Spirocyclopropanated Bicyclopropylidenes: Straightforward Preparation, Physical Properties, and Chemical Transformations**

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Dedicated to Professor Oleg Nefedov on the occasion of his 70th birthday

Abstract: Perspirocyclopropanated bicyclopropylidene (**6**) was prepared in three steps from 7-cyclopropylidenedispiro[2.0.2.1]heptane (**4**) (24% overall) or, more efficiently, through dehalogenative coupling of 7,7-dibromo[3]triangulane (**15**) (82%). This type of reductive dimerization turned out to be successful for the synthesis of (*E*)- and (*Z*)-bis(spiropentylidene) **14** (67%) and even of the "third-generation" spirocyclopropanated bicyclopropylidene **17** (17% overall from **15**). Whereas the parent bicyclopropylidene **1** dimerized at 180 °C to yield [4]rotane, dimerization of **6** at 130 °C under 10 kbar pressure occured only with opening of one three-membered ring to yield the polyspirocyclopropanated (cyclopropylidene)cyclopentane derivative **19** (34% yield), and at the elevated temperature the polyspirocyclopropanated 2-cyclopropylidene[3.2.2]propellane derivative **20** (25% yield). Perspirocyclopropanated bicyclopropylidene **6** and the "third-generation" bicyclopropylidene **17** gave addition of bromine, hydrogen bromide, and various dihalocarbenes without rearrangement. The functionally substituted branched [7]triangulane **28** and branched dichloro-C_{2v}-[15]triangulane **32** were used to prepare the perspirocyclopropanated [3]rotane (D_{3h}-[10]triangulane) **49** (six steps from **6**, 1.4% overall yield) and the C_{2v}-[15]triangulane **51** (two steps from **17**, 41% overall). Upon catalytic hydrogenation, the perspirocyclopropanated bicyclopropylidene **6** yielded 7,7′-bis(dispiro[2.0.2.1]-heptyl) (**52**) and, under more forcing conditions, 1,1′-bis(2,2,3,3-tetramethylcyclopropyl) (**53**). The bromofluorocarbene adduct **33** of **17** reacted with butyllithium to give the unexpected polyspirocyclopropanated 1,4-di-*n*-butyl-2-cyclopropylidenebicyclo[2.2.0]hexane derivative **37** as the main product (55% yield) along with the expected "third-generation" perspirocyclopropanated dicyclopropylidenemethane **38** (21% yield). Mechanistic aspects of this and the other unusual reactions are discussed. The structures of all new unusual hydrocarbons were proven by X-ray crystal structure analyses, and the most interesting structural and crystal packing features are presented.

Keywords: bicyclopropylidene · carbenoids · cyclopropanation · small ring systems · strained molecules

Introduction

Although tetraalkyl-substituted alkenes are by definition more electron-rich than lesser substituted ones, they are often less reactive than the latter due to the steric influences of the alkyl groups. Bicyclopropylidene (**1**), however, in spite of being a tetrasubstituted ethene, in many transformations is more reactive than methylenecyclopropane and tetramethylethylene. As a result of its unique reactivity, bicyclopropylidene (**1**)[1] has developed into a useful model alkene to probe

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[**] Preliminary communications: a) S. Zöllner, H. Buchholz, R. Boese, R. Gleiter, A. de Meijere, *Angew. Chem.* **1991**, *103*, 1544–1546; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1518–1520; b) M. von Seebach, S. I. Kozhushkov, R. Boese, J. Benet-Buchholz, D. S. Yufit, J. A. K. Howard, A. de Meijere, *Angew. Chem.* **2000**, *112*, 2617–2620; *Angew. Chem. Int. Ed.* **2000**, *39*, 2495–2498.

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certain reaction principles,[2] and a versatile multifunctional C_6 building block for organic synthesis, especially since it has become available in multigram quantities.[3] The synthetic value of **1** covers a wide range from various cycloadditions all the way to its applicability in novel three-component reactions involving palladium-catalyzed cascade transformations.[4] Among other purposes, it serves as the best starting material for various branched [*n*]triangulanes **2**—hydrocarbons consisting exclusively of spiroannelated cyclopropane units.[5]

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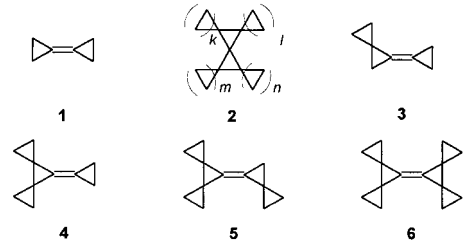
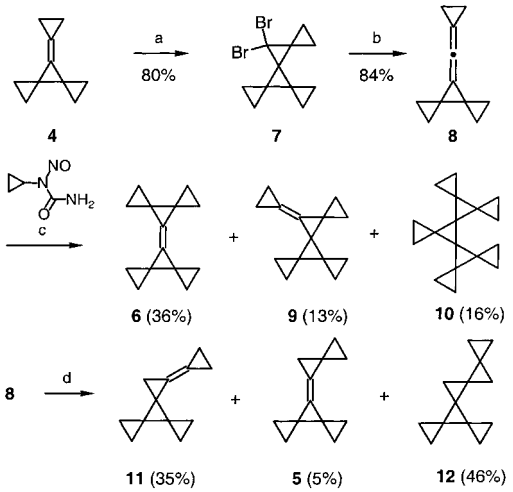


Results and Discussion

Consecutive spirocyclopropanation of the three-membered rings in **1** not only increases the total strain in the molecule,[6] but also adds some specificity to its reaction modes.[4] Bicyclopropylidenes **3** and **4** with an additional one and two spirocyclopropane annelations on the same ring can be easily prepared according to the same methodology as bicyclopropylidene itself.[3a] The trispirocyclopropanated and perspirocyclopropanated analogues of **1**, 7-spiropentylidenedispiro[2.0.2.1]heptane (**5**) and 7,7′-bis(dispiro[2.0.2.1]heptylidene) (**6**) were first prepared along a tedious multistep sequence[7] starting from 7-cyclopropylidenedispiro[2.0.2.1]heptane (**4**).[3a, 8] Treatment of its dibromocarbene adduct **7** with methyllithium gave the allene **8**[9] which, upon reaction with diazocyclopropane in situ generated from *N*-nitroso-*N*-cyclopropylurea,[10] yielded **6** (36%) along with 11-cyclopropylidenetetraspiro[2.0.0.2.0.2.0.1]undecane (**9**) (13%) and the branched [8]triangulane **10** (16%) (Scheme 1).



