[6]Radialenes Revisited[‡]

Thomas Höpfner,[a] Peter G. Jones,[b] Birte Ahrens,[b] Ina Dix,[a] Ludger Ernst,[c] and Henning Hopf*[a]

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[6]Radialene (**2d**) and its hexa- (**2a**) and dodecamethyl (**2c**) derivatives were subjected to several novel chemical reactions. Pyrolysis of **2a** under flash vacuum conditions provided a mixture of 1,5-hydrogen shift products **9** and **10**, and the benzocyclobutenes **5** and **6**, produced by electrocyclization of an intermediate *o*-xylylene derivative **7**. At the higher end of the investigated temperature range (200–400 °C) the formation of cyclization products **11** was also observed. The hydrocarbon **2c** isomerized to the benzocyclobutene **12** under these conditions. Photolysis at 254 nm converted **2c** into a novel isomer that, according to X-ray structural analysis, has the unusual twist configuration **14**. Compound **2c** was photoisomerized through photoinduced hydrogen shift reactions to **15**, and the stable *p*-xylylenes **16** and **17**. Dichloro- and dibromocarbene add to **2d** with formation of the rotaradialene *anti* adducts **19a** and **19b**, respectively, the structures of which were also established by X-ray structural analysis. With dichlorocarbene, **2a** provided the three dichlorocarbene adducts **20**, **22**, and **23**, whereas methylenation with diiodomethane/trimethylaluminium afforded a complex product mixture from which the monoadduct **21** could be isolated. The analogous product **24** and the bisadduct **25** were obtained from **2c** under the same conditions. Epoxidation of **2a** with *m*-chloroperbenzoic acid gave the monoadduct **26**, together with higher epoxidation products, which, however, could not be separated. Depending on the reaction conditions, **2c** could be oxidized with *m*-chloroperbenzoic acid to give the epoxides **27**, **28**, and **29**. Hydrochlorination of **2a** gave a complex mixture of addition products, which was converted into the olefins **9** and **10** by base treatment, showing that the addition step takes place less regioselectively than previously assumed. With $Fe_2(CO)_9$, **2a** was converted into the iron tricarbonyl complex **33** in poor yield. Repetition of the literature procedure for the preparation of **2a** allowed the isolation of novel diastereomers of this oldest hexaradialene; according to NMR experiments the methyl substituents of this hydrocarbon are arranged as shown in the structure **cccaca-2a.**

Introduction

Radialenes are cross-conjugated alicyclic hydrocarbons in which all ring carbon atoms are sp^2-hybridized and show as many exocyclic double bonds as possible. Originally more or less a laboratory curiosity, radialenes and their derivatives have recently been receiving growing attention from preparative chemists, spectroscopists, and materials scientists.[2,3] The introduction of polarizing substituents can convert radialenes into novel π-donors and π-acceptors, of interest, inter alia, for the preparation of novel charge-transfer complexes.[4] In another recent application, radialenes have been employed in molecular scaffolding.[5] The first radialene to be prepared was 7,8,9,10,11,12-hexamethyl[6]radialene (**2a**), synthesized in 30% yield in 1961 by Hopff and Wick, by treatment of the hexabromide **1a** or the corresponding chloride **1b** with magnesium in methanol/benzene.[6] The analogous hexaethyl[6]radialene (**2b**) was obtained by the same method from the corresponding hexakis(1-bromopropyl)benzene (**1c**).[7] In these elimination reactions, the two radialenes, which according to X-ray structural analysis possess the so-called bucket wheel configuration (see Scheme 1),[1b,3,8] were reported to be the only products. The fully alkylated dodecamethyl[6]radialene (**2c**) was obtained when tetramethylbutatriene (**3**), generated in situ, was trimerized in the presence of a Ni^0 catalyst.[9] The unsubstituted parent system **2d** was not synthesized until more than 15 years after **2a**.[10–12]

Although the chemical behavior of the [6]radialenes has been studied to some extent (inter alia, addition of HCl,

[‡] Alicyclic Chemistry, VIII. Part VII: Ref.[1]
[a] Institute of Organic Chemistry, Technical University of Braunschweig,
Hagenring 30, 38106 Braunschweig, Germany
Fax: (internat.) +49-(0)531-3915388
E-mail: H.Hopf@tu-bs.de
[b] Institute of Inorganic and Analytical Chemistry, Technical University of Braunschweig,
P. O. Box 3329, 38106 Braunschweig, Germany
Fax: (internat) +49-(0)531-3915387
E-mail: p.jones@xray36.anchem.nat.tu-bs.de
[c] NMR-Laboratory of the Chemical Institutes, Technical University of Braunschweig,
Fax: (internat) +49−(0)531/3918192
E-mail: L.Ernst@tu-bs.de

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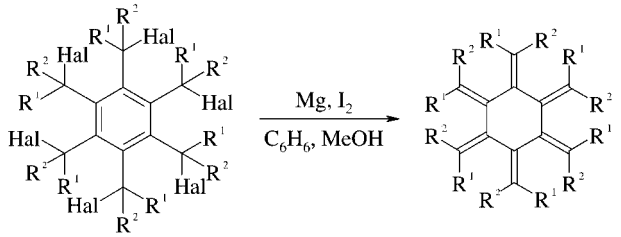
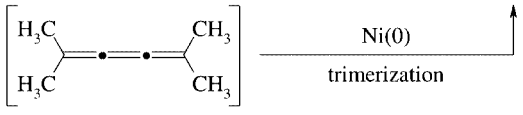


1	Hal	R¹	R²
a	Br	H	CH_3
b	Cl	H	CH_3
c	Br	H	C_2H_5

2	R¹	R²
a	H	CH_3
b	H	C_2H_5
c	CH_3	CH_3
d	H	H



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Scheme 1. Preparation of [6]radialenes

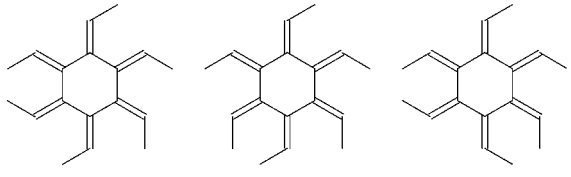
HBr, Br_2, and H_2 to **2a**,[6,7] various Diels−Alder additions to **2a**[13] and **2d**[11,14]), we thought it worthwhile to take another look at these highly unsaturated compounds. In particular, we wanted to study the isomerization behavior of [6]radialenes and also the addition of divalent species (carbenes, epoxidation) to them. In a comprehensive previous study on the chemical behavior of [4]radialene we had shown that this hydrocarbon could be cyclopropanated to yield novel derivatives of [4]rotane.[15] Before we performed the corresponding experiments with various [6]radialenes (see below), however, we were interested in the stereochemistry of the elimination reactions affording **2a** − was this really the only stereoisomer produced?

Results

The Stereochemistry of the Elimination of 1a to 2a

Elimination experiments under the classical conditions (see above) indeed yielded **2a** as the main product (isolated yield 34%), but GC/MS analysis quickly showed that other isomers − up to five were detected − were also produced. Because of their low concentrations, however, it was impossible to separate any of these for spectral identification. Only with methyl or *n*-butyllithium as dehalogenation reagent could a new isomer of **2a** be generated in sufficient amounts for structure assignment (see below). The reason for this behavior is unclear; the difficulty in finding a reasonable explanation begins with the unknown stereostructure of **1a**. According to B3LYP/6-31G(d) geometry optimization calculations,[16] and through analogy with the crystal structure of hexakis(bromomethyl)benzene,[17] **1a** should possess an all-*anti* configuration with the bromine substituents oriented alternatively above and below the carbocyclic plane. If it is assumed that debromination occurs as 1,4-elimination process, this configuration of **1a** represents the ideal stereochemical prerequisite and the resulting hydrocarbon has the shown bucket-wheel structure **2a**. If, on the other hand, the dehalogenation process takes place stepwise − by a single-electron transfer process, for example − the initially generated benzyl radical intermediates could undergo *cis*/*trans*-isomerization reactions and cause the formation of isomers of **2a** in the product mixture.

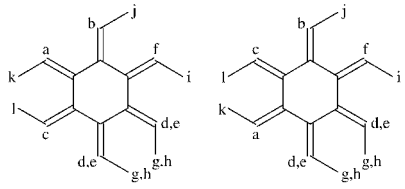
For the following reasons we believe that the second isomer of **2a**, which could be separated from the product mixture by preparative thick layer chromatography (but with substantial loss of material), has the structure ***cccaca*-2a** (Scheme 2). The ^1H NMR spectrum of this isomer shows five different signals both for the CH and for the CH_3 groups, of which one signal in each set has a twofold intensity (Table 1). This can only be explained in terms of an unsymmetrical molecule displaying accidental chemical equivalence of two CH and of two CH_3 moieties. Similarly, in the ^{13}C NMR spectrum, there are five >C= signals (one with twofold intensity), five CH_3 signals (one with twofold intensity) and six =CH− signals (see Exp. Sect.). Among the nine possible diastereomers of **2a** there are only three unsymmetrical ones that would be compatible with the observed NMR spectra. These are ***ccccca*-2a**, ***cccaa*-2a**, and ***cccaca*-2a**. NOE difference measurements with saturation of the methyl signals were carried out in order to decide between these three possibilities. Because of the very close chemical shifts, the spectra had to be recorded at an observation frequency of 600 MHz. Methine and methyl protons belonging to the same =CH−CH_3 unit were identified by H,H-COSY spectroscopy. The NOE results showed that the two =CH−CH_3 pairs b/j, f/i, and one of the two accidentally equivalent d,e/g,h pairs are arranged in a clockwise fashion in the order described. As no inter−CH_3 NOEs were observed, it appears logical to orient the three remaining =CH−CH_3 moieties such that the methyl groups with identical shifts (g, h) and with very similar shifts (k, l) are pointing toward each other. The resulting diastereomer is ***cccaca*-2a**, and its methyl group orientation accounts for the missing NOEs, since it is not possible to observe a signal intensity increase at the point of irradiation or very close to it. If the isomer in question were ***ccccca*-2a** or ***cccaa*-2a**, one would expect at least one NOE between proton a, b, or c and one non-vicinal methyl group. Since this is not the case, we favor structure ***cccaca*-2a** over the alternatives ***ccccca*-2a** and ***cccaa*-2a**. Scheme 3 shows the two possible assignments of the ^1H NMR signals for ***cccaca*-2a**.



Scheme 2. The three unsymmetrical diastereomers of hexamethyl[6]radialene (**2a**)

Table 1. ^{1}H NMR chemical shifts, nuclear Overhauser effects, and H,H-COSY cross-peaks for ***cccaca*-2a**

Signal	δ_H	Signal	δ_H
a	5.49	g,h	1.81
b	5.43	i	1.79
c	5.41	j	1.74
d,e	5.36	k	1.61
f	5.33	l	1.60
NOEs (irradiated signal → enhanced signal)		H,H-COSY crosspeaks	
g,h →d,e		a ⇄ k	
i → d,e and f		b ⇄ j	
j → b and f		c ⇄ l	
k → a		d,e ⇄ g,h	
l → c		f ⇄ i	



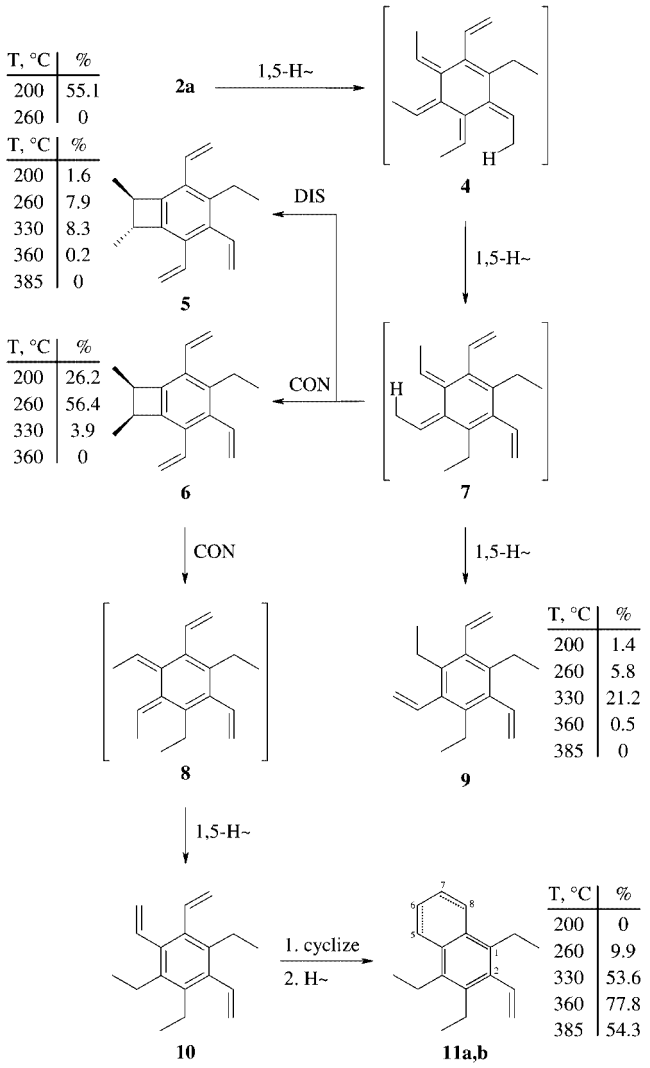
***cccaca*-2a**

Scheme 3. Alternative signal assignments of ***cccaca*-2a**

The Thermal Isomerization of Hexamethyl- (2a) and Dodecamethyl[6]radialene (2c)

In comparison with the highly reactive parent hydrocarbon **2d**, the polymethyl derivatives **2a** and **2c** are quite stable. They can be handled readily in air and melt without decomposition at 133 and 210 °C, respectively. To study their behavior under harsher conditions we sealed small samples of these hydrocarbons under vacuum in glass ampoules and heated them for one hour at temperatures between 200 and 460 °C. While **2a** had reacted completely after 1 hour at 230 °C, **2c** only began to isomerize around 330 °C. In both cases the formation of primary products was accompanied by secondary reactions at longer pyrolysis times or at higher temperatures, as shown by GC, GC/IR, and GC/MS analyses of the pyrolysate.

With regard to the structure of **2a**, which is formally composed of three 2,4-hexadiene units, it comes as no surprise that its thermal isomerization begins with a 1,5-hydrogen shift, producing hydrocarbon **4**, in which one double bond has moved into the ring, and another to the periphery. Double repetition of this process provides the aromatic isomer **9**, a known compound,[18] reaching its highest concentration at 330 °C. The route to **9** passes through the "doubly-rearranged" hydrocarbon **7**, a highly substituted *o*-xylylene that can undergo one of the reactions typical of this class of polyenes, electrocyclic ring-closure to produce benzocyclobutenes. That this cyclization actually occurs was verified by the isolation of isomer **6**, which at intermediate temperatures (260 °C) is the main product of the thermal isomerization of **2a**. The formation of the *cis* isomer **6** is in agreement with orbital-symmetry requirements, which demand a conrotatory closure pathway of **7**. However, as shown by Roth and co-workers in a comprehensive study on the stereochemistry of the thermal ring-opening of *trans*-7,8-dimethyl-benzocyclobutene,[19] this hydrocarbon − besides undergoing the allowed conrotatory isomerization − on heating also epimerizes to its *cis* isomer via a "forbidden" disrotatory reaction. Not surprisingly, this latter isomerization requires a higher activation energy. Indeed in the case of **7**, the disrotatory cyclization product **5** is generated as a minor product only, never being able to surpass **6** in yield over the whole temperature range studied (Scheme 4).

