**47**	**48**	**49**
25	12	214 mg	45		
50	12	420 mg	40	11	3
50	24	820 mg	28	54	6

t-BuOH. Reaction time was 1 h at rt. For workup 20 mL of H_2O was used. After column chromatography the two isomeric tetraenes **43** and **44** could be isolated as well as the dieneyne **42**. **42**: yield 49 mg (49%); mp 77 °C, white solid; R_f (SiO_2, petroleum ether) 0.08; IR (CCl_4) 992 cm^{-1}; UV (CH_2Cl_2) 238 nm (lg ϵ 4.36), 264 (4.33), 330 (4.13); ^1H NMR ($CDCl_3$) δ 8.12 (dd, ^3J = 16.1, 10.8 Hz, 1H, PhHC=C*H*), 7.77 (s, 1H, C20-H_{aromat}), 7.51 (d, ^3J = 7.5 Hz, 1H, H_{aromat}), 7.35−7.14 (m, 6H, H_{aromat}), 6.79 (d, ^3J = 10.9 Hz, 1H, PhHC=CHHC=C*H*), 6.73 (d, ^3J = 16.1 Hz, 1H, Ph*H*C=CH), 6.53 (t, ^3J = 10.8 Hz, 1H, PhHC=CH*H*C=CH), 2.93−2.84 (m, 4H, CH_2); ^{13}C NMR ($CDCl_3$) δ 140.0, 138.2, 137.4, 135.8, 132.1, 131.7, 131.1, 131.0, 130.9, 130.7, 128.3, 127.7, 126.6, 126.5, 120.1, 94.2, 83.5, 33.0, 23.0 (one signal missing); HRMS *m*/*z* calcd for $C_{20}H_{16}$ (M^+) 256.1252, found 256.1241. **43**: yield 11 mg (11%); mp 76 °C, white solid; R_f (SiO_2, petroleum ether) 0.20; IR (CCl_4) 977 cm^{-1}; UV (CH_2Cl_2) 244 nm (lg ϵ 4.17), 270 (4.12), 322 (3.75); ^1H NMR ($CDCl_3$) δ 7.72 (s, 1H, C20-H_{aromat}), 7.38−7.33 (m, 3H, *o*-Ph-*H*, C17-H_{aromat}), 7.27 (dd, ^3J = 5.8 Hz, ^4J = 3.4 Hz, 2H, *o*-Ph-*H*), 7.20 (d, ^3J = 7.1 Hz, 2H, C16-H_{aromat}, C18-H_{aromat}), 6.89 (d, ^3J = 16.2 Hz, 2H, Ph*H*C=CH), 6.77 (d, ^3J = 11.5 Hz, 2H, PhHC=CHHC=C*H*), 6.61 (dd, ^3J = 16.2, 7.6 Hz, 2H, PhHC=C*H*), 6.45 (dd, ^3J = 11.5, 7.6 Hz, 2H, PhHC=CH*H*C=CH); ^{13}C NMR ($CDCl_3$) δ 137.1, 136.3, 133.6, 131.2, 130.4, 129.5, 129.3, 129.0, 128.0, 127.2, 127.1; HRMS *m*/*z* calcd for $C_{20}H_{16}$ (M^+) 256.1252, found 256.1200. **44**: yield 1 mg (1%); mp 87 °C, white solid; R_f (SiO_2, petroleum ether) 0.23; UV (CH_2Cl_2) 220 nm (lg ϵ 4.02), 242 (4.10), 286 (3.97); ^1H NMR ($CDCl_3$) δ 7.05 (dd, ^3J = 5.5 Hz, ^4J = 3.3 Hz, 2H, *o*-Ph-*H*), 6.85 (t, ^3J = 7.3 Hz, 1H, C17-H_{aromat}), 6.74 (d, ^3J = 7.3 Hz, 2H, C16-H_{aromat}, C18-H_{aromat}), 6.73 (s, 1H, C20-H_{aromat}), 6.67 (dd, ^3J = 5.5 Hz, ^4J = 3.3 Hz, 2H, *o*-Ph-*H*), 6.53 (d, ^3J = 12.8 Hz, 2H, Ph*H*C=CH), 6.19 (dd, ^3J = 12.8, 6.2 Hz, 2H, PhHC=C*H*), 6.17 (d, ^3J = 13.6 Hz, 2H, PhHC=CHHC=C*H*), 5.95 (dd, ^3J = 13.6, 6.2 Hz, 2H, PhHC=CH*H*C=CH); ^{13}C NMR ($CDCl_3$) δ 137.8, 137.5, 131.4, 130.9, 129.8, 128.0, 126.9, 125.9, 125.7, 124.9, 122.5. Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.44; H, 6.31.

