Dichlorocarbene Addition to [5]Metacyclophane; Experimental and Calculational Evidence for a [1,5] Sigmatropic Chlorine Shift in a Bridged Cycloheptatriene

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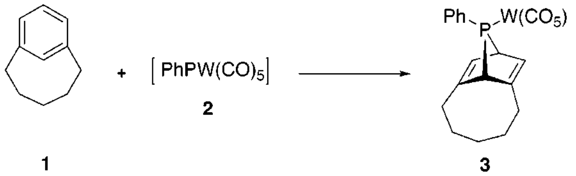
In contrast to the terminal phosphinidene complex $PhPW(CO)_5$ (**2**), which adds to [5]metacyclophane (**1**) in a 1,4-fashion, dichlorocarbene preferentially adds in a 1,2-fashion to the formal “anti-Bredt” type double bond of the aromatic ring of **1** to afford the norcaradiene **11b**, which immediately rearranges to the bridged cycloheptatriene **12b** and further by a [1,5] sigmatropic chlorine migration to the isomeric **13b** as the first observable product. More slowly, the latter isomerizes via a dissociative mechanism to give **15b**. A computational study supports the notion that the [1,5] chlorine migration in the rearrangement **12b** → **13b**, for which an activation barrier of 70.2 kJ mol^{-1} was calculated, is essentially concerted with minor charge separation. In contrast, the analogous [1,5] chlorine migration in the flat model compound 7,7-dichlorocycloheptatriene (**12a**) displays features of a dissociative pathway.

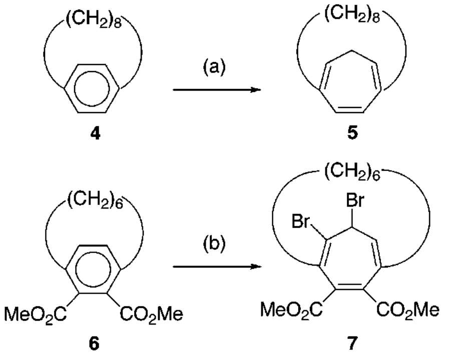
Introduction

Small strained cyclophanes keep capturing the imagination of many scientists.[1] The recent synthesis of a kinetically stabilized derivative of [1.1]paracyclophane by Tsuji et al. may serve to illustrate how the boundaries are being pushed toward ever more strained representatives of this class of compounds.[1c,2] With regard to the metacyclophanes, progress is being made in the investigation of their reactivity. We recently reported the unprecedented 1,4-addition of the terminal phosphinidene complex $PhPW(CO)_5$ (**2**) to [5]metacyclophane (**1**), the smallest member of this series that is stable at room temperature, to furnish the 7-phosphanorbornadiene derivative **3** (Scheme 1).[3] In this context, it became desirable to study the behavior of carbenes, the parent analogues of phosphinidenes, to investigate if they add to **1** in an analogous 1,4 fashion under formation of a bridged norbornadiene derivative.

Scheme 1



Scheme 2[a]



[a] (a) CH_2N_2, CuCl, rt; (b) $CHBr_3$, TEBA, NaOH, CH_2Cl_2, 6 h, rt.

At this point it is appropriate to briefly discuss the current knowledge about carbene additions to benzene rings in general and to strained cyclophanes in particular. Carbene additions to benzene are well known. Thus, methylene or dicyanocarbene add under formation of a cycloheptatriene or a stable norcaradiene, respectively.[4] In contrast, the more widely applied dichlorocarbene, which is conveniently generated from chloroform and a strong base, does not react with benzene itself. It does, however, react with aromatics in which the benzene ring is incorporated in a more extended conjugated system; this reduces the loss of resonance energy on addition. For instance, addition to naphthalene or anthracene proceeds smoothly.[5] In the case of small, strained paracyclophanes, addition of methylene (Scheme 2, **4** → **5**)[6a] and of dibromocarbene (**6** → **7**) [6b] to an isolated benzene ring has been

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(1) For recent reviews, see: (a) Bodwell, G. J. *Angew. Chem.* **1996**, *108*, 2221; *Angew. Chem., Int. Ed. Eng.* **1996**, *35*, 2085. (b) Bickelhaupt, F.; de Wolf, W. H. *J. Phys. Org. Chem.* **1998**, *11*, 362. (c) Tsuji, T. In *Advances in Strain and Interesting Organic Molecules*; Halton. B., Ed.; JAI Press: Stamford, 1999; Vol. 7, 103−152.

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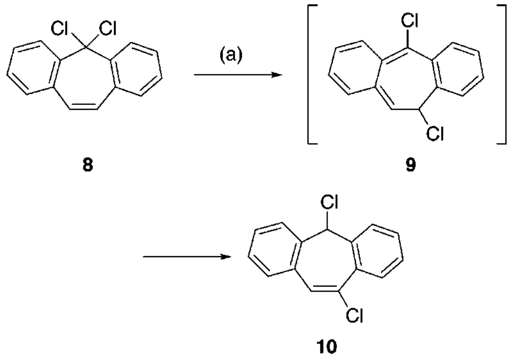
10.1021/jo000197d CCC: $19.00

Scheme 3[a]



[a] (a) 180 °C (ref 10).

reported; relief of strain in the cyclophane is a driving force for the addition in these cases.