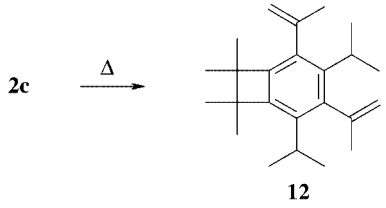


Scheme 4. Thermolysis of hexamethyl[6]radialene (**2a**)

Under pyrolysis conditions **6** can undergo conrotatory ring-opening: presumably back to **7** but also "on" to the isomeric *o*-xylylene **8**. If this reacts by a 1,5-hydrogen shift, an isomer of **9**, the trivinyl derivative **10**, is produced. Although this $C_{18}H_{24}$ isomer could not be isolated from the pyrolysis mixture it was shown to be present by GC and GC/MS comparison with an authentic sample available from another experiment (see below). With its two adjacent

vinyl substituents, **10** can ring-close to afford the dihydronaphthalene derivatives **11a** and **11b**, two isomers that could not be separated by chromatography. Their structures were derived from their NMR spectroscopic data (see Exp. Sect.) as well as from several chemical transformations. Whereas dehydrogenation with DDQ transformed this mixture into 2-vinyl-1,3,4-triethylnaphthalene, hydrogenation over Pd/C yielded 1,2,3,4-tetraethyltetralin. It is not surprising that **11a/b**, which according to the ^{13}C NMR spectrum of their mixture are produced in about equal amounts (doubling of carbon signals), are formed only at higher temperatures, since the cyclization step of **10** involves the temporary loss of an aromatic ring system. Once the cyclization has occurred, hydrogen shifts are necessary to arrive at **11a/b**.

As already mentioned, dodecamethyl[6]radialene (**2c**) is thermally much more stable than the hexamethyl derivative **2a**. Up to 360 °C the pyrolysis mixture is dominated by the benzocyclobutene **12**, which was isolated from an experiment at 350 °C in 17% yield by preparative thick layer chromatography and sublimation (Scheme 5). Its structure was assigned from the usual spectroscopic and analytic data (see Exp. Sect.), and for its formation we postulate a mechanism analogous to the conversion of **2a** into **6**.



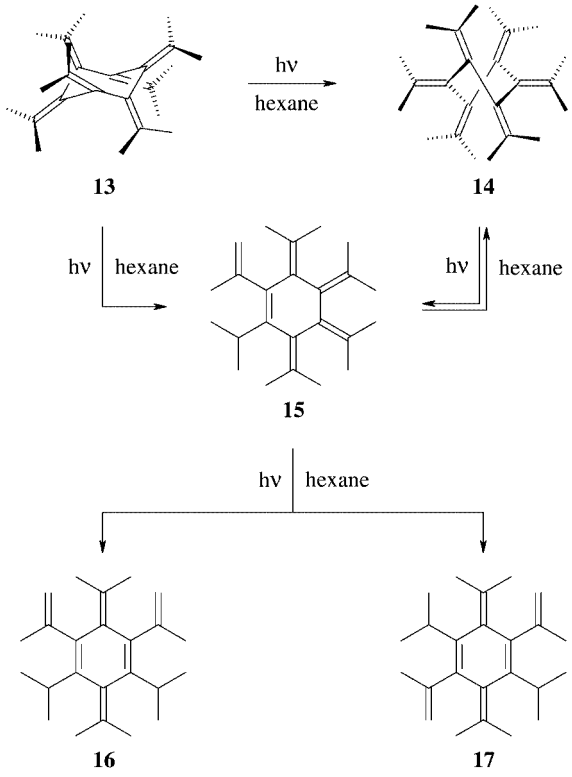
Scheme 5. Thermolysis of dodecamethyl[6]radialene (**2c**)

Although hydrocarbon **12** was shown to be homogeneous by GC and HPLC analysis, its ^1H NMR spectrum indicated the presence of at least two conformers. Line-broadening was apparent for all signals at room temperature, and although many signals became sharper on an increase in temperature this process had not come to an end even at 100 °C. No attempt was made to quantify this phenomenon.

When the pyrolysis temperature was increased further, the result was a most complex product mixture that we were unable to separate.

The Photochemical Isomerization of Dodecamethyl[6]radialene (2c)

When **2a** is irradiated either in the absence or in the presence of a sensitizer it undergoes cycloaddition reactions to provide various oligomers and polymers.[20] Since repetition of these experiments in our hands in a 2-methylbutan/2-methylpentane glass at −196 °C also did not provide monomeric isomerization products (formation of oligomers of unknown structure), we decided to subject the sterically more shielded [6]radialene derivative **2c** to photolysis. Although initial experiments were also disappointing (formation of viscous oils of undetermined structure), we were pleased to find that irradiation with a 15 W low-pressure mercury lamp at a wavelength of 254 nm in hexane solution for short reaction times (minutes, see below and Exp. Sect.) produced isomerization products of dodecamethyl[6]radialene (**2c**, Scheme 6).



Scheme 6. Photolysis of dodecamethyl[6]radialene (**2c**) in conformation **13**

The structure of **2c** in the solid state has been determined by Wilke and co-workers;[21] as shown in the scheme, the hydrocarbon prefers the chair-like structure **13**. On irradiation it isomerizes either to a new conformational isomer **14** or to a polyene that has undergone a 1,5-hydrogen shift: the hydrocarbon **15**. For orbital symmetry reasons, photochemically induced 1,5-hydrogen shifts must occur antarafacially, and, indeed, with its twisted geometry, **2c** (see three-dimensional structure **13**) fulfills this condition. The structure of **15** was determined spectroscopically. When the conformational isomer **14** was used as a substrate no reaction back to **2c** was observed, but a hydrogen shift process took place, yielding **15**. Finally, this polyene either photoisomerizes back to **14** or undergoes a second 1,5-hydrogen shift to yield the two *p*-xylylenes **16** and **17**. The yields of the isomers strongly depend on the irradiation time. After 4 minutes, **15** can be isolated in 22% yield (together with largely unchanged substrate), but after 18 minutes it cannot be detected in the photolysate. After this relatively long time, hydrocarbons **14**, **16**, and **17** were produced in 19, 16, and 4% yields, respectively. Whereas the structure of **17** was also determined spectroscopically (largely by NMR spectroscopy, see Exp. Sect.), both **14** and **16** could be crys-

tallized and subjected to X-ray structural analysis. Unfortunately the structure of **16** proved to be severely disordered, but that of **14** was of satisfactory quality and proved to be a different modification from that previously determined, which was reported briefly in a review article[21] and is deposited in the Cambridge Database (refcode GAYTIJ).

The structure of the new polymorph of the radialene **14** is, to the best of our knowledge, only the fifth of a simple radialene, the previously determined structures being the first polymorph of **14**[19] and the hexamethyl,[8] hexaethyl,[1b] and hexa-bromomethyl[22] derivatives. All these structures displayed crystallographic inversion symmetry and almost ideal chair conformations, with absolute ring torsion angles of ca. 46−48° in the hexasubstituted compounds and 56° in the previous polymorph of the dodecasubstituted **14**. The new polymorph involves two independent molecules, which are, however, closely similar (Figure 1); a least-squares fit of all atoms reveals an r.m.s. deviation of only 0.13 Å, and this is reduced to 0.07 Å if the methyl groups are omitted. Ring bond lengths lie in the 1.496−1.511 Å range, and ring angles (at sp^2 carbon atoms) in the 109.1−110.8° range. The major and surprising difference from the earlier polymorph is that the ring conformation is an almost ideal twist, with torsion angles (for molecule 1) of 32, −70, 35, 31, −70, and 33° (starting with the bond C1−C2, then C2−C3, etc.); the local twofold axis passes through C1 and C4 and is valid for all atoms to a reasonable approximation. This is the first observation of the twist conformation in a radialene. Also in contrast to the previous polymorph, and presumably as a consequence of the twist conformation, there are substantial deviations from planarity about the double bonds, especially C1−C7 and C4−C10, in which all torsion angles deviate by ca. 15° from the ideal values of 0 and 180°. Associated with this are short contacts that represent steric pressure between the methyl carbon atoms of neighboring C=CMe_2 moieties (C13···C24 3.07, C14···C15 3.05, C18···C19 3.09, C20···C21 3.06 Å). The shortest such distance in the previous polymorph was 3.29 Å.

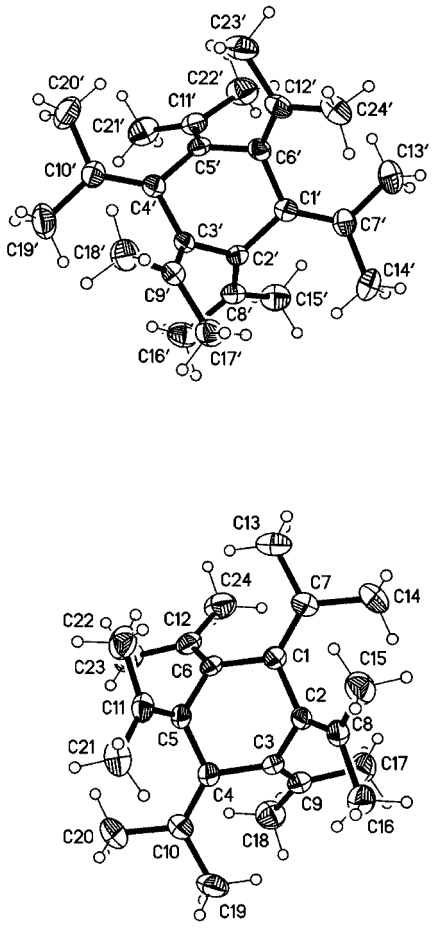
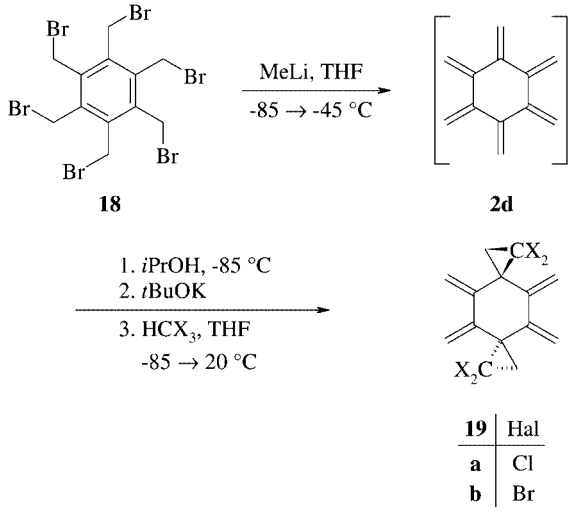


Figure 1. The two independent molecules of compound **14** in the crystal; ellipsoids represent 50% probability levels; hydrogen radii are arbitrary

Carbene Additions to [6]Radialenes

As pointed out in the introduction, radialenes can be converted into rotanes (or into "rotaradialenes" if not fully cyclopropanated) by cyclopropanation. Having demonstrated the usefulness of this concept for [4]radialene,[15] we were interested in extending it to the [6]radialenes. The simplest model for such a reaction is, of course, [6]radialene (**2d**) itself. Since we had no access to its various precursor compounds, we decided to try to debrominate hexakis(bromomethyl)benzene (**18**), since the multiple elimination route had already shown its practical usefulness in the cases of **2a** and **2b**. Because of the known high reactivity of **2d**[10−12,14] a trapping experiment was designed, in which [6]radialene generated in situ could be intercepted by either dichloro- or dibromocarbene produced from chloroform or bromoform in the same flask under two-phase conditions. As illustrated in Scheme 7, this experiment was successful, although the two carbene adducts **19a** and **19b** were isolated only in yields of 2 and 5%, respectively.



Scheme 7. Dihalocarbene addition to [6]radialene (**2d**)

Still, enough material was available to allow a structure determination by X-ray structural analysis for both adducts.

The halo derivatives **19a** and **19b** are not isostructural, but both molecules (Figures 2 and 3) display crystallographic inversion symmetry. The rings both display the chair conformation, with absolute torsion angles in the range of 49−54°. The bond lengths in the three-membered rings display the same pattern, with C1−C2 < C2−C3 < C1−C3, although the differences are not large (see refs.[23,24]). Each C-halogen bond is synperiplanar to a ring bond across C1−C3, and this may be the reason for the longer bonds. A similar effect is observed in the six-membered rings, in which the bond C4−C5 is not involved in synperiplanar contacts and is the shortest, although the differences are not great.

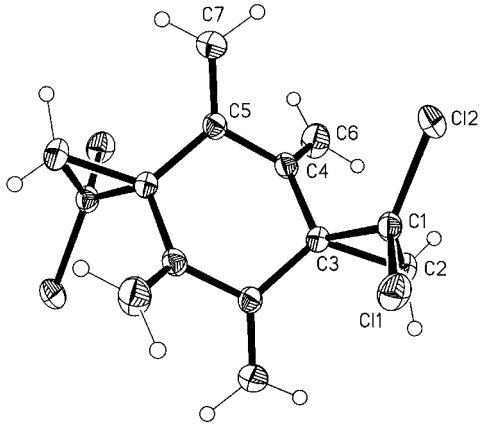


Figure 2. The molecule of compound **19a** in the crystal; ellipsoids represent 50% probability levels; hydrogen radii are arbitrary; selected molecular dimensions (Å,°): C(1)−C(2) 1.491(2), C(1)−C(3) 1.527(2), C(2)−C(3) 1.518(2), C(3)−C(5)#1 1.502(2), C(3)−C(4) 1.502(2), C(4)−C(5) 1.487(2); Cl(1)−C(1)−C(3)−C(5)#1 2.89(14), Cl(2)−C(1)−C(3)−C(4)−2.60(14)

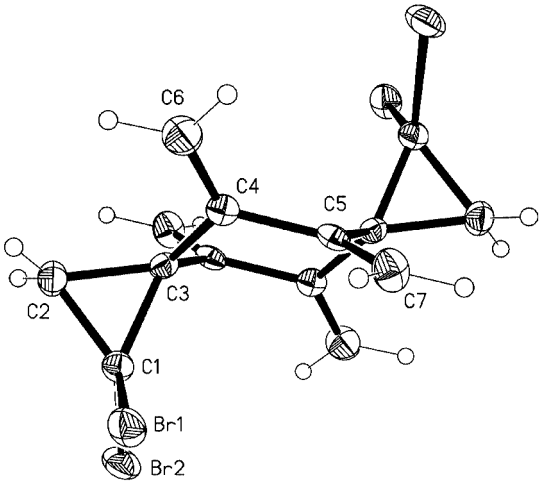


Figure 3. The molecule of compound **19b** in the crystal; ellipsoids represent 50% probability levels; hydrogen radii are arbitrary; selected molecular dimensions (Å,°): C(1)−C(2) 1.489(4), C(1)−C(3) 1.523(4), C(2)−C(3) 1.514(3), C(3)−C(4) 1.502(4), C(3)−C(5)#1 1.504(3), C(4)−C(5) 1.493(3); Br(1)−C(1)−C(3)−C(4) 2.6(3), Br(2)−C(1)−C(3)−C(5)#1 −3.6(3)

The crystal packings of both compounds each involve one independent halogen···halogen contact. In **19a** the contact C1−Cl1···Cl2−C1, via the *c* glide plane, displays a distance of 3.548 Å and angles of 84.1 and 173.5° at Cl1 and Cl2 respectively, making this a classical "type 2" contact,[25] and resulting in the formation of layers of molecules parallel to (10−1) (Figure 4). In **19b** the contact is C1−Br1···Br2−C1, through an inversion center, with a distance of 3.532 Å and angles of 173.8 and 115.3° at Br1 and Br2 respectively; this is also a "type 2" contact, and results in the formation of layers of molecules parallel to the *yz* plane (Figure 5).