Isomerization of (*Z*)-[10]Metacyclophane-5-ene-2,8-diyne (6). The isomerization of **6** was carried out in three different variations, using 150 mg (0.73 mmol) of **6** in 35 mL of dry THF as starting material. Quenching was achieved with 25 mL of H_2O. The other reaction conditions and yields are summarized in Table 3. **47**: mp 35 °C, yellowish solid; R_f (SiO_2, petroleum ether) 0.09; IR (neat) 990 cm^{-1}; UV (CH_2Cl_2) 258 nm (lg ϵ 4.20), 344 (3.91); ^1H NMR ($CDCl_3$) δ 7.98 (dd, ^3J = 15.1, 11.0 Hz, 1H, C3-*H*), 7.59 (s, 1H, C16-H_{aromat}), 7.30 (t, ^3J = 8.0 Hz, 1H, C13-H_{aromat}), 7.16 (d, ^3J = 8.5 Hz, 1H, H_{aromat}), 7.13 (d, ^3J = 8.0 Hz, 1H, H_{aromat}), 6.76 (d, ^3J = 10.9 Hz, 1H, C1-*H*), 6.46 (t, ^3J = 10.9 Hz, 1H, C2-*H*), 6.25−6.15 (m, 2H, C4-*H*, C5-*H*), 5.57 (dt, ^3J = 11.5, 2.2 Hz, 1H, C6-*H*), 2.82−2.72 (m, 4H, CH_2); ^{13}C NMR ($CDCl_3$) δ 140.0, 137.3, 134.6, 132.4, 132.2, 130.9, 130.3, 128.3, 127.3, 126.9, 126.2, 108.0, 98.1, 82.8, 32.7, 23.4; HRMS *m*/*z* calcd for $C_{16}H_{14}$ (M^+) 206.1096, found 206.1064. **48**: yellow, waxy solid; R_f (SiO_2, petroleum ether) 0.22; IR (neat) 967 cm^{-1}; UV (CH_2Cl_2) 242 nm (lg ϵ 4.40), 270 (4.25); ^1H NMR ($CDCl_3$) δ 7.36 (t, ^3J = 7.0 Hz, 1H, C13-H_{aromat}), 7.33 (s, 1H, C16-H_{aromat}), 7.21 (d, ^3J = 7.0 Hz, 2H, C12-H_{aromat}, C14-H_{aromat}), 6.71 (d, ^3J = 11.2 Hz, 2H, C1-*H*, C10-*H*), 6.53 (dd, ^3J = 16.9, 6.3 Hz, 2H, C3-*H*, C8-*H*), 6.46 (dd, ^3J = 11.2, 6.3 Hz, 2H, C2-*H*, C9-*H*), 6.44 (ddd, ^3J = 16.9, 3.4 Hz, ^4J = 1.4 Hz, 2H, C4-*H*, C7-*H*), 6.15 (dd, ^3J = 3.4 Hz, ^4J = 1.4 Hz, 2H, C5-*H*, C6-*H*); ^{13}C NMR ($CDCl_3$) δ 136.2, 131.7, 130.6, 130.3, 130.0, 129.6, 128.3, 127.1, 125.7; HRMS *m*/*z* calcd for $C_{16}H_{14}$ (M^+) 206.1096, found 206.1106. **49**: yellow, waxy solid; R_f (SiO_2, petroleum ether) 0.13; UV (CH_2Cl_2) 232 nm (lg ϵ 3.46), 250 (3.50), 288 (3.36); ^1H NMR ($CDCl_3$) δ 7.47−7.39 (m, 3H), 7.31−7.23 (m, 3−4H), 6.91 (d, ^3J = 11.5 Hz, 1H, C1-*H*), 6.81−6.67 (2−3H, two signals could be assigned: 6.80 (d, ^3J = 10.9 Hz, 1H, C10-*H*), 6.71 (t, ^3J = 10.9 Hz, 1H, C9-*H*)), 6.52−6.40 (2−3H, two signals could be assigned: 6.49 (dd, ^3J = 11.0, 5.9 Hz, 1H, C4-*H*), 6.43 (dd, ^3J = 9.6, 5.9 Hz, 1H, C5-*H*)), 6.17 (dd, ^3J = 11.5, 3.8 Hz, 1H, C2-*H*), 5.90 (dd, ^3J = 11.0, 3.8 Hz, 1H, C3-*H*); ^{13}C NMR (50.33 MHz, $CDCl_3$) δ 138.5, 136.7, 135.7, 134.9, 133.4, 129.8, 129.5, 129.4, 129.1, 128.8, 127.9, 118.8, 108.9, 107.6 (two signals missing); HRMS *m*/*z* calcd for $C_{16}H_{14}$ (M^+) 206.1096, found 206.1094.