During our investigations on the addition of a dichlorocarbene to **1**, it was found that the initially formed cycloheptatriene underwent successive rearrangements to more stable products. One of these rearrangements appeared to proceed by a [1,5] sigmatropic chlorine migration, which added a new and promising dimension to our research as a literature survey revealed that examples of sigmatropic chlorine migrations are limited.[7−9] Both [1,3] and [1,5] sigmatropic chlorine migrations have been reported for chloromethyl isocyanate[8a−c] and for chlorocyclohexadienones,[8d,e] respectively; this has also been subject to theoretical analysis.[9] It was demonstrated that in both cases the Cl shift is accelerated by the interaction of a chlorine lone pair with a low-lying LUMO (lone pair-LUMO-mediated pericyclic reaction). In the case of cycloheptatrienes, only one clear-cut example has been reported.[10] The rearrangement of the dibenzo-annelated cycloheptatriene **8** to **10** was assumed to proceed via the intermediate **9**, which was believed to arise from a [1,5] chlorine migration (Scheme 3). The driving force for this migration was ascribed to the relief of crowding between the equatorial chlorine substituent and the peri-hydrogen atoms in **8**. Neither 5,5-dichloro-5*H*-benzocycloheptene nor 7,7-dichlorocycloheptatriene (**12a**) undergo this migration. However, it has been documented that in apolar solvents (toluene, THF), **12a** is in rapid equilibrium with covalent 1-, 2-, and 3-chlorosubstituted 7-chlorocycloheptatriene.[11] In more polar solvents (CH_2Cl_2), dissociation to ion paired and free chlorotropylium ions was observed. The nature of the interconversion of the covalently bonded species remained unclear; it was suggested that both a dissociative mechanism or a mechanism with a limited charge separation in the transition state might be operating.

[1,5] Sigmatropic rearrangements in cycloheptatrienes have been the subject of extensive research.[7] Hydrogen,[12] tin,[13] and boron[14] migrations have been reported. Against this background, the relative paucity of [1,5] chlorine migrations may find its origin in the tendency of a halogen-substituted cycloheptatriene to generate a tropylium cation, so that normally this mode of reaction will prevail. In this paper, evidence for the occurrence of a *genuine* [1,5] sigmatropic chlorine migration in a bridged cycloheptatriene is presented and supported by ab initio calculations.

Results and Discussion

Addition of Dichlorocarbene to [5]Metacyclophane (1). Addition of dichlorocarbene, generated from chloroform and *t*-BuOK in pentane, to **1** afforded a single product, which was identified as the cycloheptatriene **13b** (Scheme 4). Its structure could be firmly established only with the aid of extensive 1D and 2D NMR techniques (NOE, HH−COSY, CH−COSY) in conjunction with a ^{13}C-labeling experiment involving the addition of ^{13}C-labeled dichlorocarbene; the latter permitted the identification of the original carbene carbon atom and its surroundings in **13b** (and in **15b**, vide infra) via signal intensity and coupling constants (see Experimental Section). To our knowledge, **13b** is the smallest representative of the 1,4-bridged cycloheptatrienes (cf. **5** and **7**,[6] Scheme 2).

The formation of **13b** can only be rationalized by invoking the intermediacy of **11b**. This implies that contrary to the 1,4-addition of the phosphinidene complex **2** (Scheme 1), dichlorocarbene adds to **1** in a 1,2-fashion at C10 and C11, as it would to a strained "anti-Bredt double bond". Note that presumably this mode of addition is also operative in the transformation **6** → **7**. We rationalize the difference in behavior between dichlorocarbene and **2** by a difference in size of the central atoms. As the $sp^3{-}sp^3$ carbon−carbon bond (1.54 Å) is considerably shorter than the analogous carbon−phosphorus bond (average,[15] 1.87 ± 0.02 Å; in **3**,[3] 1.864(4), 1.874(4) Å), carbon apparently is too small to achieve sufficient overlap between the frontier orbitals in the transition state for the 1,4-addition.[3] For similar reasons, the strain in the 1,4-adduct **16**, a bridged derivative of norbornadiene, is higher than in the corresponding 7-phosphanorbornadiene **3**, and according to the Hammond postulate, the thermodynamics of the reaction will be reflected (to some extent) in the transition state. Another consequence of the smaller size of dichlorocarbene compared to **2** is that the former is less sensitive to steric hindrance, which probably seriously hampers the approach of **2** to

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(7) For a review on sigmatropic rearrangements, see: Sprangler, C. W. *Chem. Rev.* **1976**, *76*, 187.

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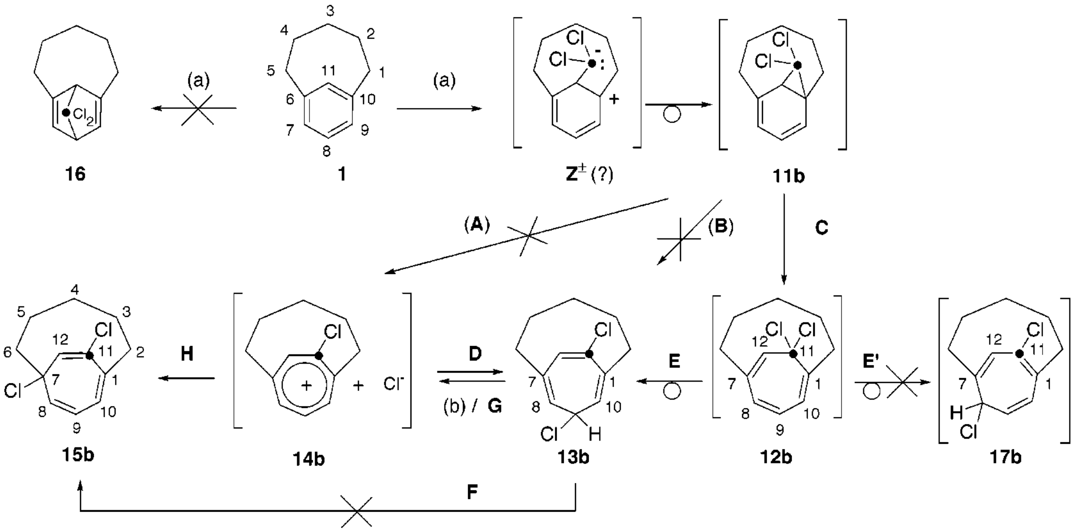
Scheme 4[a]