Scheme 1. First preparation of perspirocyclopropanated bicyclopropylidene **6** and cyclopropanation of the allene **8**. a) $CHBr_3$, KOH (powder), TEBACl, CH_2Cl_2, $0 \rightarrow 20\,^{\circ}C$, 5 h; b) MeLi, Et_2O, $0\,^{\circ}C$, 1.5 h; c) MeONa, pentane, $0\,^{\circ}C$, 8 h; d) CH_2I_2, $ZnEt_2$, Et_2O, $34\,^{\circ}C$, 3 h.

This cyclopropylidenation proceeds with a 2.8:1 regioselectivity for the attack at the less sterically encumbered double bond in the allene **8**, whereas Simmons–Smith

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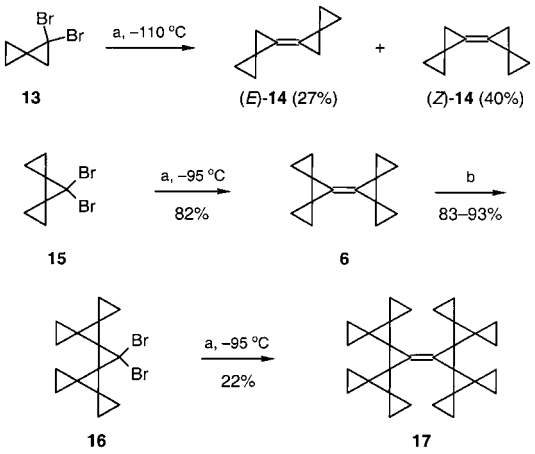
cyclopropanation of **8** occurs preferentially at the more crowded, but more highly strained double bond in **8** to yield predominantly cyclopropylidene[3]rotane **11** (35%) along with 7-spiropentylidenedispiro[2.0.2.1]heptane (**5**) (5%) and the branched [6]triangulane **12** (46%).

The very first approach to substituted bicyclopropylidenes by dehalogenative coupling of 1-halo-1-lithiocyclopropanes generated from 1,1-dihalocyclopropanes by treatment with alkyllithium reagents,[11] has recently been significantly improved. Neuenschwander et al. found that copper(II) salts assist in the coupling of 1-bromo-1-lithiocyclopropanes generated from 1,1-dibromocyclopropanes, to give a variety of substituted bicyclopropylidenes in reasonable to good and well reproducible yields.[12] Yet, under the conditions developed by the authors, the reaction of 1,1-dibromospiropentane **13**[13] did not yield any of the expected bisspirocyclopropanated bicyclopropylidenes **14**.[12d] By working at lower temperature, however, a mixture of (*E*)- and (*Z*)-bis(spiropentylidene) (*E*)-**14** and (*Z*)-**14** was readily obtained in 67% yield (Scheme 2), and the structure of the (*E*)-diastereomer (*E*)-**14** was unequivocally established by X-ray analysis (Figure 1 and Table 1). It is quite remarkable that this method can also be applied to 7,7-dibromodispiro[2.0.2.1]heptane (**15**),[13d, 14] the dibromocarbene adduct of bicyclopropylidene (**1**), to yield the perspirocyclopropanated bicyclopropylidene **6** (82% isolated yield) making this exotic hydrocarbon—a super-bicyclopropylidene—easily available in preparatively useful quantities (Scheme 2). It is even more spectacular that the dibromide **16**, the dibromocarbene adduct of **6**,[15] can be reductively "dimerized" again to give the "third-generation" perspirocyclopropanated bicyclopropylidene **17** (Figure 1).[16]



Scheme 2. Cupric-chloride-assisted dehalogenative dimerizations of spirocyclopropanated dibromocyclopropanes to yield spirocyclopropanated bicyclopropylidenes. a) $CuCl_2$, THF, temperature given, addition of BuLi over 1 h, then temperature given $\rightarrow 20\,^{\circ}C$, 2 h; b) $CHBr_3$, KOH (powder), TEBACl, CH_2Cl_2, $0 \rightarrow 20\,^{\circ}C$, 5 h.

The typical difference between proximal and distal bond lengths observed for the outer spirocyclopropane rings in [3]rotane[17] and perspirocyclopropanated [3]rotane[15] is also observed for the outer-sphere cyclopropane rings in **17** (Figure 1), but the lengths of the central double bond turned out to be essentially the same in bicyclopropylidene (**1**)

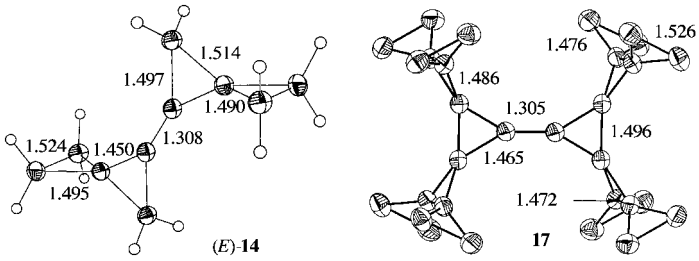
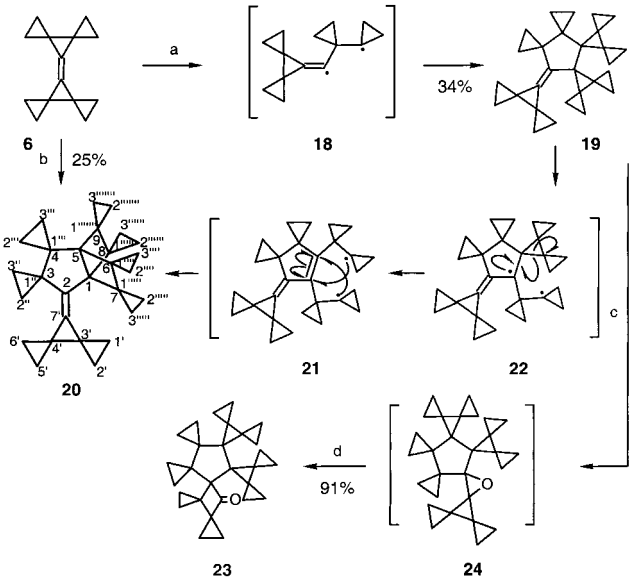


Figure 1. Structures of bis(spirocyclopropanated) bicyclopropylidene (*E*)-**14** and the "third-generation perspirocyclopropanated bicyclopropylidene" **17** in the crystals.