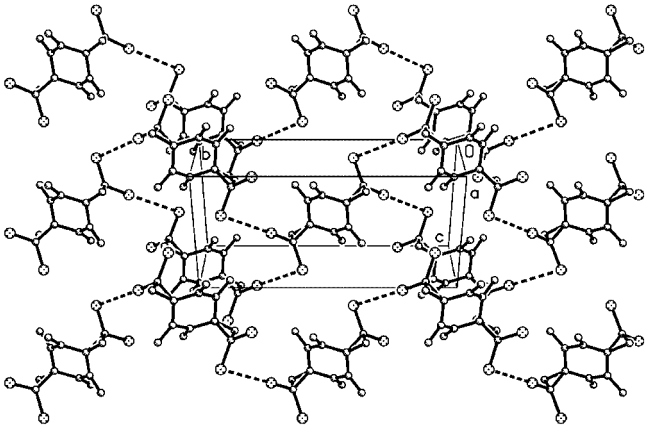


Figure 4. Packing diagram for compound **19a**; the view direction is perpendicular to (10−1); hydrogen atoms are omitted; chlorine−chlorine interactions are indicated by dashed bonds

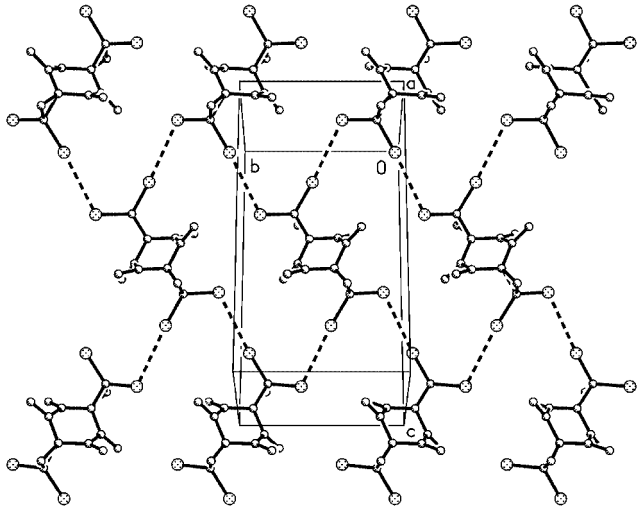
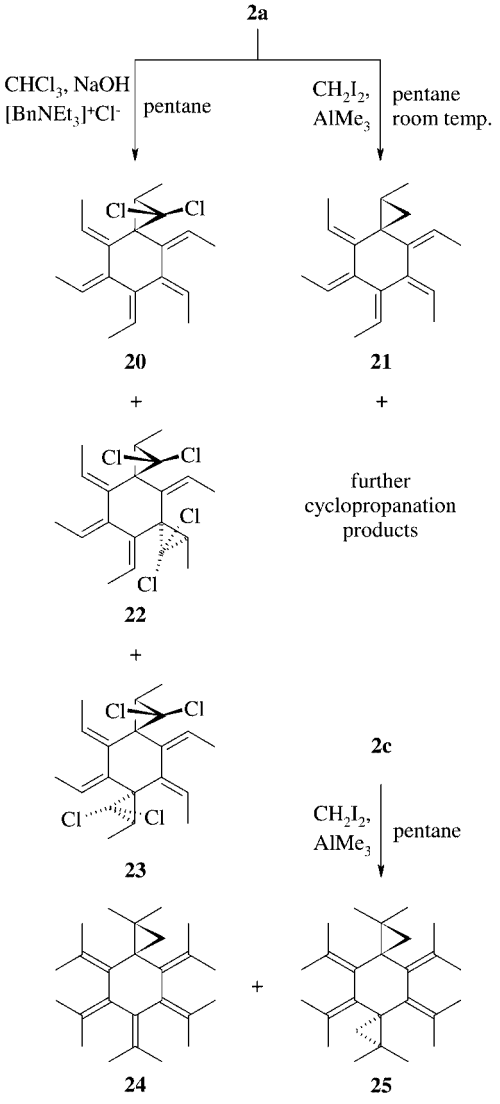


Figure 5. Packing diagram for compound **19b**; the view direction is perpendicular to the *yz* plane; hydrogen atoms are omitted; bromine−bromine interactions are indicated by dashed bonds

No higher cyclopropanation products were obtained in these two experiments, and the amounts of **19a/b** available did not suffice to subject them to further carbene addition.

Unlike **2d**, the hexamethyl derivative **2a** does not react with dibromocarbene. With dichlorocarbene − generated from chloroform under phase-transfer conditions − however, three cyclopropanation products were obtained: the

monoadduct **20** (8%), and the isomeric bisadducts **22** (17%) and **23** (1%, Scheme 8).



Scheme 8. Carbene addition to hexamethyl[6]radialene (**2a**) and dodecamethyl[6]radialene (**2c**)

Whereas the structure of **20** follows from the spectroscopic and analytical data (see Exp. Sect.), the structures of the bisadducts were determined by X-ray structural analysis.

The "pseudo-*meta*"-substituted compound **22** (Figure 6) crystallizes without imposed symmetry. Because of the somewhat lower precision, comparison of the bond lengths of the three-membered rings is less meaningful, but the CH(Me)−CCl_2 bonds are the shortest, corresponding to the situation in **19a** and **19b**. The other bonds may be affected by the steric pressure of the chlorine substituents and also the extra methyl group. The conformation of the six-membered ring approximates well to a twist form with the local twofold axis through C2 and C5, but the axis does not hold for the methyl groups C14,16,17,18. The shortest bonds in the ring, C4−C5 and C5−C6, are those not involved in syn-periplanar contacts. There are no unusually short intermolecular contacts.

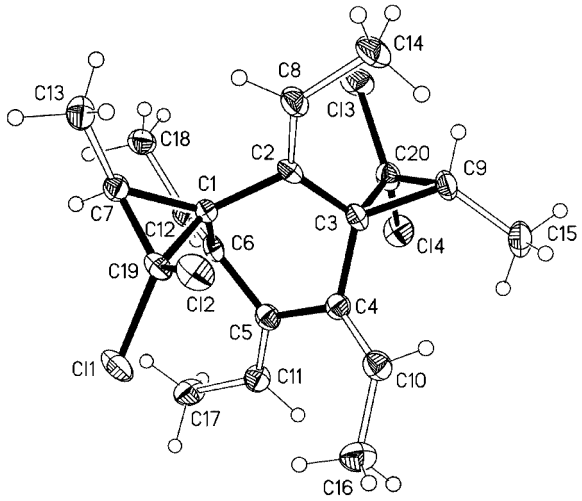


Figure 6. The molecule of compound **22** in the crystal; ellipsoids represent 30% probability levels; hydrogen radii are arbitrary; selected molecular dimensions (Å,°): C(1)−C(6) 1.521(6), C(1)−C(2) 1.524(6), C(1)−C(19) 1.527(6), C(1)−C(7) 1.538(6), C(2)−C(3) 1.501(7), C(3)−C(4) 1.503(7), C(3)−C(20) 1.534(6), C(3)−C(9) 1.550(6), C(4)−C(5) 1.475(6), C(5)−C(6) 1.480(7), C(7)−C(19) 1.495(7), C(9)−C(20) 1.489(7), C(2)−C(1)−C(7)−C(13) 7.8(8), C(4)−C(3)−C(9)−C(15) −6.2(7), C(2)−C(1)−C(19)−Cl(2) 8.6(6), C(6)−C(1)−C(19)−Cl(1) −0.6(6)

The "pseudo-*para*" compound **23** crystallizes with imposed inversion symmetry (Figure 7). The ring displays an almost ideal chair conformation, with absolute torsion angles of 53−54°. Bond lengths follow the pattern established above, in that bonds without syn-periplanar interactions are shorter [e.g. C4−C10 1.494(2), C3−C2′ 1.497(2) Å]. The crystal packing shows only one unusual contact, the weak[26] hydrogen bond C8−H8a···Cl2, with H···Cl 2.78 Å, angle 139°, via the *n* glide plane; this connects the molecules into layers parallel to (101) (Figure 8).

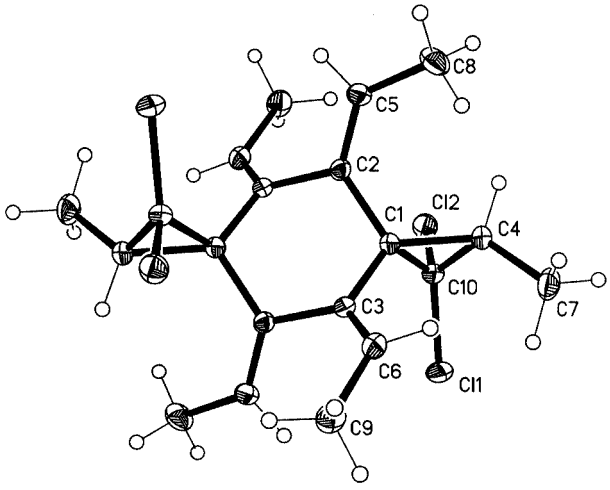


Figure 7. The molecule of compound **23** in the crystal; ellipsoids represent 50% probability levels; hydrogen radii are arbitrary; selected molecular dimensions (Å,°): C(1)−C(3) 1.505(2), C(1)−C(2) 1.506(2), C(1)−C(10) 1.535(2), C(1)−C(4) 1.541(2), C(2)−C(3)#1 1.497(2), C(4)−C(10) 1.494(2), C(3)−C(1)−C(4)−C(7) −9.3(2), C(3)−C(1)−C(10)−Cl(1) −7.4(2), C(2)−C(1)−C(10)−Cl(2) 0.8(2)

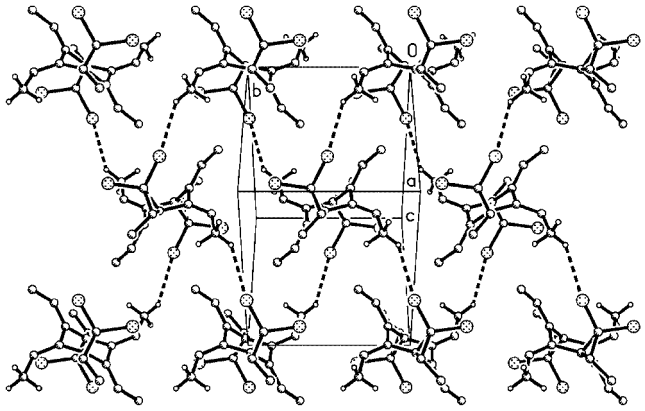


Figure 8. Packing diagram for compound **23** seen perpendicular to (10−1); weak hydrogen bonds CH···Cl are shown as broken lines

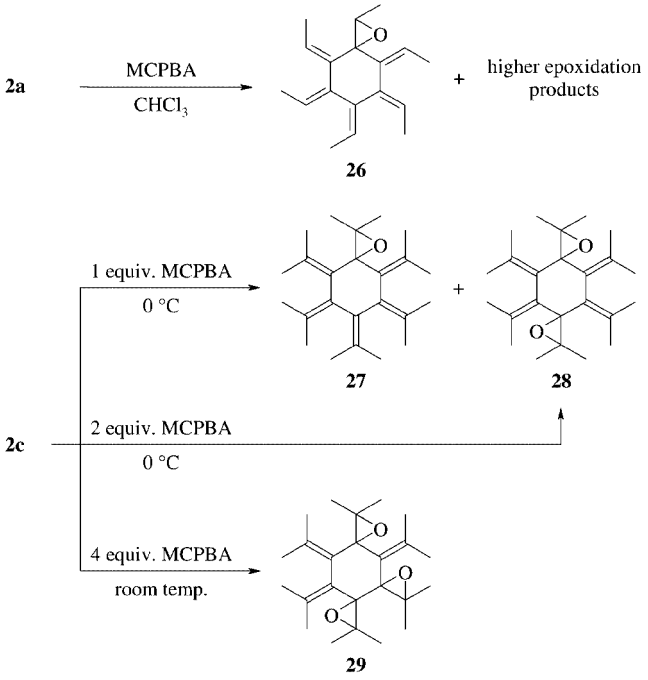
Since, once more, no further cyclopropane derivatives could be isolated from the product mixture, the reactivity of the carbene was increased further by use of the diiodomethane/trimethylaluminium reagent.[27] As hoped, multiple addition of methylene carbene occurred, as demonstrated by GC/MS analysis, but only the monoadduct **21** could be isolated in poor yield (8%) by thick layer chromatography on silica gel.

The fully methylated [6]radialene **2c** did not react with dichloro- or dibromocarbene. Changing to the more reactive methylene carbene, generated as above, provided two products: the monoadduct **24** (47%) and a bisadduct **25** (Scheme 8). The X-ray structure analysis of **25** was unfortunately again accompanied by severe disorder problems. We propose the *trans* orientation of the cyclopropane rings, in analogy with structure **23** of the dichlorocarbene adduct of **2a**.

Epoxidation of [6]Radialenes

The epoxidation of **2a** with one equivalent of *meta*-chloroperbenzoic acid (MCPBA) at 0 °C furnished the monoadduct **26** in 12% yield, together with several bis-epoxides and higher oxidation products as shown by GC/MS analysis. Epoxide **26** was separated by medium pressure chromatography on an octyl-derivatized silica gel phase, but the higher adducts turned out to be inseparable. Purification on neutral aluminium oxide had to be abandoned because of poor separation efficiency, and on normal silica gel the epoxides decomposed by ring-opening (Scheme 9).

Epoxidation of the less reactive permethyl derivative **2c** was more successful. With one equivalent of MCPBA at 0 °C a mixture consisting of the starting material **2c**, the mono-epoxide **27**, and the bis-epoxide **28**, produced in 1:2:1 ratio, was obtained. Separation was again accomplished on octyl-derivatized silica gel. Working with two equivalents of the epoxidizing agent at 0 °C provided the bis-adduct exclusively, and only at higher temperature (20 °C) and with a large excess of MCPBA was the tris-adduct **29** produced. Clearly, the rate of oxidation is decreasing with increasing degree of epoxidation; in fact, in no experiment were we able to isolate a product possessing more oxirane rings than



Scheme 9. Epoxidation of hexamethyl[6]radialene (**2a**) and dodecamethyl[6]radialene (**2c**)

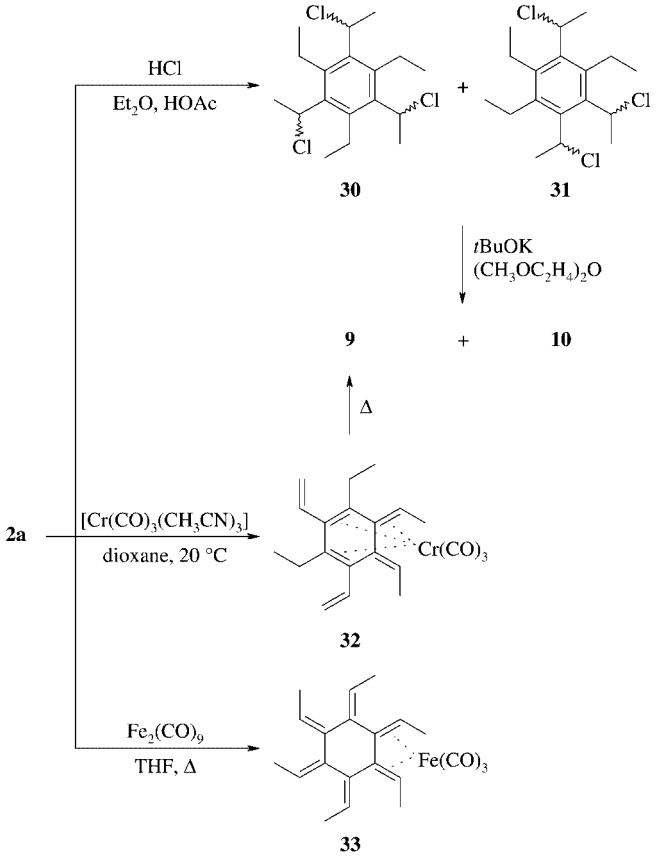
29. The structure elucidation of the three epoxides **27**−**29** rests largely on their ^{1}H NMR spectra (see Exp. Sect.), the number of methyl signals being of particular diagnostic value (6 for **27**, 3 for **28**, and 12 for **29**). The relative orientation of the three-membered rings is unproven, since we could not obtain suitable crystals for X-ray structural analysis for either of these adducts.

Miscellaneous Additions to [6]Radialenes

In their classical studies on [6]radialenes, Hopff and Wick[7] reported that **2a** reacts with hydrochloric acid in acetic acid/diethyl ether to provide a single adduct, the trichloride **30**, in 66% yield. Since there is no a priori reason why only this regioisomer should be produced, we decided to repeat the addition experiment under the original conditions. In fact, RP-HPLC analysis quickly showed that at least five adducts were produced, all of which had practically identical UV spectra, each with an absorption maximum at 220 nm. GC/MS analysis showed that three equivalents of hydrochloric acid had been added to the radialene, but chromatographic separation on a preparative scale failed. We therefore subjected the product mixture to dehydrochlorination with potassium *tert*-butoxide in diethyleneglycol dimethyl ether. Triple elimination occurred readily and provided a 1:1-mixture of the 1,3,5- and the 1,2,4-trivinyl benzene derivatives **9** and **10**, respectively (Scheme 10).