[a] (a) $CHCl_3$ (or $^{13}CHCl_3$), *t*-BuOK, pentane, 18 h, rt (• = ^{13}C label); (b) rt; accelerated by CF_3COOH.

C10−C11 as a result of interaction with the pentamethylene bridge.

A question that remains to be answered is why the carbene preferentially adds to C10−C11 and not to C6−C7 despite the fact that the HOMO of **1** has the appropriate symmetry and high coefficients at C6 and C7[3] and that addition at C6−C7 is sterically less demanding than at C10−C11. Previous calculations have demonstrated that the HOMO-1 of **1** lies only 0.31 eV below the HOMO and has a large orbital coefficient at C11[3] and the considerable bending of the aromatic ring results in an increase of electron density at the concave side, where the carbene approaches; both factors favor attack at C11. On the other hand, the HOMO-1 coefficient at C10 is very small, which should disfavor a direct concerted 1,2-addition. Therefore, one can imagine that the initial interaction involves overlap between the empty *p*-orbital of the carbene and the HOMO-1 at C11; note that the importance of subjacent orbitals on the reactivity of benzene rings has been pointed out in other cases.[23] In the following stage, nucleophilic attack of the carbene lone pair occurs at C10, which has become part of a quasi-pentadienyl cationic system, leading to ring closure under formation of **11b**. We can thus distinguish two phases in the addition of dichlorocarbene to **1**: inital charge transfer, followed by rotation and ring closure. This view is in line with the common notion that carbenes add to a double bond in one step but two stages;[24] in the present case, our proposal implies a rather high degree of nonconcertedness, which comes close to the primary formation of a zwitterion **Z**± followed in the second stage by ring closure to **11b**.

For the conversion of the primary norcaradiene **11b** (not observed!) to **13b**, there are three plausible pathways, designated **A**/**D**, **B**, and **C**/**E** in Scheme 4. Dissociation into the tropylium cation **14b** (step **A**) followed by recombination to **13b** (step **D**) may a priori seem to be attractive, but it can be discarded on the basis of the following considerations. In agreement with calculations (vide infra), experimental data show that **13b** is not the most stable isomer as it slowly and completely rearranges to **15b**. In itself, this observation is not necessarily compelling, as a thermodynamically less stable compound may be preferentially formed for kinetic reasons. A relevant case is the addition of DCl to 1,3-dienes such as 1,3-pentadiene: initially, the 1,2-adduct is formed in larger amounts, but subsequently, it rearranges to the more stable 1,4-isomer until equilibrium is reached.[25] The rationalization offered for this phenomenon involves attack of DCl at the outer carbon C1 of the diene system to give a contact ion pair between the (deuterated) allylic cation and the chloride counterion. Thus, the chloride is formed in the vicinity of C2, which explains its preferential attack at C2 rather than C4. However, if the same reasoning is applied to the transformation of **11b** → **13b** via the contact ion pair [**14b**·Cl^-], one predicts that, for analogous reasons of proximity, the chloride should attack at C7 (a formal 1,3 migration; see Scheme 4), leading directly to **15b** (which in addition is the thermodynamically more stable product!), rather than attacking the more remote C9 (a formal 1,5-migration) to give the actually observed **13b**.

Pathway **B** concerns the electrocyclic ring opening of **11b** under simultaneous migration of chlorine and reorganization of the double bonds in one step. Although a

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similar mechanism has been postulated for the hydrogen migration in a norcaradiene,[12c] we consider it to be less likely than a stepwise process (pathway **C**/**E**); our calculations confirm this assumption (vide infra). The first reaction step **C** consists of an electrocylic ring opening to give **12b**. The activation barriers for such processes are usually very low; for the rearrangement of norcaradiene to cycloheptatriene, it was determined as 25 kJ mol^{-1}.[16] Because in our case the product of the initial electrocylic ring opening (**12b**) was not observed, this step must be followed directly by a rapid suprafacial [1,5] sigmatropic chlorine migration (**E**) leading to **13b** as the kinetically preferred (but not thermodynamically most stable!) isomer. Examples of such migrations are extremely rare (vide supra), and therefore we performed an ab initio study to gain a more thorough understanding about the nature of these processes (vide infra).