[1.304(2) Å[4b]],[7a] "super-bicyclopropylidene" **6** [1.305(4) Å],[7a] and the "third-generation" perspirocyclopropanated bicyclopropylidene **17** [1.305(3) Å]. This is not in line with the oxidation potentials of these alkenes which decrease on going from **1** (1.58 V) to **6** (1.12 V, $\Delta E = 460$ mV) and further to **17** (0.98 V, $\Delta E = 140$ mV). It is remarkable that the outer sphere cyclopropyl groups in **17** still exert a significant influence, albeit a smaller one than the outer sphere groups in **6**, as indicated by the smaller difference between the values for **17** and **6** compared with that between **6** and **1**. These values are in line with the fact that the rate of bromine addition across the double bond increases with an increasing number of spiroannelated cyclopropanes, as has experimentally been determined for a number of oligospirocyclopropanated bicyclopropylidenes.[4, 18]

Differential scanning calorimetry (DSC) traces for **6** and **17** display sharp peaks. The melting point of super-bicyclopropylidene **6** is represented by a peak at 139 °C, while the wide and flat peak with a maximum at 223.4 °C possibly stands for a rearrangement or decomposition of **6**. For **17** no sharp melting point peak is displayed. The diagram indicates a decomposition starting above 230 °C. The sharp peak at 213 °C with $\Delta G = 1.45$ kcal mol^{-1} possibly indicates a phase transition or a rearrangement reaction. For comparison, bicyclopropylidene (**1**) undergoes a phase transition at $-40.2\,^{\circ}C$ with $\Delta G = 0.038$ kcal mol^{-1}.[4b]

The thermal behavior of perspirocyclopropanated bicyclopropylidene **6** with its maximum number of spirocyclopropane rings is completely different from that of bicyclopropylidene (**1**).[4b, 5a] The steric congestion around the double bond in **6** apparently impedes its [2 + 2]-dimerization as well as the type of rearrangement observed for the parent bicyclopropylidene (**1**) leading to methylenespiropentane (for reviews, see ref. [4]). After extended heating of a toluene solution of **6** (180 °C, 144 h, sealed tube) and column chromatography on silica gel of the crude product mixture, 50% of the starting material **6** was recovered, and 25% of a dimer with an R_f value very close to that of **6** was isolated.[19] Prolonged heating (6 d) at 180 °C as well as heating to higher temperatures (220 °C) led only to an accumulation of polymeric materials. Since the structure of the dimer could not unequivocally be established on the basis of its NMR data, a single crystal of appropriate quality was grown by slow concentration of a dilute solution in ethanol/pentane, and its structure determined by an X-ray crystal structure analysis. This revealed the unexpected structure **20** (Scheme 3) containing a spirocyclopropanated



Scheme 3. Two modes of thermal dimerization of perspirocyclopropanated bicyclopropylidene **6**. a) toluene, 10 kbar, 130 °C, 48 h; b) toluene, 180 °C, 144 h; c) dimethyldioxirane, acetone, 0 → 20 °C, 12 h; d) silica gel, pentane/Et_2O 9:1.

[3.2.2]propellane fragment (Figure 2). To increase the yield in this reaction, the dimerization of **6** was attempted under high pressure conditions (toluene, 10 kbar, 130 °C, 48 h). But in this case, compound **20** was formed in only 5% yield, and the new dimer **19** (34% yield) was isolated as an oil along with 41% of

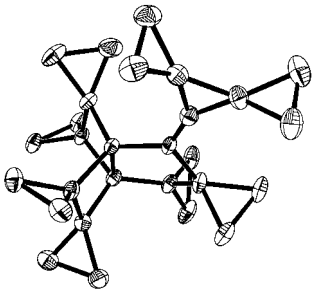


Figure 2. Structure of the oligospirocyclopropanated 2-cyclopropylidene-[3.2.2]propellane **20** in the crystal.

the starting material **6**.[20] The structure of **19** was elucidated indirectly by an X-ray crystal structure analysis of the ketone **23**[21] obtained from **19** by epoxidation with dimethyldioxirane[22] and subsequent isomerization of the epoxide **24** upon exposure to silica gel.

A speculative mechanistic rationalization of these dimerization reactions starts with a rather unreasonable cleavage of a vinylic C–C bond in **6** to form the diradical **18** (Scheme 3), which adds across the double bond of a second molecule of **6** to produce **19**. Under high pressure at 130 °C, **19** is the final product, but under the more drastic conditions (180 °C), rupture of an allylic spirocyclopropane C–C bond of the dispiro[2.0.2.1]heptane fragment adjacent to the double bond occurs, and the resulting 1,3-diradical **22** undergoes a cyclopropylcarbinyl radical to 3-butenyl radical rearrangement ("electron clock"[23]) to form the intermediate **21**. Although rather unlikely, a possible route to the propellane **20** would be by twofold four-membered ring closure of the diradical **21** attacking the double bond.