Clearly, an isomer of **30** must have been present in the original mixture, in the form of the trichloride **31**, both isomers evidently being formed as mixtures of diastereomers.

Very little is currently known about the potential for the use of radialenes as ligands for metal organic compounds.



Scheme 10. Miscellaneous reactions of hexamethyl[6]radialene (**2a**)

The first use of **2a** for such a purpose was described by Wilke and co-workers,[18] who obtained the η^6-stabilized *o*-quinodimethane complex **32** in 83% yield on treatment of this radialene with tris(acetonitrile)tricarbonylchromium in dioxane at room temperature. On heating in dioxane under carbon monoxide, metal complex **32** fragments and rearranges to the trivinylbenzene derivative **9**, the yield again being excellent (95%). When we heated **2a** with $[Fe(CO)_5]$ in boiling dibutyl ether, only rearranged products (of undetermined structure) were obtained. Under milder conditions {$[Fe_2(CO)_9]$ in refluxing THF}, however, the η^4 complex **33** could be obtained, in which the radialene structure of the ligand is maintained. At only 7%, the isolated yield of **33** was poor, one reason being extensive product loss during the chromatographic purification of the metal complex. The fully methylated hydrocarbon **2c** did not react with $[Fe(CO)_5]$ in boiling dibutyl ether.

Experimental Section

General: Melting points: Büchi melting point apparatus (Dr. Tottoli), uncorrected. Chromatography: TLC: Macherey−Nagel Polygram Sil G/UV_{254}, Polygram Alox N/UV_{254}; SC: Merck Kieselgel 60 (230−400 mesh); octyl-derivatized silica gel: Knauer Europrep 60−30 C8 (60 Å, 20−45 μ); neutral aluminium oxide, activity I; preparative thick layer chromatography: Merck Kieselgel PF 254/366. HPLC: Merck L 6200 Intelligent Pump with a L 3000 photo diode array detector with octadecyl-derivatized silica gel LiChrosphere® 100 RP-18 (5 μm). GC: DANI 86.10 HT with a capillary column OV1-50 m with hydrogen as carrier gas; prep. GC: Shimadzu GC-8A and a packed SE-54 column. ^{1}H NMR: Bruker DMX 600, Bruker AM 400, and Bruker AC 200F at 600, 400, and 200 MHz, resp., in deuteriochloroform with TMS as int. standard. ^{13}C NMR (^{1}H broad-band decoupled): Bruker AM 300 at 75.47 MHz, Bruker AM 400 and Bruker AC 200 F at 100.6 and 50.3 MHz, resp. in deuteriochloroform with $\delta(CDCl_3) = 77.05$ as int. standard; the degree of substitution of the carbon atoms was determined by employing the DEPT-135 technique; signal assignment by H,H-COSY, H,H-NOE-difference, C,H-correlation, and C,H-COLOC spectra. MS: Finnigan MAT 8340, EI (70 eV), FAB. GC/MS: Carlo−Erba HRGC 5160 with a DB1-30W capillary column and helium as carrier gas/Finnigan MAT 4515 (EI, 70 eV). IR: Nicolet 320 FT-IR. UV: HP 8452 A Diode Array Spectrophotometer. GC/FT-IR: Carlo−Erba HRGC 5160 with a DB1-30W capillary column and helium as carrier gas/Nicolet 740 FT-IR spectrometer. Elemental analyses: Institute of Inorganic and Analytical Chemistry, Technical University of Braunschweig. Literature procedures were used for the preparation of: hexakis(1-bromoethyl)-benzene (**1a**),[6,7] 7,8,9,10,11,12-hexamethyl[6]radialene (**2a**),[6,7] dodecamethyl[6]radialene (**2c**),[9] and hexakis(bromomethyl)benzene (**18**).[11]

1. A New Diastereomer of 7,8,9,10,11,12-Hexamethyl[6]radialene (*cccaca*-2a): A *n*BuLi solution in hexane (1.6 M, 44.9 mL, 72 mmol) was added at 0 °C to a suspension of **1a** (10.80 g, 15 mmol) in anhydrous THF (300 mL). The mixture was warmed to room temp. and stirred overnight, and the reaction was terminated by the addition of water (7.5 mL) and diethyl ether (300 mL). The reaction mixture was washed carefully with water (4 × 150 mL) and dried with sodium sulfate, and the solvent was removed by distillation. Silica gel (6 g) was added to the residue (4.98 g), and the resulting mixture was prepurified by column chromatography (350 g SiO_2, pentane). One of the fractions yielded product (650 mg), which was subjected to multiple (fourfold) preparative thick layer chromatography on silica gel with hexane, the central third of a product zone always being used for the next chromatography step. Radialene **2a** was concentrated at the beginning of each zone, whereas further isomers were concentrated at its end. Finally, ***cccaca*-2a** (22 mg, 0.7%) was obtained as a colorless oil. IR (film): $\tilde{\nu}$ = 3023 cm^{-1} (m), 2972 (s), 2933 (s), 2912 (s), 2875 (m), 2856 (s), 1443 (s), 1375 (m), 1065 (m), 1035 (m), 984 (m), 877 (m), 862 (m), 848 (s), 831 (s), 781 (w). ^{1} H NMR ($CDCl_3$, 600 MHz): see Table 1; all CH have q and all CH_3 have d multiplicity, J = 6.8−7.0 Hz. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.6 ppm (2 C), 14.7, 14.9, 15.5, 15.6 (CH_3), 116.2, 118.6, 120.3, 120.9, 121.1, 122.9 (=CH−), 135.9, 139.4 (2 C), 139.7, 141.4, 144.7 (=C<). UV (hexane): λ_{max} (lg ε) = 206 nm (4.40). GC/MS (70 eV): *m*/*z* (%) = 241 (19), 240 (100) [M$^+$], 225 (37) [M$^+$ − CH_3], 211 (41), 210 (11), 197 (40), 196 (64), 195 (21), 183 (39), 182 (50), 181 (60), 180 (13), 179 (24), 178 (18), 169 (45), 168 (32), 167 (59), 166 (27), 165 (57), 155 (37), 154 (17), 153 (31), 152 (22), 142 (12), 141 (27), 129 (16), 128 (22), 115 (19). HRMS: $C_{18}H_{24}$: calcd. 240.18780, found 240.187±3 ppm.

2. Thermolysis of Hexamethyl[6]radialene (2a). a) On a Preparative Scale at 300 °C: A sample of **2a** (150 mg, 0.62 mmol) was placed in a 200 mL glass ampoule, and this was sealed after evacuation (0.1 Torr). After having been heated for 1 h at 300 °C, the pyrolysate was separated by thick-layer chromatography (silica gel, hexane) into two fractions: fraction 1 (26 mg, 17%) 1,3,5-triethenyl-2,4,6-triethylbenzene (**9**), analytical and spectroscopic data identical with the authentic hydrocarbon obtained as described below

by dehydrochlorination of **30/31**; fraction 2 (35 mg, 23%): **(*E*)- and (*Z*)-4,6-diethenyl-5,7-diethyl-1,2-dihydro-1,2-dimethylbenzocyclobutene** in 1:1.3 ratio. Preparative gas chromatography (3m SE 54 column, 200 °C, carrier gas H_2) furnished the analytically pure diastereomers: a) Compound **5** (2.5 mg, 1.6%), colorless oil. GC/IR: $\tilde{\nu}$ = 3088 cm^{-1} (w), 2969 (s), 2936 (m), 2903 (m), 2881 (m), 1316 (w), 1299 (w), 1069 (w), 993 (w), 922 (w). ^1H NMR (400 MHz): δ = 6.83 ppm (dd, $^3J_{11,12'}$ = 17.6, $^3J_{11,12}$ = 11.2 Hz, 1 H, 11-H), 6.76 (dd, $^3J_{15,16'}$ = 17.9, $^3J_{15,16}$ = 11.3 Hz, 1 H, 15-H), 5.54 (dd, $^3J_{12',11}$ = 17.6, $^3J_{12',12}$ = 2.0 Hz, 1 H, 12-H′), 5.47 (dd, $^3J_{16,15}$ = 11.3, $^3J_{16,16'}$ = 2.3 Hz, 1 H, 16-H), 5.34 (dd, $^3J_{12,11}$ = 11.2, $^3J_{12,12'}$ = 2.0 Hz, 1 H, 12-H), 5.19 (dd, $^3J_{16',15}$ = 17.9, $^3J_{16',16}$ = 2.3 Hz, 1 H, 16-H′), 3.16 (qd, $^3J_{2,10}$ = 7.0, $^2J_{2,1}$ = 2.0 Hz, 1 H, 2-H), 3.01 (qd, $^3J_{1,9}$ = 7.0, $^2J_{1,2}$ = 2.0 Hz, 1 H, 1-H), 2.69 (q, $^3J_{13,14}$ = 7.5 Hz, 2 H, 13-H), 2.55 (q, $^3J_{17,18}$ = 7.6 Hz, 2 H, 17-H), 1.43 (d, $^3J_{9,1}$ = 7.0 Hz, 3 H, 9-H), 1.39 (d, $^3J_{10,2}$ = 7.0 Hz, 3 H, 10-H), 1.10 (t, $^3J_{18,17}$ = 7.6 Hz, 3 H, 18-H), 1.07 (t, $^3J_{14,13}$ = 7.5 Hz, 3 H, 14-H). ^{13}C NMR (100.6 MHz): δ = 144.05 ppm (s), 144.00 (s), 138.60 (s), 136.88 (s), 136.52 (s), 135.49 (d), 132.45 (d), 129.39 (s), 118.94 (t), 117.13 (t), 46.39 (d), 45.65 (d), 23.44 (t), 22.46 (t), 18.15 (q), 16.13 (q), 14.97 (q), 14.96 (q). GC/MS (70 eV): *m*/*z* (%) = 241 (12), 240 (60) [M^+], 226 (18), 225 (100) [$M^+ - CH_3$], 212 (14), 211 (77) [$M^+ - C_2H_5$], 210 (12), 197 (49), 196 (61), 195 (16), 183 (40), 182 (41), 181 (48), 180 (13), 179 (23), 178 (21), 169 (37), 168 (29), 167 (58), 166 (33), 165 (69), 155 (34), 154 (18), 153 (38), 152 (29), 141 (26), 129 (14), 128 (22), 115 (19). b) Compound **6** (3.7 mg, 2.5%), colorless oil. GC/IR: $\tilde{\nu}$ = 3086 cm^{-1} (w), 2973 (s), 2940 (m), 2907 (m), 2882 (m), 1030 (w), 993 (w), 922 (w). ^1H NMR (400 MHz): δ = 6.84 ppm (dd, $^3J_{11,12'}$ = 17.6, $^3J_{11,12}$ = 11.2 Hz, 1 H, 11-H), 6.76 (dd, $^3J_{15,16'}$ = 17.9, $^3J_{15,16}$ = 11.3 Hz, 1 H, 15-H), 5.56 (dd, $^3J_{12',11}$ = 17.6, $^2J_{12',12}$ = 2.0 Hz, 1 H, 12-H′), 5.47 (dd, $^3J_{16,15}$ = 11.3, $^2J_{16,16'}$ $^2J_{16,16'}$ = 2.3 Hz, 1 H, 16-H), 5.35 (dd, $^3J_{12,11}$ = 11.2, $^2J_{12,12'}$ = 2.0 Hz, 1 H, 12-H), 5.19 (dd, $^3J_{16',15}$ = 17.9, $^2J_{16',16}$ = 2.3 Hz, 1 H, 16-H′), 3.75 (qd, $^3J_{2,10}$, $^2J_{2,1}$ = 6.9 Hz, 1 H, 2-H), 3.62 (qd, $^3J_{1,9}$, $^2J_{2,1}$, 1 H, 1-H), 2.69 (q, $^3J_{13,14}$ = 7.5 Hz, 2 H, 13-H), 2.61−2.52 (m, 2 H, 17-H, 17-H′), 1.29 (d, $^3J_{9,1}$ = 7.5 Hz, 3 H, 9-H), 1.27 (d, $^3J_{10,2}$ = 7.2 Hz, 3 H, 10-H), 1.10 (t, $^3J_{18,17}$ = 7.6 Hz, 3 H, 18-H), 1.06 (t, $^3J_{14,13}$ = 7.5 Hz, 3 H, 14-H). ^{13}C NMR (100.6 MHz): δ = 145.33 ppm (s), 145.18 (s), 138.67 (s), 136.94 (s), 136.46 (s), 135.46 (d), 132.60 (d), 129.31 (s), 118.97 (t), 117.20 (t), 40.57 (d), 39.68 (d), 23.46 (t), 22.63 (t), 14.99 (q), 14.90 (q), 13.98 (q), 11.94 (q). GC/MS (70 eV): *m*/*z* (%) = 241 (12), 240 (61) [M^+], 226 (18), 225 (100) [$M^+ - CH_3$], 212 (14), 211 (78) [$M^+ - C_2H_5$], 210 (12), 197 (49), 196 (62), 195 (16), 183 (41), 182 (42), 181 (49), 180 (13), 179 (24), 178 (20), 169 (37), 168 (29), 167 (61), 166 (33), 165 (69), (34), 154 (18), 153 (38), 152 (30), 141 (26), 129 (14), 128 (23), 115 (20).

b) On a Preparative Scale at 360 °C: A sample of **2a** (120 mg, 0.50 mmol) was placed in a 200 mL glass ampoule, and this was sealed after evacuation (0.1 Torr) After having been heated for 1 h at 360 °C the pyrolysate was separated by thick layer chromatography (silica gel, hexane), to provide an inseparable mixture of **11a** and **11b** (76 mg, 63%) as a colorless oil. ^1H NMR (400 MHz): δ = 6.82 ppm (dd, ^3J = 17.8, ^3J = 11.5 Hz, 1 H, C*H*=CH_2), 6.80 (dd, ^3J = 17.7, ^3J = 11.6 Hz, 1 H, C*H*=CH_2), 6.75 (dt, ^3J could not be determined because of signal overlap, ^4J = 1.8 Hz, 1 H, C*H*=CH−CH_2), 6.72 (dt, ^3J undeterminable, ^4J = 1.8 Hz, 1 H, C*H*=CH−CH_2), 6.10 (dt, ^3J = 9.9, ^3J = 4.9 Hz, 1 H, CH=C*H*−CH_2), 6.08 (dt, ^3J = 9.8, ^3J = 4.9 Hz, 1 H, CH=C*H*−CH_2), 5.48 (dd, ^3J = 11.3, ^2J = 2.5 Hz, 1 H, H), 5.47 (dd, ^3J = 11.4, ^2J = 2.4 Hz, 1 H), 5.20 (dd, ^3J = 17.9, ^2J = 2.3 Hz, 2 H, H′), 2.80−2.60 (m, 16 H, CH_2), 2.27−2.20 (m, 4 H, CH=CH−CH_2), 1.21−1.03 (m, 18 H, CH_3). ^{13}C NMR (100.6 MHz): δ = 138.85 ppm (s, C_{Ar}), 137.61 (s, C_{Ar}−CH=CH_2), 137.49 (s, C_{Ar}), 136.60 (d, *C*H=CH_2), 136.51 (s, C_{Ar}), 136.39 (d, *C*H=CH_2), 135.12 (s, C_{Ar}), 135.03 (s, C_{Ar}), 133.20 (s, C_{Ar}), 131.62 (s, C_{Ar}), 131.01 (s, C_{Ar}−CH=CH), 129.72 (s, C_{Ar}−CH=CH), 128.32 (d, CH=*C*H−CH_2), 127.79 (d, CH=*C*H−CH_2), 125.38 (d, *C*H=CH−CH_2), 125.34 (d, *C*H=CH−CH_2), 118.83 (t, CH=CH_2), 118.69 (t, CH=CH_2), 24.51 (t, C_{Ar}−*C*H_2−CH_2), 24.33 (t, C_{Ar}−*C*H_2−CH_2), 23.46 (t, *C*H_2−CH_3), 23.16 (t, 2 C, *C*H_2−CH_3), 23.00 (t, CH=CH-*C*H_2), 22.94 (t, CH=CH−CH_2), 22.79 (t, *C*H_2−CH_3), 21.91 (t, *C*H_2−CH_3), 21.55 (t, *C*H_2−CH_3), 15.63 (q, CH_3), 15.24 (q, 2 C, CH_3), 15.19 (q, CH_3), 14.94 (q, CH_3), 14.51 (q, CH_3), 2 quaternary carbon atoms could not be identified. GC/MS (70 eV): *m*/*z* (%) = 241 (18), 240 (100) [M^+], 225 (49) [$M^+ - CH_3$], 212 (16), 211 (97) [$M^+ - C_2H_5$], 197 (19), 196 (23), 195 (11), 183 (33), 182 (22), 181 (29), 179 (20), 178 (18), 169 (26), 168 (15), 167 (45), 166 (26), 165 (53), 155 (29), 154 (13), 153 (26), 152 (20), 141 (18), 128 (13), 115 (12).