It should be pointed out that formally two regioisomeric modes must be considered for a [1,5] sigmatropic chlorine shift in **12b**. The one actually observed proceeds via pathway **E** by migration of chlorine from C11 to C9 to furnish **13b**, the other one via pathway **E′** by migration from C11 to C8 leading to **17b**. The reason the latter process does not occur is obvious from inspection of the structure of **17b**: it contains two strained trans double bonds in a nine-membered ring (C1=C11, C7=C12), whereas the corresponding trans double bonds in **13b** (C1=C10, C7=C8) are less strained as they are trans in a 10-membered ring. In line with this reasoning, HF/3-21G calculations of the heats of formation indicate that **17b** is less stable than **13b** by 125.4 kJ mol^{-1}.

Compound **13b** rearranged slowly to **15b** (during 1 day; pathway **G**/**H**). Cycloheptatriene **15b** owns its greater stability to the fact that its pentamethylene bridge is connected to the cycloheptatriene unit by only one sp^2-hybridized bridgehead carbon (C1), whereas the other one (C7) is sp^3-hybridized; this reduces the “Bredt strain”. The rearrangement is unlikely to proceed by a [1,3] sigmatropic migration of chlorine (pathway **F**) because it was found to be catalyzed by acid: addition of 1 mol % of CF_3COOH resulted in almost immediate (<5 min) and quantitative conversion to **15b**. Although the role of the acid needs to be clarified, it is conceivable that it acts by assisting the dissociation to the highly strained [5]-paratropyliophane **14b** (step **G**) through protonation of **13b** at the leaving chloride ion. The uncatalyzed reaction is slow, presumably because it proceeds in a nonpolar solvent (pentane), and paratropyliophanes with a bridge containing less than eight carbon atoms have not been isolated, undoubtedly because of their high strain energy. Subsequent recombination of **14b** with chloride furnishes the stable end product **15b** (step **H**). Attempts to intercept **14b** with nucleophiles other than chloride have not yet been successful.

Calculated Structures and Energies. To provide a background for the calculations (at the HF/3-21G + ZPE and the B3LYP/6-31G* level of theory) on compounds **11b**−**15b**, the unbridged model compounds **11a**−**15a** were considered, too. Transition state structures **TS2a**,**b** were characterized by an imaginary frequency. For the sake of comparison, numbering schemes at variance with the IUPAC nomenclature rules were employed (Figure 1, Table 1). Detailed data of the geometric and energetic parameters are presented in the Supporting Information.

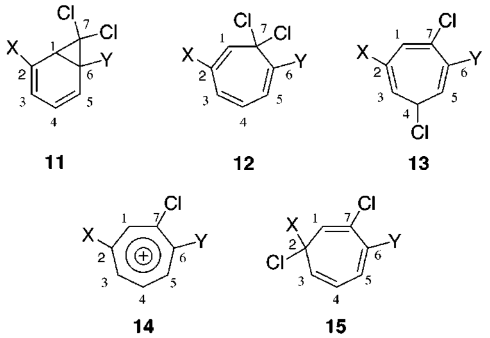

Figure 1. Compounds investigated. **a**: X = Y = H. **b**: X + Y = $(CH_2)_5$.

Table 1. Relative Energies (kJ mol^{-1}) of TS1 and TS2

	HF/3-21G		B3LYP/6-31G*	
species	Δ*E*	Δ*E* + ΔZPVE[a]	Δ*E*	Δ*E* + ΔZPVE[a]
TS1a	27.7	23.6	15.8	12.1
TS1b	27.8	23.2	15.1	10.4
TS2a[b]			79.7	76.2
TS2b	118.7	112.1	74.3	70.5

[a] Zero-point energy corrections are scaled by 0.96; see ref 31. [b] A transition state could not be located at the HF/3-21G level.

The structural parameters of **11a** closely resemble those of previously calculated norcaradienes.[14,17] The carbon atoms in the six-membered ring lie almost in one plane as indicated by the dihedral angle C1C2C3C4 (−6°). In **11b**, the influence of the bridge is apparent in the out of plane twisting of C2 (C1C2C5C6 = −14.2°); most other geometrical parameters are similar to those of **11a**. The transition state **TS1a** for the electrocyclic ring opening of **11a** to **12a** is located 23.6 kJ mol^{-1} above **11a** at the HF/3-21G + ZPE level, in good accord with the experimentally determined barrier for the ring opening of norcaradiene to cycloheptatriene.[16] It drops to 15.8 kJ mol^{-1} at the B3LYP/6-31G* level and decreases even further on the inclusion of zero-point energy corrections (12.1 kJ mol^{-1}). Surprisingly, the bridge in **11b** has only a minor influence on the activation barrier (B3LYP/6-31G*, 10.4 kJ mol^{-1}). This is in line with the similar C1C6 distance in the transition state (**TS1a**, 1.879 Å; **TS1b**, 1.889 Å). However, the relative stability of the products differs substantially. Whereas **12a** lies 43.4 kJ mol^{-1} lower in energy than **11a**, the energy gain from ring opening of **11b** amounts to no more than 12.3 kJ mol^{-1}. This comes as no surprise as **12b**, contrary to **12a**, is a strained 1,4-bridged cycloheptatriene.

Before discussing the geometries of the cycloheptatrienes (CHT) **12**, **13**, and **15**, we note that previous computational studies of the parent CHT showed that a variety of computational methodologies were capable of reproducing the experimental data for geometries[18] and energies[19] with high accuracy.[20] It was concluded that the structure is determined by an intricate interplay between ring strain forces, nonbonded interactions, and resonance effects. The net outcome of these forces is a boat-shaped geometry that can interconvert with the opposite boat through a planar transition state. The deviation of the boat conformation from planarity is expressed by the deformation angles α and β depicted in Figure 2. For the boat-shape ground state, there is evidence for homoaromatic stabilization[21] that is lost in the planar structure. This is one of the factors contributing to the inversion barrier of about 25 kJ mol^{-1}.