In view of the known routes and chemical transformations of small ring propellanes,[24] the formation of the [3.2.2]propellane skeleton under these drastic conditions is quite surprising. After all, the strain energy (SE) for the parent [3.2.2]propellane is estimated to be 65 kcal mol^{-1},[24d] and every spirofused three-membered ring contributes at least an additional 28.1 kcal mol^{-1} to the total strain of **20**,[25] not taking into account the additional strain increments due to the spiro-fusions in the [3.2.2]propellane and dispiro[2.0.2.1]heptane fragments.[6] Thus, the survival of compound **20** under the conditions of its formation is one more excellent example of the potentially enormous kinetic stability of such extremely strained compounds.[26]

The X-ray crystal structure analysis of the hydrocarbon **20** discloses two crystallographically independent molecules in the unit cell with almost identical geometries. The five-membered ring in **20** adopts an envelope conformation with atom C(3) out of the C(1)-C(2)-C(4)-C(5) plane by 0.41(1) Å. Both four-membered rings are folded along their diagonals by 16.3° (mean value for two molecules). The bond C(1)–C(5) common to the four- and five-membered rings is elongated to 1.576 Å, which is typical for [3.2.2]propellane structures.[24a] While the atoms C(1) and C(5) can thus adopt pyramidalized configurations, they are located only 0.12(1) Å out of the planes C(2)-C(7)-C(8) and C(4)-C(6)-C(9), respectively.

An increasing number of spiroannelated cyclopropanes apparently stabilizes the bicyclopropylidene skeleton against ring opening and ring enlargement upon electrophilic additions. While the addition of bromine to bicyclopropylidene (**1**) itself yields 7% of the ring-opening by-product,[18] the bisspirocyclopropanated (**4**)[18] and perspirocyclopropanated bicyclopropylidene (**6**)[6] both add bromine and hydrogen bromide virtually without ring opening. In the latter case the formation of the dibromide **25** and bromide **26** proceeds almost quantitatively. The same behavior is observed for the "third-generation" perspirocyclopropanated bicyclopropylidene **17** which rapidly adds bromine to give dibromide **27** with complete conservation of the polyspirocyclopropane skeleton (Scheme 4). On the other hand, the rhodium acetate catalyzed alkoxycarbonylcyclopropanation of **1** proceeds with good yield and without rearrangement,[3a] whereas that of the perspirocyclopropanated analogue **6** furnishes the cycloadduct **28** in only 32% yield along with 9% of the ring-enlargement product **29** (Scheme 4), the structure of which was corroborated by an X-ray crystal structure analysis.[27]

Control experiments showed that **28** did not isomerize to **29** upon continuous stirring with $[Rh(OAc)_2]_2$ in chloroform or dichloromethane, and **6** did not react with ethyl diazoacetate in the absence of rhodium acetate to form the pyrazoline **30**, apparently due to the steric congestion around the double bond. However, the addition of the carbenerhodium complex to the highly nucleophilic[18] alkene **6** may occur stepwise, since a 1,3-zwitterionic intermediate of type **31**, being an ester enolate at one and a dispiro[2.0.2.1]hept-7-yl cation[18] at the other, would be a reasonably stabilized species. Ring closure of **31** would lead to **28**, and cyclopropylmethyl to cyclobutyl

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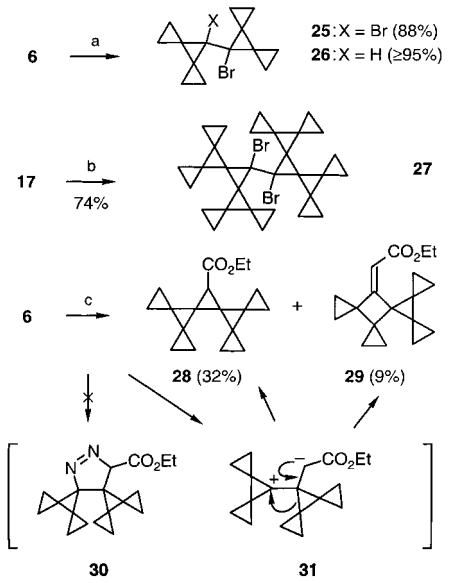
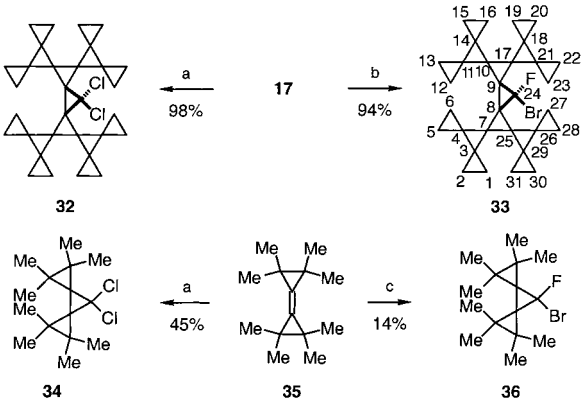


Scheme 4. Addition of various electrophiles (Br_2, HBr, :$CHCO_2Et$) to the perspirocyclopropanated **6** and the "third-generation" bicyclopropylidene **17**. a) XBr, pentane, $-15\,^{\circ}C$; b) Br_2, Py, hexane, $-15\,^{\circ}C$; c) N_2CHCO_2Et, $[Rh(OAc)_2]_2$ (1 mol%), CH_2Cl_2, $0\,^{\circ}C$, 12 h.

cation rearrangement would lead to the by-product **29** (Scheme 4).

The steric congestion around the double bond arising from the increased number of spiroannelated three-membered rings in **17** prevents certain cycloadditions that are possible with **1** and **6**. For example, dibromocarbene did not add onto the double bond in **17**,[28] neither under phase transfer catalysis nor under classical conditions as developed by Doering et al.[29] and Seyferth et al.[30] The addition of bromochlorocarbene also failed under all of these conditions, while 7-bromo-7-chlorodispiro[2.0.2.1]heptane was obtained from **1** in 77% yield using Doering's procedure. Also, **17** did neither react with diazocyclopropane, in situ generated from *N*-nitroso-*N*-cyclopropylurea,[10] nor with diazomethane in the presence of $Pd(OAc)_2$.[31] However, with less sterically demanding carbenes such as dichloro- and bromofluorocarbene the corresponding dihalo[15]triangulanes C_{2v}-**32** and C_{2v}-**33** were obtained in excellent yields (Scheme 5).