Chemical Structure Confirmation for 11a/11b. 2-Ethenyl-1,3,4-triethylnaphthalene: A sample of **2a** (120 mg, 0.5 mmol) was thermolyzed for 1 h at 360 °C as described above. The pyrolysate was dissolved in toluene (5 mL), DDQ (136 mg, 0.6 mmol) was added, and the mixture was heated for 1 h at 100 °C. After solvent removal in vacuo, column chromatography on silica gel with pentane yielded the aromatic hydrocarbon (100 mg, 84%) as a colorless oil. IR (film): $\tilde{\nu}$ = 3075 cm^{-1} (m), 2967 (s), 2932 (m), 2899 (m), 2873 (m), 1465 (m), 1452 (m), 1377 (m), 923 (m), 909 (m), 759 (s), 734 (m). ^1H NMR (400 MHz): δ = 8.15−8.00 ppm (m, 2 H, 5-H, 8-H), 7.48−7.41 (m, 2 H, 6-H, 7-H), 6.97 (dd, $^3J_{13,14'}$ = 17.9, $^3J_{13,14}$ = 11.4 Hz, 1 H, 13-H), 5.58 (dd, $^3J_{14,13}$ = 11.4, $^2J_{14,14'}$ = 2.1 Hz, 1 H, 14-H), 5.27 (dd, $^3J_{14',13}$ = 17.9, $^2J_{14',14}$ = 2.1 Hz, 1 H, 14-H′), 3.12 (q, $^3J_{11,12}$ = 7.5 Hz, 2 H, 11-H), 3.11 (q, $^3J_{17,18}$ = 7.5 Hz, 2 H, 17-H), 2.84 (q, $^3J_{15,16}$ = 7.5 Hz, 2 H, 15-H), 1.31 (t, $^3J_{18,17}$ = 7.5 Hz, 3 H, 18-H), 1.25 (t, $^3J_{12,11}$ = 7.5 Hz, 3 H, 12-H), 1.15 (t, $^3J_{16,15}$ = 7.5 Hz, 3 H, 16-H). ^{13}C NMR (100.6 MHz): δ = 137.31 ppm (s, C-3), 136.65 (d, C-13), 136.47 (s, C-2), 135.59 (s, C-1), 134.82 (s, C-4), 131.58 (s, C-10), 130.67 (s, C9), 125.14 (d, C-6 or C-7), 125.02 (d, C-5 or C-8), 124.67 (d, C-6 or C-7), 124.52 (d, C-5 or C8), 119.18 (t, C-14), 23.71 (t, C-15), 22.94 (t, C-11), 21.54 (t, C-17), 15.55 (q, 2C, C-12 and C-18), 14.92 (q, C-16). UV (hexane): λ_{max} (lg ε) = 238 nm (4.80), 294 (3.81). GC/MS (70 eV): *m*/*z* (%) = 239 (14), 238 (79) [M^+], 223 (33) [$M^+ - CH_3$], 210 (17), 209 (100) [$M^+ - C_2H_5$], 195 (20), 194 (34), 193 (16), 181 (29), 180 (21), 179 (66), 178 (59), 167 (29), 166 (26), 165 (70), 153 (16), 152 (17), 115 (10). **1,2,3,4-Tetraethyl-5,6,7,8-tetrahydronaphthalene:** A sample of **2a** (120 mg, 0.5 mmol) was pyrolyzed for 1 h at 360 °C as described above. The pyrolysate was dissolved in methanol (20 mL), Pd/C (10%, 50 mg) was added, and the mixture was hydrogenated for 4 h at room temp. under normal pressure. After filtration and solvent removal, the tetralin (122 mg, 99%) was obtained as a colorless oil. IR (film): $\tilde{\nu}$ = 2966 cm^{-1} (s), 2931 (s), 2904 (s), 2871 (s), 2835 (m), 1463 (m), 1451 (m), 1436 (m), 1376 (m), 1054 (m), 819 (w). ^1H NMR (400 MHz): δ = 2.78−2.71 ppm (m, 4 H, 5-H, 8-H), 2.66 (q, ^3J = 7.5 Hz, 4 H, 11-H, 17-H), 2.62 (q, ^3J = 7.5 Hz, 4 H, 13-H, 15-H), 1.80−1.75 (m, 4 H, 6-H, 7-H), 1.18 (t, ^3J = 7.5 Hz, 4 H, 12-H, 18-H), 1.14 (t, ^3J = 7.5 Hz, 4 H, 14-H, 16-H). ^{13}C NMR (100.6 MHz): δ = 138.08 ppm (s), 137.31 (s), 133.13 (s), 27.11 (t), 23.29 (t), 22.04 (t), 21.76 (t), 15.94 (q), 14.54 (q). UV (hexane): λ_{max} (lg ε) = 214 nm (4.61), 432 (sh, 4.07), 276 (2.57). GC/MS (70 eV): *m*/*z* (%) = 245 (19), 244 (100) [M^+], 230 (16), 229 (88) [$M^+ - CH_3$], 216 (16), 215 (90) [$M^+ - C_2H_5$], 201 (14), 200 (12), 187 (29), 185 (17), 173 (34), 171 (19), 159 (20), 157 (21), 156 (12), 155 (16), 145 (17), 143 (27), 142 (18), 141 (19), 131 (18), 129 (32), 128 (23), 117 (12), 115 (13), 105 (11).

3. Thermolysis of Dodecamethyl[6]radialene (2c): A sample of **2c** (108 mg, 0.3 mmol) was pyrolyzed for 1 h at 350 °C as described above. The pyrolysate was separated by silica gel thick layer chromatography and the least polar fraction was sublimed under high vacuum to afford **1,2-dihydro-1,1,2,2-tetramethy-4,6-bis(methylethenyl)-5,7-bis(methylethyl)lbenzocyclobutene** (**12**, 18 mg, 17%) as a colorless solid, m.p. 192 °C. IR (KBr): $\tilde{\nu}$ = 3075 cm^{-1} (w), 2959 (s), 2923 (s), 2877 (m), 1636 (m), 1449 (m), 1371 (m), 897 (s), 790 (w). ^1H NMR (400 MHz, $C_2D_2Cl_4$, 100 °C): δ = 5.23−5.20 ppm (m, 2 H, 14-H, 20-H), 4.87 (dq, $^2J_{14',14}$ = 2.6, $^4J_{14',15}$ = 0.9 Hz, 1 H, 14-H′), 4.79 (dq, $^2J_{20',20}$ = 2.6, $^4J_{20',21}$ = 0.8 Hz, 1 H, 20-H′), 3.25 [br. s, 1 H, C*H*(CH_3)$_2$], 3.07 [sept, ^3J = 7.1 Hz, 1 H, C*H*(CH_3)$_2$], 2.09 (dd, $^4J_{15,14}$ = 1.3, $^4J_{15,14'}$ = 0.9 Hz, 3 H, 15-H), 2.00 (dd, $^4J_{21,20}$ = 1.3, $^4J_{21,20'}$ = 0.9 Hz, 3 H, 21-H), 1.35 (s, 3 H, cyclobutene-CH_3), 1.34 (s, 3 H, cyclobutene-CH_3), 1.31 (d, ^3J = 7.3 Hz, 3 H, CH_3-CH-C*H*$_3$), 1.28 (d, ^3J = 7.2 Hz, 3 H, CH_3-CH-C*H*$_3$), 1.28 (s, 3 H, cyclobutene-CH_3), 1.25 (s, 3 H, cyclobutene-CH_3), 1.25 (d, ^3J = 7.1 Hz, 3 H, CH_3-CH-C*H*$_3$), 1.16 (d, ^3J = 6.9 Hz, 3 H, CH_3-CH-C*H*$_3$). ^{13}C NMR (100.6 MHz, $C_2D_2Cl_4$, 100 °C): δ = 148.52 ppm, 146.74, 146.05, 144.57, 140.86, 139.98, 136.02, 116.41 (t, C-14 or C-20), 115.24 (t, C-14 or C-20), 49.83, 47.72, 31.88, 26.68, 26.46, 25.33, 25.07, 24.22, 23.71; six ^{13}C signals could not be identified. UV (hexane): λ_{max} (lg ε) = 204 nm (4.65), 226 (sh, 4.13), 280 (3.00). MS (70 eV): *m/z* (%) = 325 (10), 324 (34) [M^+], 310 (25), 309 (100) [$M^+ - CH_3$], 281 (11), 267 (10), 253 (11), 225 (19), 211 (25). HRMS: $C_{24}H_{36}$, calcd. 324.28170, found 324.281±2 ppm.

4. Photolysis of Dodecamethyl[6]radialene (2c): A solution of **2c** (324 mg, 1 mmol) in freshly distilled hexane (340 mL) was irradiated with a low-pressure mercury lamp (Heraeus TNN 15/32, 15W) for 20 min at room temp. in an immersion well photoreactor. The solvent was removed in a rotary evaporator and the remaining oil was separated by silica gel thick layer chromatography with hexane. The obtained fractions were subjected to further thick layer chromatographic purification (silica gel, pentane) to provide, besides starting material (120 mg, 37%), three fractions.

Fraction 1. 1,4-Bis(methylethenyl)-2,5-bis(methylethyl)-3,6-bis(methylethylidene)cyclohexa-1,4-diene (17): 13 mg, 4%, colorless solid, m.p. 100−105 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2987 cm^{-1} (s), 2963 (s), 2935 (s), 2923 (s), 2910 (s), 2870 (m), 1633 (m), 1448 (m), 1366 (m), 922 (w), 904 (s), 821 (w), 811 (w). ^1H NMR (400 MHz): δ = 5.09−5.03 ppm (m, 4 H, H-8, H-8′), 2.93 (dq, $^3J_1$ = 7.07, $^3J_2$ = 6.99 Hz, 2 H, H-10), 1.85−1.83 (m, 6 H, H-9), 1.72 (s, 6 H, H-14), 1.69 (s, 6 H, H-15), 1.18 (d, $^3J_2$ = 6.99 Hz, 6 H, H-11 or H-12), 1.10 (d, $^3J_1$ = 7.07 Hz, 6 H, H-11 or H-12). ^{13}C NMR (100.6 MHz): δ = 145.60 ppm (s, C-2), 144.48 (s, C-1 or C-7), 142.03 (s, C-1 or C-7), 137.26 (s, C-3), 127.71 (s, C-13), 116.14 (t, C-8), 32.35 (d, C-10), 25.68 (q, C-11 or C-12), 25.15 (q, C-15), 24.06 (q, C-9), 23.05 (q, C-11 or C-12), 21.42 (q, C-14). UV (hexane): λ_{max} (lg ε) = 192 nm (4.38), 224 (4.20), 294 (4.03). MS (70 eV): *m/z* (%) = 325 (29), 324 (100) [M^+], 323 (16), 310 (24), 309 (94), 281 (30), 267 (13), 266 (14), 251 (27), 239 (14), 237 (14), 225 (42), 223 (30), 211 (30), 209 (19). HRMS: $C_{24}H_{36}$, calcd. 324.28170, found 324.281±2 ppm.

Fraction 2. 1,5-Bis(methylethenyl)-2,4-bis(methylethyl)-3,6-bis(methylethylidene)cyclohexa-1,4-diene (16): 51 mg, 16%, colorless solid; m.p. after recryst. from dichloromethane/acetone: 130−135 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3078 cm^{-1} (m), 2965 (s), 2925 (s), 2909 (s), 2869 (s), 2854 (s), 1626 (m), 1451 (m), 1438 (m), 1378 (m), 1367 (s), 904 (s). ^1H NMR (400 MHz): δ = 5.05−5.01 ppm (m, 4 H, H-8, H-8′), 3.10 (dq, $^3J_1$ = 7.10, $^3J_2$ = 6.90 Hz, 2 H, H-10), 1.83−1.80 (m, 6 H, H-9), 1.72 (s, 6 H, H-16), 1.67 (s, 6 H, H-14), 1.16 (d, $^3J_1$ = 7.10 Hz, 6 H, H-12), 1.07 (d, $^3J_2$ = 6.90 Hz, 6 H, H-11). ^{13}C NMR (100.6 MHz): δ = 147.40 ppm (s, C-2), 145.30 (s, C-7), 140.03 (s, C-1), 137.55 (s, C-3), 134.04 (s, C-6), 131.23 (s, C-15), 124.90 (s, C-13), 115.43 (t, C-8), 30.95 (d, C-10), 24.83 (q, C-11), 24.02 (q, C-14), 23.96 (q, C-9), 23.03 (q, C-12), 22.64 (q, C-16). UV (hexane): λ_{max} (lg ε) = 192 nm (4.46), 224 (4.25), 290 (4.00). MS (70 eV): *m/z* (%) = 325 (11), 324 (41) [M^+], 310 (25), 309 (100), 281 (36), 267 (16), 266 (11), 253 (17), 251 (22), 239 (16), 237 (11), 225 (51), 223 (21), 211 (43), 197 (14), 183 (14). HRMS: $C_{24}H_{36}$, calcd. 324.28170, found 324.281±2 ppm.

Fraction 3. Dodecamethyl[6]radialene (14): Twist boat conformation (62 mg, 19%), colorless solid m.p. after recryst. from dichloromethane: 213−218 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2992 cm^{-1} (m), 2980 (m), 2918 (s), 2850 (s), 1452 (m), 1434 (m), 1367 (m), 1029 (w), 967 (w), 950 (w). ^1H NMR (400 MHz): δ = 1.69 ppm (br. s, 12 H), 1.54 (br. s, 12 H), 1.48 (br. s, 12 H). ^{13}C NMR (100.6 MHz): δ = 137.44 ppm (s), 136.37 (s), 127.46 (s), 122.57 (s), 23.57 (q), 21.82 (q), 21.73 (q). UV (hexane): λ_{max} (lg ε) = 224 nm (4.60). MS (70 eV): *m/z* (%) = 325 (28), 324 (100) [M^+], 309 (63), 281 (25), 267 (11), 253 (11), 251 (12), 239 (11), 225 (25), 211 (20), 197 (11), 183 (11). HRMS: $C_{24}H_{36}$, calcd. 324.28170, found. 324.281±2 ppm. When the irradiation was terminated after 4 min, isomer **15** could also be isolated from the pyrolysate by thick layer chromatography. From 4 runs (65 mg **2c**, 0.2 mmol) in 200 mL of hexane a total amount of 50 mg (19%) **1-methylethenyl-2-methylethyl-3,4,5,6-tetrakis(methylethylidene)cyclohexene** (**15**) was isolated as a colorless oil. IR (film): $\tilde{\nu}$ = 3077 cm^{-1} (w), 2988 (m), 2962 (s), 2921 (s), 2907 (s), 2852 (s), 1454 (m), 1437 (m), 1368 (m), 889 (m), 816 (w). ^1H NMR (400 MHz): δ = 4.97 ppm (dq, $^2J_{8,8'}$ = 2.9, $^4J_{8,9}$ = 1.4 Hz, 1 H, 8-H or 8-H′), 4.93 (dq, $^2J_{8,8'}$ = 2.9, $^4J_{8,9}$ = 0.9 Hz, 1 H, 8-H or 8-H′), 3.07 (sept, ^3J = 6.9 Hz, 1 H, 10-H), 1.76 (s, 3 H, 9-H), 1.73 (s, 3 H, CH_3), 1.71 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3), 1.59 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.10 (d, ^3J = 7.0 Hz, 3 H, 11-H or 12-H), 0.80 (d, ^3J = 6.8 Hz, 3 H, 11-H or 12-H). ^{13}C NMR (100.6 MHz): δ = 145.64 ppm (s, C-2), 144.13 (s, C-1 or C-7), 140.26 (s, C-1 or C-7), 137.13 (s), 136.59 (s), 136.57 (s), 136.47 (s), 125.77 (s), 124.33 (s), 114.06 (t, C-8), 31.83 (d, C-10), 24.69 (q), 24.62 (q), 24.29 (q), 23.99 (q), 23.78 (q), 23.54 (q, C-11 or C-12), 23.25 (q, C-9), 22.97 (q, C-11 or C-12), 22.35 (q), 22.16 (q), 20.05 (q); two olefinic C atoms could not be identified. UV (hexane): λ_{max} (lg ε) = 222 nm (4.47), 256 (4.20). MS (70 eV): *m/z* (%) = 325 (24), 324 (91) [M^+], 310 (26), 309 (100) [$M^+ - CH_3$], 282 (13), 281 (56), 267 (24), 266 (12), 253 (19), 251 (21), 239 (21), 225 (48), 224 (15), 223 (20), 211 (34), 210 (11), 209 (15), 197 (16), 183 (17), 169 (10). HRMS: $C_{24}H_{36}$, calcd. 324.28170, found 324.281±2 ppm.