Contrary to the “normal” cycloheptatrienes just discussed, the most stable conformation of **12a** turned out

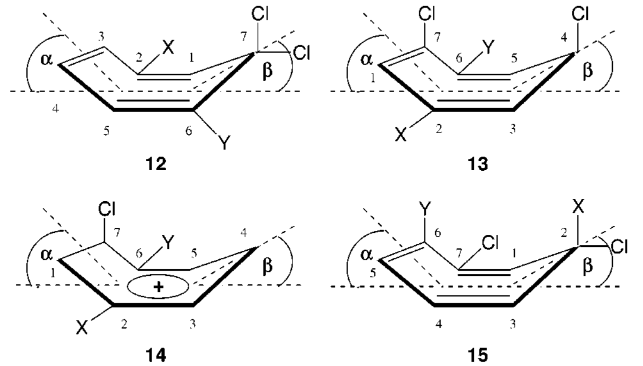

Figure 2. Definition of the nonplanarity angles in cycloheptatrienes **12**, **13**, **15**, and tropylium cation **14**. **a**: X = Y = H. **b**: X + Y = $(CH_2)_5$.

to have a planar geometry. Although it is beyond the scope of this paper to provide a profound analysis of this phenomenon, we assume that the decisive factor is the introduction of the second chlorine substituent at the 7-position, which gives rise to steric repulsion with the other side of the boat (C3, C4) in the bent structure. Apparently, the loss of repulsion in the planar structure overcomes both the loss of resonance energy and the ring strain induced by the planar geometry; note, for instance, that the sp^3 carbon adopts a C−C−C angle of 122° and the sp^2 C−C−C angles range from 127.7° to 130.9°. The bridged structure of **12b** differs markedly from that of **12a**. For **12b**, a planar structure would cause severe strain in the bridge, and as a consequence, it adopts the expected boat geometry in the CHT part of the molecule. However, several anomalies should be pointed out. (1) C1C2C5C6, which are normally located in the same plane, are now twisted (C1C2C5C6, −17.6°). (2) All single bonds in the CHT unit are slightly shortened (1.436−1.449 Å), whereas the double bonds are slightly elongated (1.359−1.369 Å). This suggests an increased degree of bond delocalization and hence gain of resonance energy (homoaromaticity). (3) The rather short C1C6 distance (2.34 Å) also indicates an increased degree of delocalization; note that this distance is 2.59 Å in **12a**. (4) The large C−C−C bond angles in the pentamethylene bridge (113.3−120.7°) reflect a substantial degree of strain, too.

The primary objective of this computational study was to assess the nature of the transition state of the [1,5] chlorine migration leading from **12** to **13**. It was therefore disappointing that no transition state could be located at the HF/3-21G level. Fortunately, a first-order B3LYP/6-31G* transition state (**TS2a**, Figure 3) was found 79.7 kJ mol^{-1} above **12a**. Again the inclusion of zero-point energy corrections reduces the barrier considerably (76.2 kJ mol^{-1}). Several arguments may be put forth that suggest that the rearrangement **12a** → **13a** proceeds by a mechanism that is very close to dissociative, although some bonding interaction is retained that governs the regioselectivity of the migration. (1) The chlorine remains only loosely bound in the transition state as indicated by the long carbon−chlorine distances (2.93−2.99 Å). (2) The same can be inferred from the small imaginary frequency (−211 cm^{-1}), which signals that the potential energy surface is rather flat around the **TS2a**. (3) Although C5C6 is short (1.365 Å), all other C−C bonds are substantially longer (1.388−1.426 Å) indicating a certain degree of delocalization. (4) This is also reflected by the limited degree of bending of the CHT backbone. (5) The migration is accompanied by a considerable amount of charge separation; chlorine bears a large negative charge of 0.63 e. (6) The HOMO is located predominantly at chlorine and is essentially a chlorine lone pair. In solution, in particular in polar solvents, one may expect this migration to occur by a fully dissociative mechanism.

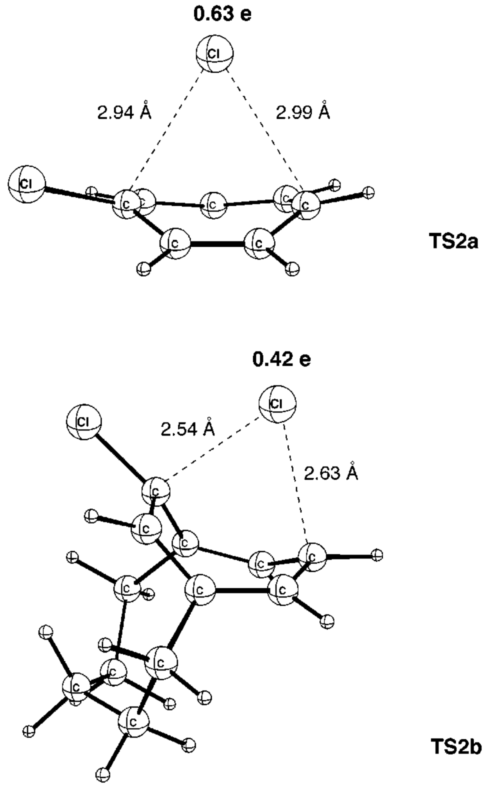

Figure 3. B3LYP/6-31G* optimized geometries of **TS2a** and **TS2b**.