Scheme 5. Dihalocarbene additions to sterically encumbered bicyclopropylidenes **17** and **35**. a) $CHBr_3$, 50% aq. NaOH, TEBACl, CH_2Cl_2, $20\,^{\circ}C$, 3 d; b) $CHBr_2F$, 50% aq. NaOH, TEBACl, CH_2Cl_2, $20\,^{\circ}C$, 3 d; c) $CHBr_2F$, 50% aq. NaOH, TEBACl, $20\,^{\circ}C$, 2 d.

Surprisingly, permethylbicyclopropylidene (**35**) is even less reactive than the overly spirocyclopropanated bicyclopropylidene **17** with respect to cycloadditions of various carbenes. Not only was compound **35** completely unreactive towards dibromocarbene under the conditions mentioned above, the dichlorocarbene adduct **34** was produced in only 45% yield. Addition of bromofluorocarbene to **35** even using $CHBr_2F$ as the solvent stopped after about 30% conversion, and the isolated yield of **36** was a mere 14% (Scheme 5).

The structures of the dihalo[15]triangulanes C_{2v}-**32** and C_{2v}-**33** both display unique features. The two spiropentane moieties making up the central dispiro[2.0.2.1]heptane units in both of them have lost their usual C_2 symmetry. In **32**, the deformation of these spiropentane units is both by twisting (i.e., rotation of the plane of one cyclopropane ring against the other one), yet by only 1° ($\psi = 89.0^{\circ}$ for the left and right spiropentane unit, see Figure 3) and bending (i.e., buckling of the C_2 axis which usually bisects the two cyclopropane rings, see Figure 3) by 10.1° ($\Phi = 169.9^{\circ}$ for both moieties).[32] The

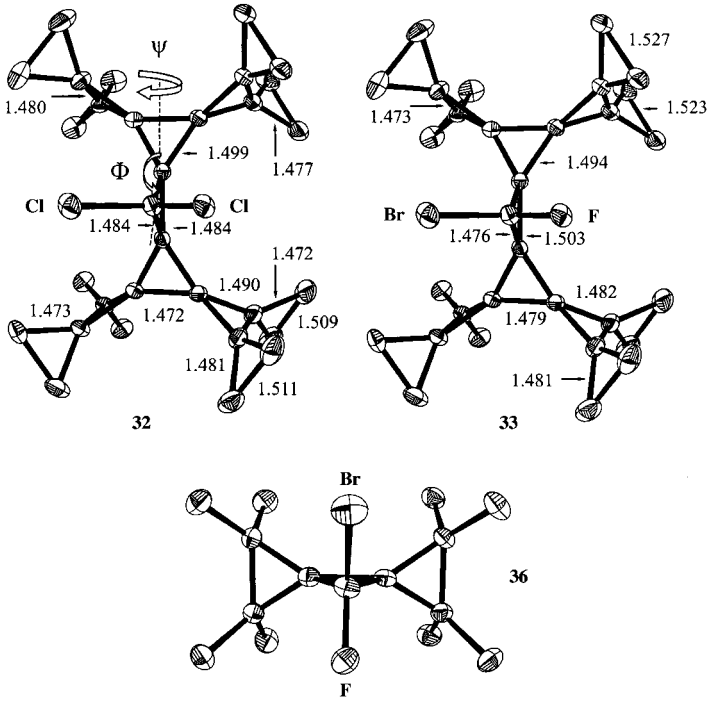


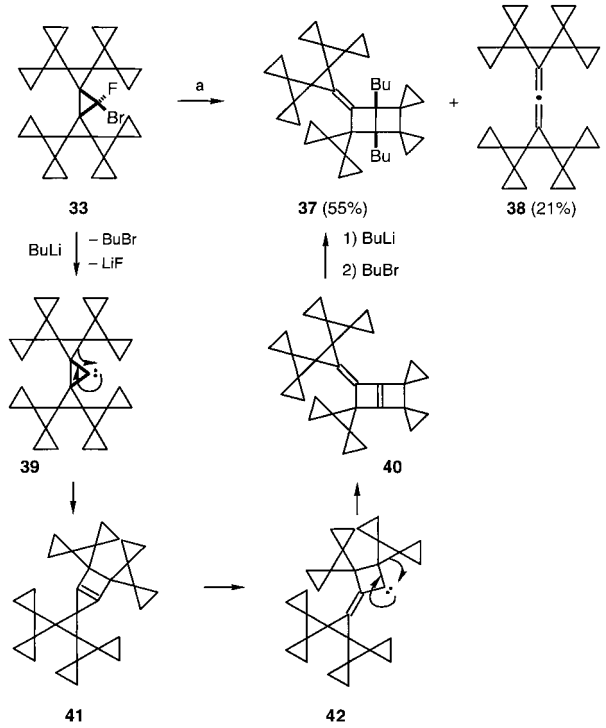
Figure 3. Structures of dihalo[15]triangulanes C_{2v}-**32** and C_{2v}-**33** and 7-bromo-7-fluorooctamethyldispiro[2.0.2.1]heptane (**36**) in the crystals.

central dispiro[2.0.2.1]heptane fragment in **33** is also twisted and bent, but the big bromine atom apparently causes a more significant twisting for the two sides to be in the same direction ($\psi = 96.6^{\circ}$ and 93.3°) as opposed to compound **32** ($\psi = 89.0^{\circ}$) while the degree of bending ($\Phi = 169.9$ and 170.5°) is approximately the same as in **32**. These deformations must arise from the mutual repulsion of the two bulky branched [7]triangulane fragments spiroannelated to the central cyclopropane moiety of **32** and **33**, and it apparently goes along with a significant change in hybridization of the two central spiro carbon atoms.