5. Dichlorocarbene Addition to [6]Radialene (2d): A solution of methyllithium in diethyl ether (1.6 M, 30 mL, 48 mmol) was added at −85 °C over 1 h to a suspension of hexakis(bromomethyl)benzene (**18**, 7.63 g, 12.0 mmol) in anhydrous THF (130 mL). The reaction mixture was allowed to warm to −45 °C over 2 h, stirred for 30 min at this temperature, and again cooled to −85 °C. After 2-propanol (1.5 mL) and potassium *tert*-butoxide (20.2 g, 0.18 mol) had been added, a solution of chloroform (21.5 g, 0.18 mol) in anhydrous THF (70 mL) was slowly added. The mixture was allowed to warm to −40 °C within 2 h and left standing at −20 °C overnight. For workup the reaction mixture was poured onto ice (400 g), and after neutralization with acetic acid, sodium chloride (100 g) and diethyl ether (400 mL) were added. The phases were separated, the aqueous phase was washed thoroughly with two 100 mL portions of ether, and the organic phases were united, washed with brine, and dried with sodium sulfate. After solvent removal, the residue (7.63 g) was adsorbed on silica gel (14 g) and

prepurified by column chromatography (400 g of silica gel, pentane/dichloromethane = 4:1 (v/v)). One fraction yielded **(*E*)-1,1,7,7-tetrachloro-4,5,9,10-tetramethylidenedispiro[2.2.2.2]decane** (**19a**, 69 mg, 2%, after recrystallization from hexane/dichloromethane) as a colorless solid, m.p. 160 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3097 cm^{-1} (w), 1637 (m), 1416 (s), 1300 (m), 1062 (s), 1035 (s), 1012 (m), 941 (m), 910 (s), 757 (s), 742 (s). ^1H NMR (400 MHz): δ = 5.35 ppm (d, $^2J_{11',11}$ = 0.68 Hz, 4 H, 11-H′), 4.97 (d, $^2J_{11',11}$ = 0.65 Hz, 4 H, 11-H), 2.03 (s, 4 H, 2-H). ^{13}C NMR (100.6 MHz): δ = 144.70 ppm (s, C-4), 113.66 (t, C-11), 64.79 (s, C-1), 43.41 (s, C-3), 25.44 (t, C-2). UV (acetonitrile): λ_{max} (lg ε) = 198 nm (4.36), 240 nm (3.86). MS (70 eV): *m*/*z* (%) = 326 (0.9), 325 (0.9), 324 (3.8), 323 (1.7), 322 (7.5), 321 (2.1), 320 (5.8) [M^+], 289 (10), 288 (20), 287 (30), 286 (51), 285 (33), 284 (49) [M^+ − HCl], 253 (11), 252 (27), 251 (53), 250 (58), 249 (78), 248 (36) [M^+ − 2 HCl], 216 (31), 215 (55), 214 (91), 213 (100), 212 (7) [M^+ − 3 HCl], 200 (11), 199 (12), 180 (25), 179 (91), 178 (92), 177 (19), 176 (16), 165 (31), 153 (19), 152 (42), 151 (17), 139 (12). HRMS: $C_{14}H_{12}Cl_4$: calcd. 321.966452; found 321.966±3 ppm.

6. Dibromocarbene Addition to [6]Radialene (2d): This preparation was as described above for the dichlorocarbene reaction, but by use of **18** (6.36 g, 10.0 mmol) and a solution of methyllithium in diethyl ether (1.6 M, 25 mL, 40.0 mmol) diluted with anhydrous THF (100 mL), potassium *tert*-butoxide (16.83 g, 0.15 mol), and bromoform (37.91 g, 0.15 mol) in anhydrous THF (70 mL), yielding **(*E*)-1,1,7,7-tetrabromo-4,5,9,10-tetramethylidenedispiro[2.2.2.2]decane** (**19b**, 243 mg, 5%) as colorless needles after chromatography and recrystallization from dichloromethane, m.p. 184 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3095 cm^{-1} (w), 1635 (m), 1420 (s), 1408 (m), 1066 (s), 1024 (s), 999 (m), 939 (m), 914 (s), 751 (s), 702 (s), 616 (s). ^1H NMR (400 MHz): δ = 5.43 ppm (d, $^2J_{11',11}$ = 0.67 Hz, 4 H, 11-H′), 5.01 (d, $^2J_{11',11}$ = 0.63 Hz, 4 H, 11-H), 2.23 (s, 4 H, 2-H). ^{13}C NMR (100.6 MHz): δ = 145.45 ppm (s, C-4), 114.73 (t, C-11), 42.42 (s, C-1), 35.62 (s, C-3), 27.63 (t, C-2). UV (acetonitrile): λ_{max} (lg ε) = 192 nm (4.36). MS (70 eV): *m*/*z* (%) = 422 (1), 420 (5), 418 (5), 416 (1) [M^+ − HBr], 342 (20), 341 (17), 340 (43), 339 (27), 338 (24), 337 (12) [M^+ − HBr − Br], 260 (23), 259 (16), 258 (24), 257 (9) [M^+ −2 HBr − Br], 180 (47), 179 (100), 178 (67). MS (CI, NH_3, pos.): *m*/*z* (%) = 520 (4), 518 (5), 516 (4) [M + NH_4^+], 505 (10), 503 (41), 502 (11), 501 (62), 499 (42), 497 (11) [M + H^+], 424 (15), 423 (23), 422 (46), 421 (41), 420 (56), 419 (33), 418 (30), 417 (10), 416 (5) [M − Br^-], 358 (29), 356 (35), 354 (15) [M − HBr − Br^- + NH_3], 343 (38), 342 (56), 341 (88), 340 (100), 339 (72), 338 (52), 337 (19) [M − HBr − Br^-], 261 (22), 260 (35), 259 (32), 258 (30), 257 (12) [M − 2 HBr − Br^-], 181 (11), 180 (53), 179 (84), 178 (46). $C_{14}H_{12}Br_4$ (499.86): calcd. C 33.64, H 2.42; found C 33.39, H 2.31.

7. Dichlorocarbene Addition to Hexamethyl[6]radialene (2a): Aqueous sodium hydroxide solution (10%, 7 mL) was added at −10 °C to a solution of **2a** (240 mg, 1 mmol) and benzyltriethylammonium chloride (46 mg, 0.2 mmol) in pentane (20 mL) and chloroform (10 mL). After stirring for 2 h at −10 °C, the mixture was poured onto water (50 mL) and ice (100 g), the phases were separated, and the aqueous layer was extracted with diethyl ether (3 × 40 mL). The combined organic phases were neutralized and dried with sodium sulfate, and the solvent was removed in vacuo. Preparative thick layer chromatography with hexane yielded **2a** (40 mg, 17%) and crude addition mixture, which was resubmitted to chromatography (aluminium oxide, activity 1; pentane), providing two fractions.

Fraction 1. 1,1-Dichloro-4,5,6,7,8-pentaethylidene-2-methylspiro[2.5]octane (20): 25 mg, 8%, colorless solid, m.p. 114 °C. IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1} (w), 3024 (m), 2999 (m), 2977 (s), 2954 (s), 2936 (s), 2913 (s), 2874 (m), 2855 (s), 1452 (s), 1438 (s), 1372 (m), 1337 (m), 1034 (m), 985 (s), 974 (m), 851 (s), 844 (s), 827 (s), 822 (s), 798 (s), 757 (m). ^1H NMR (400 MHz): δ = 5.48 ppm (q, $^3J_{16,17}$ = 7.0 Hz, 1 H, 16-H), 5.45 (q, $^3J_{14,15}$ = 7.0 Hz, 1 H, 14-H), 5.37 (q, $^3J_{18,19}$ = 7.2 Hz, 1 H, 18-H), 5.36 (q, $^3J_{10,11}$ = 6.9 Hz, 1 H, 10-H), 5.30 (q, $^3J_{12,13}$ = 7.1 Hz, 1 H, 12-H), 2.09 (q, $^3J_{2,9}$ = 6.8 Hz, 1 H, 2-H), 1.86 (d, $^3J_{13,12}$ = 7.1 Hz, 3 H, 13-H), 1.83 (d, $^3J_{15,14}$ = 7.0 Hz, 3 H, 15-H), 1.77 (d, $^3J_{17,16}$ = 7.0 Hz, 3 H, 17-H), 1.76 (d, $^3J_{19,18}$ = 7.1 Hz, 3 H, 19-H), 1.65 (d, $^3J_{11,10}$ = 6.8 Hz, 3 H, 11-H), 1.49 (d, $^3J_{9,2}$ = 6.8 Hz, 3 H, 9-H). ^{13}C NMR (100.6 MHz): δ = 139.91 ppm (s, C-6), 139.80 (s, C-4), 138.99 (s, C-8), 138.55 (s, C-5), 138.50 (s, C-7), 123.35 (d, C-18), 122.76 (d, C-12), 122.36 (d, C-16), 121.82 (d, C-14), 119.67 (d, C-10), 69.68 (s, C-1), 43.42 (s, C-3), 34.94 (d, C-2), 15.15 (q, C-15), 15.12 (q, C-17), 14.96 (q, C-13), 14.41 (q, C-11), 13.95 (q, C-19), 12.02 (q, C-9). UV (acetonitrile): λ_{max} (lg ε) = 194 nm (4.33). MS (70 eV): *m*/*z* (%) = 322 (10) [M^+], 309 (16), 307 (25) [M^+ − CH_3], 293 (13), 289 (30), 288 (21), 287 (94) [M^+ − Cl], 272 (15), 271 (22) [M^+ − HCl − CH_3], 260 (11), 259 (29), 258 (22), 257 (30), 252 (19), 251 (47) [M^+ − Cl − HCl], 245 (15), 244 (12), 243 (34), 242 (13), 237 (40), 236 (32), 235 (28), 231 (22), 229 (17), 224 (29), 223 (100), 222 (63), 221 (53), 215 (11), 209 (32), 208 (38), 207 (70), 206 (25), 205 (20), 203 (15), 196 (13), 195 (43), 194 (38), 193 (62), 192 (37), 191 (39), 190 (15), 189 (19), 181 (29), 180 (25), 179 (53), 178 (43), 167 (27), 166 (26), 165 (64), 155 (12), 153 (28), 152 (28). HRMS: $C_{19}H_{24}Cl_2$, calcd. 322.125508, found. 322.125±2 ppm.

Fraction 2. (*E*)-1,1,6,6-Tetrachloro-4,8,9,10-tetraethylidene-2,7-dimethylbispiro[2.1.2.3]decane (22): 68 mg, 17%, colorless solid, m.p. 141.5 °C. IR (KBr): $\tilde{\nu}$ = 3096 cm^{-1} (w), 2999 (m), 2962 (m), 2934 (s), 2913 (s), 2875 (m), 2855 (m), 1453 (s), 1373 (m), 835 (s), 817 (s), 778 (s), 737 (s). ^1H NMR (400 MHz): δ = 5.83 ppm (q, $^3J_{19,20}$ = 7.2 Hz, 1 H, 19-H), 5.54 (q, $^3J_{17,18}$ = 7.1 Hz, 1 H, 17-H), 5.49 (q, $^3J_{15,16}$ = 7.0 Hz, 1 H, 15-H), 5.19 (q, $^3J_{12,13}$ = 7.4 Hz, 1 H, 12-H), 2.39 (q, $^3J_{7,14}$ = 6.7 Hz, 1 H, 7-H), 2.24 (q, $^3J_{2,11}$ = 6.9 Hz, 1 H, 2-H), 1.90 (d, $^3J_{16,15}$ = 7.0 Hz, 3 H, 16-H), 1.88 (d, $^3J_{18,17}$ = 7.1 Hz, 3 H, 18-H), 1.83 (d, $^3J_{20,19}$ = 7.2 Hz, 3 H, 20-H), 1.73 (d, $^3J_{13,12}$ = 7.4 Hz, 3 H, 3-H), 1.51 (d, $^3J_{11,2}$ = 6.9 Hz, 3 H, 11-H), 1.34 (d, $^3J_{14,7}$ = 6.7 Hz, 3 H, 14-H). ^{13}C NMR 100.6 MHz): δ = 139.28 ppm (s, C-9), 139.11 (s, C-10), 136.60 (s, C-4), 136.00 (s, C-8), 128.80 (d, C-19), 126.15 (d, C-15), 122.97 (d, C-17), 122.05 (d, C-12), 73.54 (s, C-1), 71.73 (s, C-6), 45.97 (s, C-5), 42.26 (s, C-3), 36.26 (d, C-2), 33.29 (d, C-7), 15.58 (q, C-16), 15.35 (q, C-18), 15.21 (q, C-20), 14.53 (q, C-13), 12.74 (q, C-14), 9.43 (q, C-11). UV (acetonitrile): λ_{max} (lg ε) = 212 nm (4.31). MS (CI, NH_3, pos.): *m*/*z* (%) = 411 (10), 410 (11), 409 (48), 408 (22), 407 (100), 406 (11), 405 (78) [M + H]$^+$, 373 (21), 372 (11), 371 (48), 370 (11), 369 (42) [M − Cl]$^+$, 337 (32), 336 (12), 335 (50), 333 (14) [M − Cl − HCl]$^+$.

Fraction 3. 1,1,7,7-Tetrachloro-4,5,9,10-tetraethylidene-2,8-dimethylbispiro[2.2.2.2]decane (23): 4 mg, 1%, colorless, poorly soluble solid, m.p. 220 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3067 cm^{-1} (w), 2984 (m), 2954 (s), 2928 (m), 2914 (m), 1454 (s), 1438 (s), 987 (m), 966 (m), 853 (m), 830 (s), 810 (s), 774 (m), 671 (m), 641 (s). ^1H NMR (400 MHz): δ = 5.52 ppm (q, $^3J_{12,13}$ = 7.0 Hz, 2 H, 12-H), 5.45 (q, $^3J_{14,15}$ = 7.3 Hz, 2 H, 14-H), 2.16 (q, $^3J_{2,11}$ = 6.9 Hz, 2 H, 2-H), 1.81 (d, $^3J_{15,14}$ = 7.3 Hz, 6 H, 15-H), 1.63 (d, $^3J_{13,12}$ = 7.0 Hz, 6 H, 13-H), 1.57 (d, $^3J_{11,2}$ = 6.9 Hz, 6 H, 11-H). A ^{13}C NMR spectrum could not be registered because of the poor solubility of **23** in $CDCl_3$. UV (acetonitrile): λ_{max} (lg ε) = 192 nm (4.23), 196 (4.22), 204 (4.15). MS (70 eV): *m*/*z* (%) = 404 (1) [M^+], 371 (34), 369 (35) [M^+ − Cl], 335 (24), 334 (16), 333 (34) [M^+ − Cl − HCl],

321 (11), 319 (19), 307 (26), 306 (14), 305 (39), 300 (11), 299 (29), 298 (31), 297 (54) [$M^+ - Cl - 2\,HCl$], 285 (11), 284 (13), 283 (26), 282 (11), 272 (16), 271 (47), 270 (47), 269 (100), 268 (20), 267 (11), 263 (37), 262 (34), 261 (34), 257 (11), 256 (14), 255 (26), 254 (15), 253 (14), 249 (11), 248 (16), 247 (31), 246 (14), 243 (17), 242 (14), 241 (33), 240 (11), 235 (33), 234 (37), 233 (54), 232 (24), 231 (20). $C_{20}H_{24}Cl_4$, calcd. 404.0632, found 404.063±2 ppm.