The barrier for the transformation of **12b** → **13b** is only slightly lower (**TS2b** (B3LYP/6-31G*), 70.5 kJ mol^{-1} including zero-point energy correction; Figure 3). Nevertheless, the bridge appears to have a marked impact on the nature of the transition state. Several features displayed by **TS2b** support the description as a genuine concerted, suprafacial [1,5] sigmatropic chlorine migration. (1) Carbon−chlorine distances are significantly reduced (2.537−2.627 Å) as compared to **TS2a**; they are in good accord with those computed for the [1,5] chlorine migration in 6-chlorocyclohexa-2,4-dienone (2.467 Å).[9] (2) The increased value of the imaginary frequency (−327 cm^{-1}) confirms that chlorine is more tightly bound to the CHT fragment. (3) C5C6 (1.353 Å) is shortened compared to that in **12a** (1.365 Å), thus signaling a reduced degree of delocalization toward a tropylium cation. (4) The CHT fragment displays increased bending as signaled by the angles α and β (**TS2a**, $\alpha = 21.7°$, $\beta = 26.9°$; **TS2b**, $\alpha = 45.6°$, $\beta = 35.2°$). (5) The charge separation is reduced as chlorine bears a negative charge of 0.42 e only. We should also note that the overall gain of energy for the rearrangement **12** → **13** is significantly higher in the bridged species (−36.6 for **b** versus −19.7 kJ mol^{-1} for **a**).

In an attempt to assess if there exists a direct pathway from **11** to **13** (Scheme 4, pathway **B**), the transition state obtained turned out to be the same as **TS2** for step **E** of the stepwise mechanism (**C**/**E**). However, because all transition states are of first order and a linear transit calculation demonstrated that **TS2** connects **12** and **13**, it cannot at the same time be a transition state for the direct rearrangement via pathway **B**.

The structures of the products **13** differ markedly from that of CHT itself in such a way that they reflect the tendency of chlorine-substituted CHT to dissociate into a tropylium cation. The carbon *sp*^{3}-chlorine bond in **13a** is considerably elongated (1.911 Å versus a normal value of 1.767 ± 0.002 Å[15b]). Additionally, the CHT backbone is less bent as indicated by the angles α (16.7°) and β (34.8°), which normally are 30° and 50°, respectively (cf. Figure 2). In line with previous calculations,[20d] the angle β is found to be about twice as large as the angle α in B3LYP/6-31G* optimized cycloheptatrienes. In contrast, in **13b**, α and β are 42.4° and 46.1°, respectively. The bridge thus appears to have a profound effect on the CHT framework. The reduced tendency of **13b** toward dissociation also manifests itself by an intermediate carbon−chlorine bond length (1.854 Å) and a diminished degree of bond delocalization as reflected by the carbon−carbon bond lengths (**13a**, 1.353−1.485 Å; **13b**, 1.1.345−1.509 Å).

For the slow transformation of **13b** to **15b**, we postulate that the reaction involves the intermediacy of the tropylium cation **14b**. A crude estimate of the additional strain energy of **14b** compared to **13b** may be derived by comparing the energetics for the transformation **13a** → **14a** with that of **13b** → **14b**. A value of $\Delta\Delta H = 52.7$ kJ mol^{-1} is thus obtained. Not surprisingly, **14b** exhibits a high degree of bending ($\alpha = 42.6°$, $\beta = 17.1°$). The system responds to the geometrical constraints imposed by the bridge mainly by twisting instead of pyramidalization as indicated by the sum of the three angles around the *sp*^{2}-hybridized carbon atoms, which are all close to 360°. Interestingly, **14b** retains its aromaticity with remarkable tenacity, despite its high strain energy and considerable deviations from planarity. This is, for example, expressed by the carbon−carbon bond lengths, which fall into the aromatic range and display little bond alternation (1.375−1.419 Å).

Finally, we wish to point out that the calculated stability order **11b** < **12b** < **13b** < **15b** correlates nicely with the postulated and the experimentally observed sequence of events. In the unstrained **a**-series, accurate experimental data on the relative stability of the reference compounds are not available; our calculations predict **13a** to be the most stable member of this series.

Conclusions

As a result of the high strain present in [5]metacyclophane (**1**), it is one of the few compounds containing an unconjugated benzene ring that is susceptible to attack by dichlorocarbene. The primary product, norcaradiene **11b**, undergoes ring opening to the cycloheptatriene (CHT) **12b**; both are too short-lived to be observed directly. It is proposed that **12b** undergoes a rarely encountered [1,5] sigmatropic chlorine shift to furnish the CHT **13b**, which slowly isomerizes to **15b**; this process is strongly accelerated by acid catalysis. Compounds **13b** and **15** are of interest as CHT derivatives with short cyclophane-type bridges.