The sterically congested skeleton in bromofluoro[15]triangulane **33** apparently accommodates the larger bromine and the smaller fluorine substituents at C(24) best with different orientations of the C–F and C–Br bonds. The angle between the C–Br bond axis and the C(9)-C(8)-C(24) plane is only 49.1°, while that between the C–F axis and the same plane is 58.2°. The crystal packing of the molecules **33** is also noteworthy. The terminal three-membered rings attached at C(4), C(11), C(18), and C(26) form a large enough cavity which accommodates the Br substituent of the adjacent molecule quite nicely: the shortest intermolecular contact Br(1)···H(28B) 2.97(1) Å is the same as the shortest intramolecular ones Br(1)···H(312) 2.96(1) and Br(1)···H(152) 2.98(1) Å, while the sum of van der Waals radii of hydrogen (1.20 Å) and bromine (1.85 Å)[33] atoms is 3.05 Å (Figure 4).

The crystal structure of 7-bromo-7-fluorooctamethyldispiro-[2.0.2.1]heptane (**36**) was also determined for comparison (Figure 3). The dispiroheptane unit in **36** was found to be distorted, too, but with $\psi = 89.8$ and 92.1° and $\Phi = 174.4°$ in the two spiropentane moieties to a significantly lesser extent than in **33**. The angle between the C–Br bond axis and the C(3)-C(4)-C(7) plane in **36** is 51.7°, while that between the C–F axis and the same plane is 56.7°. The interatomic distances are equal to C(7)–C(2) 2.746, C(7)–C(5) 2.715, C(7)–C(1) 2.747, and C(7)–C(6) 2.768 Å.

In order to test the possibility of reductively dimerizing a carbenoid from **33** to an even more highly spirocyclopropanated analogue of **17**, the bromofluoro-C_{2v}-[15]triangulane **33** was treated with alkyllithium reagents. While no reaction was observed with methyllithium in the temperature range from −78 to 0 °C, treatment of **33** with *n*-butyllithium at −10 to −5 °C led to a remarkable skeletal rearrangement and incorporation of two *n*-butyl groups to give the hydrocarbon **37** containing a bicyclo[2.2.0]hexane fragment, as the main product (Scheme 6). The structure of **37** was proved by X-ray analysis (Figure 5). In addition, the expected allene **38** was isolated in 21% yield. Essentially the same results were obtained at +65 °C. When the reaction was performed at −90 to −75 °C in the presence of $CuCl_2$, 32% of the starting material **33** was recovered, and the major product fraction was a mixture of unidentified soluble oligomers. Only a trace of the bicyclohexane derivative **37** could be detected.



Scheme 6. Treatment of bromofluoro-C_{2v}-[15]triangulane **33** with *n*-butyllithium. a) *n*BuLi, THF, −10 → −5 °C, 0.5 h.

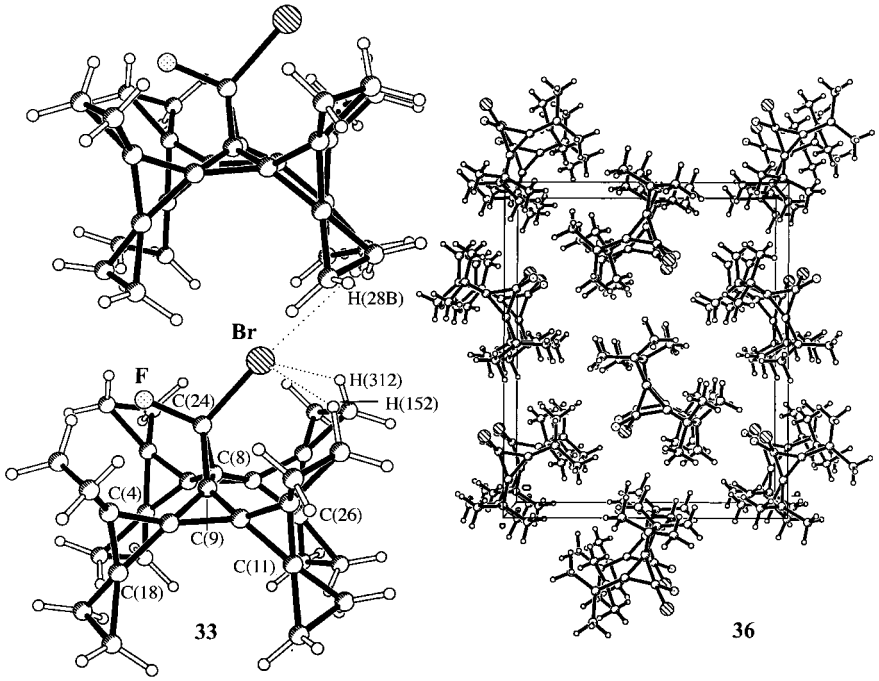


Figure 4. Adjacent molecules in the crystal of 24-bromo-24-fluoro-C_{2v}-[15]triangulane (**33**) and a section showing the crystal packing of 7-bromo-7-fluorooctamethyldispiro[2.0.2.1]-heptane (**36**).

Based on literature precedents for the individual steps, the transformation of **33** to **37** can be rationalized as follows: Bromine–lithium exchange in **33** leads to a carbenoid which may α-eliminate lithium fluoride to form the cyclopropylidene intermediate **39**. A minor fraction of this undergoes the usual ring opening (corresponding to the so-called Doering–Skattebøl–Moore reaction[9]) to allene **38** ("third-generation" perspirocyclopropanated dicyclopropylidenemethane), the major fraction experiences a cyclopropylcarbene to cyclobutene ring enlargement.[34] The resulting excessively strained bicyclo[2.1.0]pent-1(4)-ene derivative **41** then opens its cyclopropene to a vinylcarbene