Isomerization of [10]Metacyclophane-2,8-diyne (7). A solution of 100 mg (0.48 mmol) of **7** in 25 mL of THF was treated with 250 mg (2.2 mmol) of *t*-BuOK and 250 mg of *t*-BuOH. Reaction time was 12 h at rt. For workup 20 mL of H_2O was used. After column chromatography two compounds could be isolated, but one of them (R_f (SiO_2, petroleum ether) 0.33) decomposed during ^1H NMR analysis. Signals in the region between δ = 6.1 and 5.8 indicated that this compound could have the bisallenic structure **38**. The second compound was assigned to the alleneyne **39**: yield 46 mg (46%); yellow, viscous oil; R_f (SiO_2, petroleum ether) 0.22; IR (neat) 2222, 1937 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.28 (s, 1H), 7.20 (t, ^3J = 8.2 Hz, 1H), 7.00 (d, ^3J = 8.2 Hz, 1H), 6.97 (d, ^3J = 8.4 Hz, 1H), 6.14 (d, ^4J = 6.3 Hz, 1H), 5.90 (q, J = 7.5 Hz, 1H), 3.62 (d, ^2J = 20.4 Hz, 1H), 3.52 (d, ^2J = 20.4 Hz, 1H), 2.49 (m, 2H), 2.13−1.60 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 207.4, 137.0, 135.0, 128.3, 126.0, 125.4, 124.8, 95.5, 94.6, 85.9, 78.0, 32.0, 27.4, 27.3, 24.5, 19.3; HRMS *m*/*z* calcd for $C_{16}H_{16}$ (M^+) 208.1252, found 208.1209.

Isomerization of *m*-Dipropargylbenzene (10). A solution of 154 mg (1.0 mmol) of **10** in 60 mL of THF was treated with 561 mg (5.0 mmol) of *t*-BuOK and 561 mg of *t*-BuOH. Reaction time was 12 h at 50 °C. For workup 30 mL of H_2O was used. After column chromatography 1,3-bis(1-propynyl)-benzene (**35**) could be isolated quantitatively as a colorless oil; bp 85 °C (0.61 mbar) (lit.[21] bp 86 °C (0.53 mbar)); R_f (SiO_2, petroleum ether) 0.13; ^1H NMR (200 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.23−7.06 (m, 3H), 1.95 (s, 6H). The analytical data correspond to those described in the literature.[21]

He I PE spectra. The PE spectra of **3** and **6**−**8** were recorded on a Perkin-Elmer PS18 spectrometer. The recording temperatures were as follows: **3**, 40 °C; **6**, 95 °C; **7**, 45 °C; **8**, 70 °C. In the case of **4** and **5** the samples decomposed during recording. The calibration was performed with Ar (15.76 and 15.94 eV) and Xe (12.13 and 13.44 eV). A resolution of 20 meV on the $^2P_{3/2}$ Ar line was obtained.

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Supporting Information Available: ^1H NMR and ^{13}C NMR spectra of **3**, **8**, **10**, **29**−**34**, **36**, **37**, **39**−**43** and **47** (25 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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