A theoretical analysis of the proposed reaction scheme revealed that, depending on the structure, two reaction channels can be distinguished for the [1,5] chlorine migration **12** → **13** in CHT; they constitute the limits of a range of mechanistic possibilities. At one end of this range, we find the dissociative path that involves formation of a tropylium cation, followed by recombination; at the other end, the concerted [1,5] chlorine migration is located. The [1,5] chlorine shift in the model compound 7,7-dichlorocycloheptatriene (**12a**) displays distinct features of the dissociative pathway (long carbon−chlorine distance, charge separation, bond delocalization in the carbon framework). Interestingly, a shift toward a more concerted mechanism is calculated for the bridged CHT **12b**; in addition, the observation that it leads to **13b** and not directly to the more stable **15b** excludes the intermediacy of a tropylium cation (**14b**).

Thus, we have presented both experimental and computational evidence for the occurrence of a genuine [1,5] sigmatropic chlorine migration in this type of compounds. As anticipated, the computed activation barrier for this process (70.5 kJ mol^{-1}) is markedly lower than for the corresponding [1,5] hydrogen migration, for which values in the range of 105−146 kJ mol^{-1} have been reported.[7]

Experimental Section

General Procedures. ^{1}H NMR Spectra were recorded at 400.13 MHz (Bruker MSL 400). ^{13}C NMR Spectra were recorded at 100.62 MHz. All NMR samples were measured at 298 K in $CDCl_3$ with $CHCl_3$ ($\delta = 7.27$ ppm) as a reference for the ^{1}H spectra and $CDCl_3$ ($\delta = 77.0$ ppm) for the ^{13}C spectra. The assignment of NMR signals is based on HH-COSY, CH-correlation, and NOE experiments. HRMS spectra were recorded at an ionization potential of 70 eV. Aluminum oxide: Merck, aluminum oxide 90, standardized (activity II−III), 0.063−0.200 mm. Silica gel: Riedel-de Haën, silica gel S, 0.2−0.5 mm. All chemicals used were commercially available from either Acros or Aldrich Chemicals.

9,11-Dichlorobicyclo[5.3.2]dodeca-1(10),7,11-triene (13b). To a solution of **1**[22] (60 mg, 0.41 mmol) and $CHCl_3$ (180 mg, 1.5 mmol) in dry pentane (10 mL) was carefully added *t*-BuOK at 0 °C under nitrogen over a period of 2 h using a solid addition tube. After stirring for another 18 h at room temperature, the reaction mixture was partitioned between ice−water and pentane. The water layer was extracted three times with pentane. The combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated under vacuum. The product thus obtained was subjected to this same sequence repeated three times to achieve a conversion of more than 95%. Attempted purification of **13b** by column chromatography (silica gel/pentane) led to rapid conversion into **15b**. Yield: 75 mg **13b** (0.33 mmol, 80%) as a slightly yellow oil. ^{1}H NMR: δ 6.73 (d, ^4J (H,H) = 0.9 Hz, H12), 6.11 (dd, ^3J (H,H) = 6.8 Hz, ^4J (H,H) = 1.4 Hz, H10), 6.07 (dd, ^3J (H,H) = 6.8 Hz, ^4J (H,H) = 1.5 Hz, H8), 4.86 (t, ^3J (H,H) = 6.8 Hz, H9), 2.83−2.75 (m, 2H), 2.53−2.43 (m, 2H), 1.94−0.83 (m, 5H), 0.44−0.38 (m, 1H). ^{13}C NMR: δ 141.2 (s, C7), 137.2 (s, C1), 135.4 (s, C11), 132.4 (s, C10), 131.5 (s, C12), 130.4 (s, C8), 50.1 (s, C9), 36.0 (s), 35.3 (s), 31.8 (s), 30.4 (s), 17.1 (s, C4). HRMS calcd for $C_{12}H_{14}{}^{35}Cl_2$ 228.0473, found 228.0477 ± 0.0005.

[11-^{13}C]-9,11-Dichlorobicyclo[5.3.2]dodeca-1(10),7,11-triene ([11-^{13}C]-13b). This compound was prepared from **1** as described above using pure $^{13}CHCl_3$. ^{1}H NMR: δ 6.73 (dd, ^2J (C,H) = 7.5 Hz, ^4J (H,H) = 0.9 Hz, H12), 6.11 (ddd, ^3J (C,H) = 12.9 Hz, ^3J (H,H) = 6.8 Hz, ^4J (H,H) = 1.4 Hz, H10), 6.07 (ddd, ^3J (H,H) = 6.8 Hz, ^4J (C,H) = 1.7 Hz, ^4J (H,H) = 1.5 Hz, H8), 4.86 (t, ^3J (H,H) = 6.8 Hz, H9), 2.83−2.75 (m, 2H), 2.53−2.43 (m, 2H), 1.94−0.83 (m, 5H), 0.44−0.38 (m, 1H). ^{13}C NMR: δ 141.2 (s, C7), 137.2 (d, ^1J (C,C) = 57.1 Hz, C1), 135.4 (s, C11), 132.4 (s, C10), 131.5 (d, ^1J (C,C) = 77.5 Hz, C12), 130.4 (d, ^{3}J (C,C) = 2.1 Hz, C8), 50.1 (s, C9), 36.0 (d, J (C,C) = 4.5 Hz), 35.3 (s), 31.8 (s), 30.4 (d, J (C,C) = 1.5 Hz), 17.1 (s, C4).