8. Cyclopropanation of Hexamethyl[6]radialene (2a): A solution of trimethylaluminium (2 M, 3.6 mL, 7.2 mmol) in toluene was added at −10 °C to a solution of **2a** (240 mg, 1 mmol) and diiodomethane (2.68 g, 10 mmol) in pentane (75 mL). After stirring for 3 h, the mixture was allowed to warm to 0 °C and the reaction was terminated by the addition of aqueous sodium hydroxide (10%, 20 mL). The phases were separated, the aqueous phase was extracted with pentane (3 × 10 mL), and the combined organic phases were neutralized and dried with sodium sulfate. The solvent and excess diiodomethane were removed in vacuo (0.1 Torr), and the remaining oil was fractionated by preparative thick layer chromatography (silica gel) with hexane to yield **4,5,6,7,8-pentaethylidene-1-methylspiro[2.5]octane** (**21**, 20 mg, 8%) as a colorless oil. IR (KBr): $\tilde{\nu}$ = 3073 cm^{-1} (w), 2995 (s), 2974 (s), 2932 (s), 2914 (s), 2858 (s), 1444 (s), 1390 (m), 1375 (m), 1095 (m), 1035 (m), 991 (m), 864 (m), 848 (s), 832 (m), 817 (m). ^1H NMR (400 MHz): δ = 5.37 ppm (q, ^3J = 7.0 Hz, 1 H), 5.30 (q, ^3J = 6.8 Hz, 1 H), 5.24 (q, ^3J = 6.9 Hz, 1 H), 5.19 (q, ^3J = 7.0 Hz, 1 H), 5.12 (q, ^3J = 7.1 Hz, 1 H), 1.81 (d, ^3J = 7.0 Hz, 3 H), 1.80 (d, ^3J = 6.9 Hz, 3 H), 1.71 (d, ^3J = 7.0 Hz, 3 H), 1.71 (d, ^3J = 6.9 Hz, 3 H), 1.70 (d, ^3J = 6.7 Hz, 3 H), 1.28 (br. s, 1 H, 2-H), 0.87 (d, $^3J_{9,1}$ = 6.1 Hz, 3 H, 9-H), 0.77 (br. s, 1 H, 2-H), 0.56 (br. s, 1 H, 1-H). ^{13}C NMR (100.6 MHz): δ = 141.95 ppm (s), 141.58 (s), 140.80 (s), 140.47 (s), 140.36 (s), 120.82 (d), 120.53 (d), 119.44 (d), 118.76 (d), 116.50 (d), 34.27 (s, C-3), 18.37 (d, C-1), 17.28 (t, C-2), 14.69 (q), 14.66 (q), 14.54 (q), 14.42 (q), 14.10 (q), 13.82 (q). UV (hexane): λ_{max} (lg ε) = 198 nm (4.32). GC/MS (70 eV): *m/z* (%) = 254 (8) [M^+], 240 (19), 239 (100) [$M^+ - CH_3$], 226 (12), 225 (66), 211 (51), 210 (76), 209 (23), 197 (38), 196 (48), 195 (74), 193 (13), 184 (11), 183 (65), 182 (47), 181 (85), 180 (25), 179 (43), 178 (24), 170 (14), 169 (78), 168 (31), 167 (54), 166 (35), 165 (75), 156 (14), 155 (54), 154 (25), 153 (43), 152 (26), 143 (13), 142 (16), 141 (39), 129 (24), 128 (29), 115 (23), 105 (11), 91 (27), 79 (11), 77 (23). HRMS: $C_{19}H_{26}$, calcd. 254.2035, found 254.203±3 ppm.

9. Cyclopropanation of Dodecamethyl[6]radialene (2c): A solution of **2c** (162 mg, 0.5 mmol) and diiodomethane (1.34 g, 5 mmol) in pentane (40 mL) was treated with a solution of trimethylaluminium (2 M, 2 mL, 4 mmol) in toluene, and the reaction mixture was stirred for 4 h at room temp. The methylenation was terminated by the addition of aqueous sodium hydroxide solution (20%, 20 mL), the phases were separated, and the aqueous phase was extracted with ether (2 × 20 mL). After the combined organic layers had been neutralized and dried (sodium sulfate), the solvent was removed under vacuum and the product mixture was fractionated by thick layer chromatography (silica gel, pentane): Fraction 1: substrate (18 mg, 11%).

Fraction 2. 1,1-Dimethyl-4,5,6,7,8-pentakis(methylethylidene)spiro[2.5]octane (24): 79 mg, 47%, as a colorless solid, m.p. 240 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1} (w), 3011 (m), 2986 (s), 2977 (s), 2956 (m), 2923 (s), 2908 (s), 2853 (s), 1456 (m), 1439 (m), 1367 (m), 1142 (m), 1125 (m), 1096 (m), 1072 (m), 981 (m). ^1H NMR (400 MHz): δ = 1.78 ppm (s, 3 H, 11-H), 1.63 (s, 6 H, H-15, H-17), 1.55 (s, 3 H, 12-H), 1.50 (s, 3 H, 14-H), 1.26 (s, 3 H, 9-H), −0.05 (s, 2 H, 2-H). ^{13}C NMR (100.6 MHz): δ = 138.69 ppm (s, C-5), 137. 82 (s, C-6), 137.53 (s, C-4), 122.71 (s, C-16), 122.46 (s, C-10), 121.52 (s, C-13), 41.66 (s, C-3 or C-1), 30.83 (s, C-1 or C-3), 25.26 (q, C-9), 24.01 (t, C-2), 22.92 (q, C-11), 22.12 (q, C-12), 21.70 (q, C-15 or C-17), 21.00 (q, C-14 and C-15 or C-17). UV (hexane): λ_{max} (lg ε) = 196 nm (4.44), 234 (4.22). MS (70 eV): *m/z* (%) = 339 (22), 338 (79) [M^+], 324 (27), 323 (100), 296 (11), 295 (41), 281 (21), 280 (12), 265 (15), 253 (16), 239 (35), 238 (11), 237 (19), 225 (22), 224 (11), 223 (12), 211 (24), 209 (15), 197 (20). $C_{25}H_{38}$ (338.58): calcd. C 88.69, H 11.31; found C 88.33, H 11.67.

Fraction 3: 1,1,7,7-Tetramethyl-4,5,9,10-tetrakis(methylethylidene)-dispiro[2.2.2.2]decane (25): 48 mg, 27%, as a colorless solid, m.p. 250 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3063 cm^{-1} (w), 3013 (m), 2980 (s), 2951 (s), 2921 (s), 2907 (s), 2867 (s), 2852 (s), 1452 (m), 1441 (m), 1368 (s), 1125 (m), 1088 (s), 1032 (m), 988 (m), 734 (m). ^1H NMR (400 MHz): δ = 1.80 ppm (s, 12 H, 13-H), 1.44 (s, 12 H, 14-H), 1.25 (s, 12 H, 11-H), −0.10 (s, 4 H, 2-H). ^{13}C NMR (100.6 MHz): δ = 139.09 ppm (s, C-4), 121.25 (s, C-12), 43.09 (s, C-3 or C-1), 31.49 (s, C-1 or C-3), 25.25 (q, C-11), 23.09 (t, C-2), 22.45 (q, C-13), 22.20 (q, C-14). UV (hexane): λ_{max} (lg ε) = 194 nm (4.44). MS (70 eV): *m/z* (%) = 352 (23), 338 (28) [M^+], 337 (100), 310 (14), 309 (48), 295 (23), 294 (12), 281 (20), 279 (25), 267 (15), 253 (39), 252 (11), 251 (20), 239 (22), 238 (11), 237 (13), 225 (29), 224 (11), 223 (19), 211 (36), 210 (11), 209 (16), 197 (22), 195 (15), 193 (12), 183 (22), 181 (11), 179 (12). $C_{25}H_{38}$ (338.58): calcd. C 88.57, H 11.43; found C 88.31, H: 11.69.

10. Epoxidation of Hexamethyl[6]radialene (2a): A solution of **2a** (240 mg, 1 mmol) and 3-chloroperbenzoic acid (69%, 250 mg, 1 mmol) in chloroform (25 mL) was stirred for 90 min at −10 °C. Ether was added (50 mL) and the reaction mixture washed thoroughly with sodium carbonate solution (10%, 3 × 20 mL). The organic phase was neutralized and dried with sodium sulfate, the solvent was removed in vacuo, and the remaining oil was chromatographed on octyl-derivatized silica gel with methanol/water (85:15, v/v): besides starting material (9 mg), **4,5,6,7,8-pentaethylidene-9-methyl-1-oxaspiro[2.5]octane** (**26**, 30 mg, 12%) was isolated as a colorless solid m.p. 102 °C. IR (KBr): $\tilde{\nu}$ = 3024 cm^{-1} (w), 2988 (m), 2968 (s), 2928 (s), 2914 (s), 2871 (m), 2855 (s), 1441 (m), 1376 (m), 1368 (m), 995 (m), 986 (m), 911 (m), 870 (m), 862 (m), 848 (s), 832 (s), 827 (m), 783 (m). ^1H NMR (400 MHz): δ = 5.50 ppm (q, $^3J_{10,11}$ = 7.0 Hz, 1 H, 10-H), 5.40 (q, ^3J = 6.9 Hz, 1 H), 5.39 (q, ^3J = 7.0 Hz, 1 H), 5.29 (q, ^3J = 7.0 Hz, 1 H), 5.27 (q, ^3J = 7.1 Hz, 1 H), 2.90 (q, $^3J_{2,9}$ = 5.3 Hz, 1 H, 2-H), 1.88 (d, ^3J = 7.1 Hz, 3 H), 1.81 (d, ^3J = 6.7 Hz, 3 H), 1.79 (d, ^3J = 6.5 Hz, 3 H), 1.75 (d, ^3J = 6.9 Hz, 3 H), 1.75 (d, $^3J_{11,10}$ = 7.0 Hz, 3 H, 11-H), 1.12 (d, $^3J_{9,2}$ = 5.3 Hz, 3 H, 9-H). ^{13}C NMR (100.6 MHz): δ = 139.24 ppm (s), 138.90 (s, C-4), 138.43 (s), 137.47 (s), 135.43 (s), 122.53 (d), 122.00 (d), 121.72 (d), 121.29 (d), 117.75 (d, C-10), 67.95 (s, C-3), 60.59 (d, C-2), 14.84 (q), 14.61 (q), 14.47 (q), 13.84 (q, C-11), 13.09 (q, C-9), 13.02 (q). UV (hexane): λ_{max} (lg ε) = 194 nm (4.39). MS (70 eV): *m/z* (%) = 257 (16), 256 (71) [M^+], 242 (19), 241 (100) [$M^+ - CH_3$], 228 (12), 227 (60), 226 (11), 213 (40), 212 (55), 211 (16), 199 (30), 198 (27), 197 (37), 185 (24), 184 (16), 183 (26), 182 (15), 181 (11), 171 (17), 169 (22), 168 (19), 167 (27), 166 (12), 165 (24), 157 (16), 156 (11), 155 (26), 154 (14), 153 (26), 152 (17), 143 (14), 142 (12), 141 (20), 129 (15), 128 (17), 115 (16).

11. Mono- and Bis-Epoxidation of Dodecamethyl[6]radialene (2c): A solution of 3-chloroperbenzoic acid (64 mg, 0.25 mmol) in CH_2Cl_2 (2 mL) was slowly added at −22 °C to a solution of **2c** (81 mg, 0.25 mmol) in CH_2Cl_2 (5 mL). After the reaction mixture had been stirred for 1 h at −22 °C, sodium carbonate solution (10%, 5 mL) was added and the mixture was diluted with CH_2Cl_2 (40 mL) and water (40 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL), and the combined organic phases were neutralized and

dried with sodium sulfate. After solvent removal the residue was separated on RP-8-silica gel with methanol/water (9:1, v/v), yielding two fractions.

Fraction 1. 2,2-Dimethyl-4,5,6,7,8-pentakis(methylethylidene)-1-oxaspiro[2.5]octane (27): 40 mg, 47%, colorless solid, m.p. 248 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2985 cm^{-1} (s), 2966 (m), 2958 (m), 2927 (s), 2910 (s), 2852 (s), 1453 (s), 1442 (s), 1375 (s), 1367 (s), 1245 (m), 1137 (m), 1117 (m), 1100 (s), 875 (s), 801 (m). ^{1}H NMR (400 MHz): δ = 1.77 ppm (s, 6 H, 11-H), 1.67 (s, 6 H, 15-H), 1.65 (s, 6 H, 17-H), 1.59 (s, 6 H, 12-H), 1.54 (s, 6 H, 14-H), 1.41 (s, 6 H, 9-H). ^{13}C NMR (100.6 MHz): δ = 136.71 ppm (s, C-6), 135.14 (s, C-5), 134.75 (C-4), 125.79 (C-13), 123.39 (s, C-16), 122.92 (s, C-10), 73.20 (s, C-3), 69.72 (s, C-2), 23.23 (q, C-9), 22.39 (q, C-11), 21.65 (q, C-17), 21.52 (q, C-12), 21.17 (q, C-15), 20.88 (q, C-14). UV (hexane): λ_{max} (lg ε) = 194 nm (4.46), 236 (4.22). MS (70 eV): *m/z* (%) = 341 (17), 340 (60) [M^+], 326 (16), 325 (58) [$M^+ - CH_3$], 323 (23), 322 (90) [$M^+ - H_2O$], 308 (11), 307 (42), 297 (25), 283 (16), 282 (11), 269 (20), 268 (22), 267 (100), 255 (12), 241 (16), 239 (39), 237 (17), 225 (42), 224 (24), 223 (17), 213 (11), 210 (16), 209 (30), 207 (12), 199 (12), 197 (17), 196 (11), 195 (15), 194 (11), 193 (14), 185 (14), 181 (11), 179 (14), 171 (14), 169 (11), 167 (11), 165 (14), 157 (13), 105 (13). HRMS: $C_{24}H_{36}O$: calcd. 340.2766, found 340.276±2 ppm.

Fraction 2. 2,2,8,8-Tetramethyl-4,5,9,10-tetrakis(methylethylidene)-1,7-dioxadispiro[2.2.2.2]decane (28): 25 mg, 28%, colorless solid, m.p. 245 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3005 cm^{-1} (m), 2982 (m), 2970 (m), 2956 (m), 2927 (s), 2912 (s), 2855 (m), 1454 (m), 1442 (m), 1381 (m), 1369 (m), 1116 (m), 1100 (m), 972 (m). ^{1}H NMR (400 MHz): δ = 1.72 ppm (s, 12 H), 1.49 (s, 12 H, 13-H), 1.26 (s, 12 H). ^{13}C NMR (100.6 MHz): δ = 133.96 ppm (s), 126.61 (s), 74.14 (s, C-3 or C-2), 67.10 (s, C-2 or C-3), 25.94 (q), 23.07 (q), 21.91 (q). UV (hexane): λ_{max} (lg ε) = 192 nm (4.23), 216 (4.29). MS (70 eV): *m/z* (%) = 356 (22) [M^+], 342 (21), 341 (74) [$M^+ - CH_3$], 338 (14) [$M^+ - H_2O$], 324 (12), 323 (42), 313 (29), 299 (12), 298 (22), 297 (22), 295 (19), 285 (14), 284 (22), 283 (100), 271 (14), 257 (12), 256 (12), 255 (50), 253 (14), 241 (26), 240 (11), 239 (11), 227 (24), 225 (25), 213 (26), 211 (12), 210 (12), 199 (23), 197 (12), 195 (11), 185 (14), 171 (15). $C_{24}H_{36}O_2$: calcd. 356.27153, found 356.271±2 ppm.