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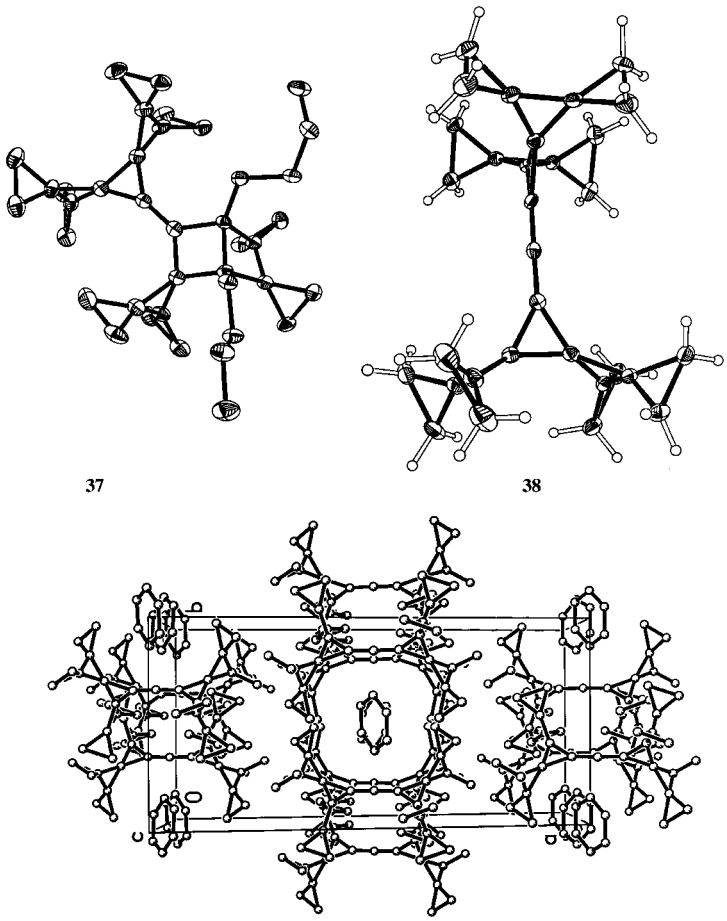
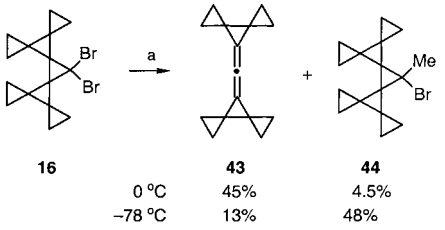


Figure 5. Structures of the oligospirocyclopropanated bicyclo[2.2.0]hexane **37** as well as the "third-generation" perspirocyclopropanated dicyclopropylidenemethane **38** and a section showing the crystal packing of the latter with benzene solvent molecules in the channels.

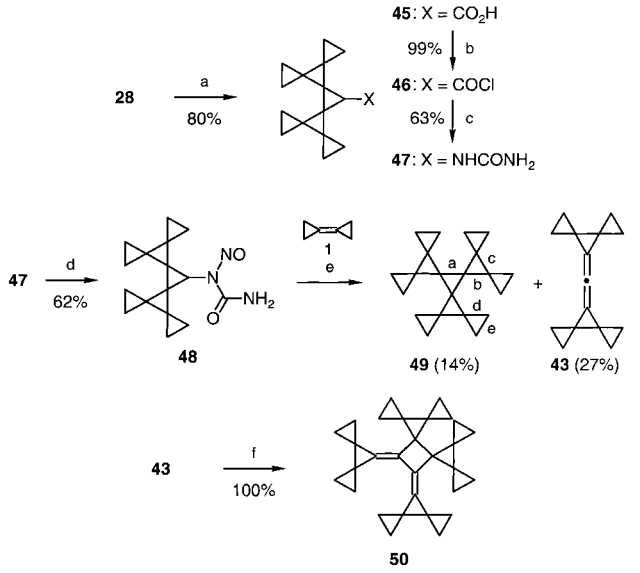
unit[35] to give **42** which can undergo a cyclopropylcarbene to cyclobutene rearrangement[34] once more. The resulting bicyclo[2.2.0]hex-1(4)ene **40**[36] with its highly strained bridgehead–bridgehead double bond[36, 37] then adds a molecule of *n*-butyllithium, and the bridgehead lithio derivative finally reacts with the initially formed butyl bromide.[38]

Such type of rearrangement was not observed for the carbenoid derived from 15,15-dibromo-C_{2v}-[7]triangulane **16** which reacted with methyllithium in the presence of lithium iodide to produce the expected allene (perspirocyclopropanated dicyclopropylidenemethane) **43** and 7-bromo-7-methyl-C_{2v}-[7]triangulane **44** in different proportions at different temperatures (Scheme 7).



Scheme 7. Reaction of dibromo-C_{2v}-[7]triangulane **16** with methyllithium. a) MeLi/LiI, Et_2O, 1 h.

The oligospirocyclopropanated bicyclopropylidenes **6** and **17**, as well as some of their transformation products, appeared to be appropriate starting materials for the synthesis of higher branched triangulanes. Towards this goal, the ester **28** was hydrolyzed to the acid **45** (80% yield), which was transformed into the acid chloride **46** (99% yield) with thionyl chloride. Analogous to the synthesis of *N*-cyclopropyl-*N*-nitrosourea,[10] the acid chloride **46** was converted to the *N*-nitroso-*N*-[7]triangulanylurea **48** in 31% overall yield (Scheme 8).



Scheme 8. Preparation of perspirocyclopropanated [3]rotane (D_{3h}-[10]triangulane) **49** and perspirocyclopropanated dicyclopropylidenemethane **43**. a) NaOH, H_2O, 100 °C, 5 h; b) $SOCl_2$, 80 °C, 2 h; c) 1. NaN_3, acetone, 0 °C, 2 h; 2. C_6H_6, 80 °C, 2 h; 3. NH_3, C_6H_6, 5 °C; d) N_2O_4, Et_2O, 0 °C, 2 h; e) MeONa, 0 °C, 10 h; f) 0 °C, one year. Bond lengths [Å] (averaged over D_{3h} symmetry) for **49**: $a = 1.484(1)$, $b = 1.479(1)$, $c = 1.476(2)$, $d = 1.481(1)$, $e = 1.529(2)$.