7,11-Dichlorobicyclo[5.3.2]dodeca-1(10),8,11-triene (15b). To an NMR tube containing **13b** (11.4 mg, 0.05 mmol) in $CDCl_3$ (0.5 mL) was added a catalytic amount (1 μL) of CF_3COOH. This resulted in the immediate and quantitative conversion to **15b** according to the internal standard (Me_4Si). Yield: 100%. ^{1}H NMR: δ 6.52 (dd, ^{3}J (H,H) = 5.1 Hz, ^{4}J (H,H) = 1.6 Hz, H10), 6.12 (d, ^{3}J (H,H) = 9.9 Hz, H8), 5.95 (s, H12), 5.85 (ddd, ^{3}J (H,H) = 9.9 Hz, 5.1 Hz, ^{4}J (H,H) = 1.8 Hz, H9), 2.96−2.91 (m, H2), 2.25 (dddd, ^{2}J (H,H) = −16.8 Hz, ^{3}J (H,H) = 10.6 Hz, 2.0 Hz, ^{4}J (H,H) = 0.7 Hz, H3), 1.97 (m, H2′), 1.91 (ddd, ^{2}J (H,H) = −16.8 Hz, ^{3}J (H,H) = 7.5 Hz, 2.0 Hz, H3′), 1.81−1.66 (m, 3H), 0.95 (m, 1H), 0.89−0.82 (m, 2H). ^{13}C NMR: δ 145.4 (s, C1), 142.2 (s, C8), 132.7 (s, C12), 129.6 (s, C10), 128.4 (s, C11), 121.9 (s, C9), 69.9 (s, C7), 42.3 (s, C3), 35.8 (s, C2), 30.6 (s), 29.6 (s), 25.0 (s). HRMS calcd for $C_{12}H_{14}{}^{35}Cl_2$ 228.0473, found 228.0477 ± 0.0005.

[11-^{13}C]-7,11-Dichlorobicyclo[5.3.2]dodeca-1(10),8,11-triene ([11-^{13}C]-15b). Prepared from [11-^{13}C]-**13b** according to the same procedure as described for **15b**. ^{1}H NMR: δ 6.52 (ddd, ^{3}J (C,H) = 13.3 Hz, ^{3}J (H,H) = 5.1 Hz, ^{4}J (H,H) = 1.6 Hz, H10), 6.12 (d, ^{3}J (H,H) = 9.9 Hz, H8), 5.95 (d, ^{2}J (H,H) = −5.4 Hz, H12), 5.85 (dddd, ^{3}J (H,H) = 9.9 Hz, 5.1 Hz, ^{4}J (C,H) = 2.1 Hz, ^{4}J (H,H) = 1.8 Hz, H9), 2.96−2.91 (m, H2), 2.25 (dddd, ^{2}J (H,H) = −16.8 Hz, ^{3}J (H,H) = 10.6 Hz, 2.0 Hz, ^{4}J (H,H) = 0.7 Hz, H3), 1.97 (m, H2′), 1.91 (ddd, ^{2}J (H,H) = −16.8 Hz, ^{3}J (H,H) = 7.5 Hz, 2.0 Hz, H3′), 1.81−1.66 (m, 3H), 0.95 (m, 1H), 0.89−0.82 (m, 2H). ^{13}C NMR: δ 145.4 (d, ^{1}J (C,C) = 59.3 Hz, C1), 142.2 (s, C8), 132.7 (d, ^{1}J (C,C) = 77.3 Hz, C12), 129.6 (d, ^{2}J (C,C) = 3.4 Hz, C10), 128.4 (s, C11), 121.9 (s, C9), 69.9 (d, ^{2}J (C,C) = 6.9 Hz, C7), 42.3 (s, C3), 35.8 (s, C2), 30.6 (s), 29.6 (s), 25.0 (s).

Computational Details. All input structures were generated graphically and preoptimized using the semiempirical PM3 Hamiltonian as implemented in Cerius 3.5.[26] To ensure well-converged results the keyword PRECISE was included. Care was taken to perform all further calculations on the lowest energy conformers. Ab initio and density functional theory calculations were carried out with the Gaussian98 suite of programs.[27] For the conventional ab initio calculations we used the Hartree−Fock method with the 3-21G basis set (HF/3-21G). For the DFT calculations we employed Becke's three-parameter exchange-correlation[28] functional including the nonlocal gradient corrections described by the Lee−Yang−Parr correlation functional,[29] denoted as B3LYP, in conjunction with Pople's split valence basis set 6-31G*. This functional has proven to be among the most successful in providing accurate structures and energies. Previous studies showed convincingly that DFT methods in conjunction with double-ζ basis sets are suitable for studying transition states of pericyclic reactions.[30] Geometry optimizations were performed without imposing geometry constraints. In many cases, it proved to be convenient to initially optimize the structures at the HF/3-21G level and to refine the located structures at the B3LYP/6-31G* level. Frequency calculations were used to confirm the nature of the stationary points thus located and to obtain zero-point vibrational energies (ZPVEs). All ZPVEs were scaled by a factor of 0.96.[31] All transition states were of first order as indicated by a single negative value for the Hessian. The restricted B3LYP wave functions are stable with respect to expansion to an unrestricted (UB3LYP) approach. Unless stated otherwise, the discussion is based on the geometries obtained at the B3LYP/6-31G* level.

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Supporting Information Available: Mass spectra of **13b** and **15b**; tables with geometrical and energetic parameters calculated for **11**, **15**, **TS1**, and **TS2**; and ^{1}H and ^{13}C NMR spectra of **13b** and **15b**, with and without ^{13}C label. This material is available free of charge via the Internet at http://pubs.acs.org.

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