12. Threefold Epoxidation of Dodecamethyl[6]radialene (2c): A solution of 3-chloroperbenzoic acid (256 mg, 1 mmol) in CH_2Cl_2 (4 mL) was slowly added to a solution of **2c** (81 mg, 0.25 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred for 1 h at 20 °C. The oxidation was terminated by addition of sodium carbonate solution (10%, 5 mL), and a mixture of CH_2Cl_2 (40 mL) and water (40 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL), and the combined organic phases were neutralized and dried with sodium sulfate. After solvent removal the residue was purified by column chromatography (Alox, CH_2Cl_2) to yield **13,14,15,16,17,18-hexamethyl-7,11,13-tris(methylethylidene)-1,5,9-trioxatrispiro[2.0.2.1.2.2]dodecane** (**29**, 56 mg, 60%) as colorless solid, m.p. > 250 °C. IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (m), 2965 (m), 2929 (s), 2911 (s), 2877 (m), 2855 (m), 1459 (m), 1455 (m), 1386 (m), 1371 (s), 1099 (m), 890 (m), 884 (m), 824 (m), 781 (m). ^{1}H NMR (400 MHz): δ = 1.86 ppm (s, 3 H), 1.84 (s, 3 H), 1.69 (s, 3 H), 1.63 (s, 3 H), 1.60 (s, 3 H), 1.53 (s, 3 H), 1.49 (s, 3 H), 1.46 (s, 3 H), 1.45 (s, 3 H), 1.38 (s, 3 H), 1.34 (s, 3 H), 1.25 (s, 3 H). ^{13}C NMR (100.6 MHz): δ = 132.83 ppm (s), 130.74 (s), 129.95 (s), 129.50 (s), 128.57 (s), 126.41 (s), 74.32 (s), 73.23 (s), 72.57 (s), 71.89 (s), 67.15 (s), 65.48 (s), 25.58 (q), 25.27 (q), 23.51 (q), 23.49 (q), 22.97 (q), 22.65 (q), 22.56 (q), 22.25 (q), 22.15 (q), 21.62 (q), 21.37 (q), 20.94 (q). UV (hexane): λ_{max} (lg ε) = 192 nm (4.25), 224 (4.12). GC/MS (70 eV): *m/z* (%) = 372 (0.5) [M^+], 299 (39), 271 (27), 243 (20), 241 (19), 229 (23), 215 (16), 213 (18), 201 (15), 199 (14), 198 (14), 187 (18), 185 (16), 173 (16), 171 (18), 159 (16), 157 (14), 135 (11), 133 (14), 121 (11), 119 (15), 107 (16), 105 (17), 93 (11), 91 (17), 43 (100). No HRMS could be obtained because of the very low intensity of the molecular ion signal.

13. 1,3,5-Triethenyl-2,4,6-triethylbenzene (9) and 1,2,4-Triethenyl-3,5,6-triethylbenzene (10): A stream of hydrogen chloride was passed through a solution of **2a** (120 mg, 0.5 mmol) in diethyl ether (15 mL) and acetic acid (2 mL) at −22 °C for 30 min. The reaction mixture was diluted cautiously with ice water (40 mL) and extracted several times with ether. The combined organic phases were neutralized with sodium carbonate solution and dried with sodium sulfate. After solvent removal the residual oil was taken up in diethyleneglycol dimethyl ether (5 mL), potassium *tert*-butoxide (336 mg, 3 mmol) was added, and the mixture was heated for 2 h at 100 °C. After the mixture had cooled to room temp., water was added (30 mL), the mixture was extracted thoroughly with diethyl ether, and the combined organic phases, after neutralization, were dried with sodium sulfate. After solvent removal under vacuum, preparative thick layer chromatography (silica gel, hexane) furnished two fractions.

Fraction 1: 1,3,5-Triethenyl-2,4,6-triethylbenzene (9): 22 mg, 18%), colorless solid, m.p. 56.5 °C (ref.[18] 55−56 °C). IR (KBr): $\tilde{\nu}$ = 3087 cm^{-1} (m), 3001 (m), 2976 (s), 2942 (m), 2882 (m), 995 (m), 924 (m), 840 (w). ^{1}H NMR (400 MHz): δ = 6.79 ppm (dd, $^3J_{7,8'}$ = 17.9, $^3J_{7,8}$ = 11.3 Hz, 3 H, 7-H), 5.48 (dd, $^3J_{8,7}$ = 17.9, $^2J_{8,8'}$ = 2.3 Hz, 3 H, 8-H), 5.23 (dd, $^3J_{8',7}$ = 11.3, $^2J_{8',8}$ = 2.3 Hz, 3 H, 8-H′), 2.67 (q, $^3J_{9,10}$ = 7.4 Hz, 6 H, 9-H), 1.01 (t, $^3J_{10,9}$ = 7.4 Hz, 9 H, 10-H). ^{13}C NMR (100.6 MHz): δ = 138.79 ppm (s, C-1), 135.76 (s, C-2), 135.76 (d, $^1J_{C,H}$ = 154 Hz, C-7), 119.04 (t, $^1J_{C,H}$ = 156 Hz, C-8), 24.03 (t, $^1J_{C,H}$ = 127, $^2J_{C,H}$ = 4 Hz, C-9), 14.51 (q, $^1J_{C,H}$ = 127, $^2J_{C,H}$ = 5 Hz, C-10). UV (hexane): λ_{max} (lg ε) = 220 nm (4.47). MS (70 eV): *m/z* (%) = 241 (12), 240 (64) [M^+], 226 (18), 225 (100) [$M^+ - CH_3$], 212 (13), 211 (70) [$M^+ - C_2H_5$], 210 (11), 197 (50), 196 (46), 183 (37), 182 (27), 181 (34), 179 (11), 178 (12), 169 (28), 168 (19), 167 (37), 166 (20), 165 (39), 155 (23), 154 (11), 153 (22), 141 (14).

Fraction 2. 1,2,4-Triethenyl-3,5,6-triethylbenzene (10): 26 mg, 22%, colorless solid, m.p. 58 °C. IR (KBr): $\tilde{\nu}$ = 3078 cm^{-1} (m), 2965 (s), 2931 (s), 2895 (m), 2871 (s), 1629 (m), 1464 (m), 1452 (m), 1436 (m), 1368 (m), 1289 (m), 991 (s), 916 (s), 837 (m). ^{1}H NMR (400 MHz): δ = 6.82 ppm (dd, $^3J_{13,14'}$ = 17.9, $^3J_{13,14}$ = 11.3 Hz, 1 H, 13-H), 6.71 (dd, $^3J_{7,8'}$ = 18.0, $^3J_{7,8}$ = 11.4 Hz, 1 H, 7-H), 6.69 (dd, $^3J_{9,10'}$ = 17.9, $^3J_{9,10}$ = 11.4 Hz, 1 H, 9-H), 5.49 (dd, $^3J_{14,13}$ = 11.4, $^2J_{14,14'}$ = 2.2 Hz, 1 H, 14-H), 5.44 (dd, $^3J_{8,7}$ = 11.4, $^2J_{8,8'}$ = 2.2 Hz, 1 H, 8-H), 5.41 (dd, $^3J_{10,9}$ = 11.4, $^2J_{10,10'}$ = 2.2 Hz, 1 H, 10-H), 5.23 (dd, $^3J_{14',13}$ = 17.9, $^2J_{14',14}$ = 2.2 Hz, 1 H, 14-H′), 5.18 (dd, $^3J_{10',9}$ = 17.9, $^2J_{10',10}$ = 2.3 Hz, 1 H, 10-H′), 5.18 (dd, $^3J_{8',7}$ = 18.0, $^2J_{8',8}$ = 2.3 Hz, 1 H, 8-H′), 2.73−2.64 (m, 6 H, 11-H, 15-H, 17-H), 1.11 (t, ^3J = 7.5 Hz, 3 H, 16-H or 18-H), 1.10 (t, ^3J = 7.4 Hz, 3 H, 16-H or 18-H), 1.02 (t, $^3J_{12,11}$ = 7.4, 3 H, 12-H). ^{13}C NMR (100.6 MHz): δ = 138.90 ppm (s, C-5 or C-6), 137.74 (s, C-4), 137.42 (s, C-3), 137.25 (s, C-5 or C-6), 136.74 (d, C-7), 136.61 (s, C-1), 136.59 (d, C-9), 136.06 (d, C-13), 134.95 (s, C-2), 119.44 (t, C-8), 119.27 (t, C-10), 118.94 (t, C-14), 23.78 (t, C-11), 23.11 (t, C-15 or C-17), 22.79 (t, C-15 or C-17), 15.26 (q, C-16 or C-18), 15.12 (q, C-16 or C-18), 14.65 (q, C-12). UV (hexane): λ_{max} (lg ε) = 194 nm (4.28), 226 (4.46). MS (70 eV): *m/z* (%) = 241 (16), 240 (82) [M^+], 226 (18), 225 (100) [$M^+ - CH_3$], 212 (16), 211 (96) [$M^+ - C_2H_5$], 197 (42), 196 (42), 195 (11), 163 (44), 162 (31), 161 (37), 159 (14), 158 (12), 169 (31), 168 (22), 167 (42), 166 (22), 165 (42), 155

Table 2. Crystallographic data for compounds **19a**, **19b**, **14**, **22**, and **23**

Compound	**19a**	**19b**	**14**	**22**	**23**
Empirical formula	$C_{14}H_{12}Cl_4$	$C_{14}H_{12}Br_4$	$C_{24}H_{36}$	$C_{20}H_{24}Cl_4$	$C_{20}H_{24}Cl_4$
M_r	322.04	499.88	324.53	406.19	406.19
Habit	colorless prism	colorless prism	colorless tablet	colorless tablet	colorless tablet
Cryst. size [mm]	0.62×0.40×0.28	0.52×0.36×0.24	0.7×0.4×0.2	0.7×0.4×0.15	0.54×0.54×0.35
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P(-1)$	$P2_1/n$	$P2_1/n$
Cell constants					
a [Å]	5.9349(12)	6.1303(8)	9.1841(10)	9.652(2)	10.542(2)
b [Å]	15.115(2)	8.4097(10)	14.0705(16)	13.253(3)	8.079(2)
c [Å]	8.3711(12)	15.2847(16)	17.656(2)	15.574(3)	11.373(2)
α [°]	90	90	71.027(8)	90	90
β [°]	107.798(12)	101.378(8)	88.748(6)	90.29(3)	101.92(2)
γ [°]	90	90	81.716(6)	90	90
V [Å^3]	715.0(2)	772.50(16)	2134.4(4)	1992.2(7)	947.8(3)
Z	2	2	4	4	2
D_x [Mg·m^{-3}]	1.496	2.149	1.010	1.354	1.423
μ [mm^{-1}]	0.81	10.4	0.06	0.59	0.62
F(000)	328	472	720	848	424
T [°C]	−130	−100	−100	−130	−130
$2\theta_{max}$	55	50	50	50	55
Refl. measured	3242	2846	10949	5666	2455
Refl. indep.	1639	1353	7355	3467	2182
R_{int}	0.012	0.037	0.024	0.056	0.012
Parameters	83	83	457	223	112
$wR(F^2$, all refl.)	0.062	0.040	0.108	0.188	0.078
R [F, >4σ(F)]	0.023	0.019	0.045	0.070	0.029
S	1.08	0.95	0.85	1.04	1.08
max. Δρ [e·Å^{-3}]	0.36	0.39	0.15	1.2	0.4

(28), 154 (13), 153 (28), 152 (20), 141 (16), 128 (11). $C_{18}H_{24}$: calcd. 240.18780, found 240.187±2 ppm.

14. Tricarbonyliron Complex 33 of Hexamethyl[6]radialene (2a): A suspension of **2a** (0.240 g, 1.0 mmol) and $Fe_2(CO)_9$ (2.18 g, 6.0 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temp. the reaction mixture was filtered, the solvent was removed in vacuo, and the remainder was purified twice by preparative silica gel thick layer chromatography with hexane. Besides unchanged **2a**, **33** (28 mg, 7%) was isolated as a colorless solid, m.p. 98 °C, still containing traces of **2a**. IR (KBr): $\tilde{\nu}$ = 3067 cm^{-1} (w), 2970 (m), 2937 (m), 2915 (m), 2874 (m), 2857 (m), 2029 (s), 1969 (s), 1962 (s), 1955 (s), 1948 (s), 1925 (m), 1915 (m), 1442 (m), 664 (m), 618 (m), 607 (s). ^{1}H NMR (400 MHz): δ = 5.98 ppm (q, $^3J_{11,17}$ = 7.2 Hz, 1 H, 11-H), 5.76 (q, $^3J_{9,15}$ = 7.1 Hz, 1 H, 9-H), 5.70 (q, $^3J_{12,18}$ = 7.1 Hz, 1 H, 12-H), 5.67 (q, $^3J_{10,16}$ = 7.5 Hz, 1 H, 10-H), 2.74 (q, $^3J_{7,13}$ = 7.1 Hz, 1 H, 7-H), 2.24 (q, $^3J_{8,14}$ = 6.3 Hz, 1 H, 8-H), 2.01 (d, $^3J_{16,10}$ = 7.5 Hz, 3 H, 16-H), 1.93 (d, $^3J_{18,12}$ = 7.1 Hz, 1 H, 18-H), 1.91 (d, $^3J_{15,9}$ = 7.1 Hz, 3 H, 15-H), 1.85 (d, $^3J_{17,11}$ = 7.2 Hz, 3 H, 17-H), 1.55 (d, $^3J_{14,8}$ = 6.3 Hz, 3 H, 14-H), 1.28 (d, $^3J_{13,7}$ = 7.1 Hz, 3 H, 13-H). ^{13}C NMR (100.6 MHz): δ = 138.88 ppm (s, C-5), 137.18 (s, C-3), 136.49 (s, C-6), 134.72 (s, C-4), 128.84 (d, C-12), 125.98 (d, C-9), 124.21 (d, C-10), 123.66 (d, C-11), 112.06 (s, C-2), 99.06 (s, C-1), 51.88 (d, C-8), 50.08 (s, C-7), 18.61 (q, C-14), 16.93 (C-16), 16.66 (q, C-17), 16.30 (q, C-15), 15.12 (q, C-18), 14.66 (q, C-13). The carbonyl signals could not be identified. UV (hexane): λ_{max} (lg ε) = 198 nm (4.64), 228 nm (4.53). MS (70 eV): *m/z* (%) = 378 (0.7) [M$^+$], 352 (25), 325 (16), 324 (68), 297 (22), 296 (100), 295 (15), 294 (61), 292 (11) [M$^+$ − 3 CO].

15. X-ray Structure Determinations: Single crystals were grown as follows: **19a** by slow evaporation from $CDCl_3$ in a NMR tube; **19b** by cooling of a saturated solution in CH_2Cl_2; **14** by slow evaporation of a CH_2Cl_2 solution at −18 °C; **22** from ethanol; **23** from ethanol. Numerical details are presented in Table 2. *Data collection and reduction:* Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (**19a**, **22**, **23**: Stoe STADI-4; **19b**, **14**: Siemens P4, with appropriate low temperature attachments). Measurements were performed by use of monochromated Mo-K_α radiation. An absorption correction for compound **19b** was performed on the basis of ψ-scans. *Structure solution and refinement:* The structures were solved with direct methods and refined anisotropically against F^2 (program SHELXL-97, G.M. Sheldrick, University of Göttingen). H atoms were included with a riding model or rigid methyl groups.

CCDC-202808 (**19a**), -202809 (**19b**), -202810 (**14**), -202811 (**22**), and -202812 (**23**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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