The crucial step in the synthesis of **49**—the in situ generation of the diazo[7]triangulane[39]—was performed by treatment with ten equivalents of solid sodium methanolate at 0 °C in a large excess of bicyclopropylidene (**1**). The perspirocyclopropanated [3]rotane (D_{3h}-[10]triangulane) **49** was isolated in 14% yield by column chromatography, and its structure was examined by X-ray crystal structure analysis.[15] The main product obtained from this reaction was the allene **43**. Upon storage in a refrigerator for one year, the allene **43** completely transformed to its "head-to-head" dimer **50** which was characterized by an X-ray crystal structure analysis.[40]

In view of a total strain energy of about 360 kcal mol^{-1},[6] it is particularly noteworthy that D_{3h}-[10]triangulane **49** is stable for an extended period of time even at its melting point of 200–201 °C. Thermal decomposition occurs only above 250 °C, as revealed by differential scanning calorimetry (DSC).[41] The bonds in the central three-membered ring of **49** (1.484 Å with a standard deviation of 0.001 Å) are significantly longer than those in the central ring of [3]rotane [1.475(2) Å].[17] This might be attributable to an additional electronic interaction in terms of spiro conjugation between six outer rings and the central cyclopropane ring.[15]

The perspirocyclopropanated [3]rotane **49** turned out not to be the ultimate achievable size of a branched triangulane. The dichlorocarbene adduct **32** (Scheme 5) from the "third-generation" perspirocyclopropanated bicyclopropylidene **17** was reductively dechlorinated to the hydrocarbon **51** (Scheme 9 and Figure 6) which, with its 15 spirofused cyclopropane rings,

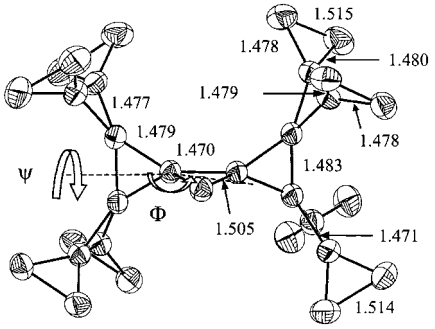
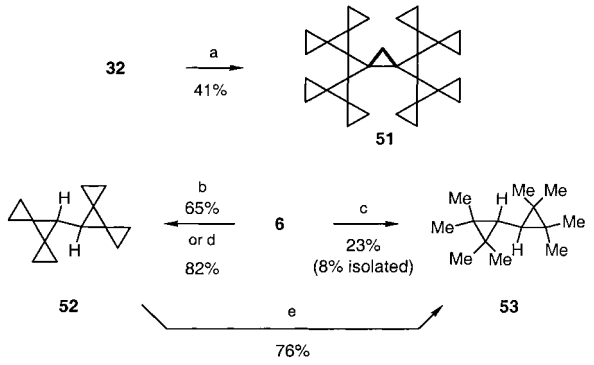


Figure 6. Structure of C_{2v}-[15]triangulane **51** in the crystal.

already sets a new record. The successful generation of the carbenoid from the bromofluoro-C_{2v}-[15]triangulane **33** fuels new hope that the limits for generating even higher aggregates of spiroannelated cyclopropane rings can be pushed forward even further.

The structure of the branched C_{2v}-[15]triangulane **51** also displays twisting by -4.3° and $+5.8^\circ$ ($\psi = 85.7^\circ$ and 95.8°, respectively, for the left and right spiropentane unit, see Figure 6) and bending by 11.7° ($\Phi = 168.3^\circ$ for both moieties) of the two spiropentane fragments making up the central dispiro[2.0.2.1]heptane unit, caused by the mutual repulsion of the two bulky branched C_{2v}-[7]triangulane fragments spiroannelated to the central cyclopropane ring of **51**, and it apparently goes along with a significant change in hybridization of the two central spiro carbon atoms leading to a shortening of the proximal C–C bond [1.470(2) Å] in the central ring.



Scheme 9. Preparation of the branched C_{2v}-[15]triangulane **51** and catalytic hydrogenation of the perspirocyclopropanated bicyclopropylidene **6**. a) Li, *t*BuOH, THF, 20 °C, 2 d; b) H_2, Pd/$BaSO_4$, hexane/MeOH, 20 °C, 2 h; c) H_2, PtO_2, hexane/AcOH, 20 °C, 2.5 h; d) H_2, PtO_2, hexane/MeOH/AcOH, −15 °C, 1.5 h; e) H_2, PtO_2, hexane/Et_2O/AcOH/MeOH, −15 °C, 6 d.

As permethylbicyclopropylidene **35** did not add dibromocarbene and, therefore, a reductive "dimerization" of the corresponding bromocuprocyclopropylidenoid to give the permethylated "super-bicyclopropylidene" could not be attempted, an alternative approach to this hydrocarbon by hydrogenolytic ring opening[42, 43] of the outer-sphere spirocyclopropane rings in the "third-generation" bicyclopropylidene **17** has been examined. Unfortunately, however, the attempted hydrogenolysis of **17** in acetic acid at room temperature under platinum catalysis led to a complex mixture of at least eight hydrocarbons, and no reaction was observed at −15 °C. Control experiments with "super-bicyclopropylidene" **6** (Scheme 9) demonstrated that the double bond in **6** reacts first. Thus, no reaction was observed under Pd/C catalysis in MeOH or HOAc. Hydrogenolysis over a Pd/$BaSO_4$ catalyst at ambient temperature or over a PtO_2 catalyst at −15 °C led to the predominant formation of 7,7′-bis(dispiro[2.0.2.1]heptyl) (**52**), which was isolated in 65 and 82% yield, respectively. Hydrogenation of **6** under PtO_2 catalysis at ambient temperature resulted also in hydrogenolytic ring opening of all four outer-sphere spirocyclopropanes to produce the octamethylbicyclopropyl (**53**)[44] in 23% yield, as indicated by GC analysis (the isolated yield was only 8%). Catalytic hydrogenation of **52** over PtO_2 at −15 °C also led to **53** in 76% yield, but the latter could not be isolated in pure form from this hydrogenation.

The vicinal coupling constants between the methine protons in **52** were $^3J(H,H) = 7.50 \pm 0.25$ (20 °C), 7.25 ± 0.25 (−8 °C), 7.00 ± 0.25 (−25 °C), and 7.00 ± 0.25 Hz (−50 °C), as determined in the ^{13}C satellites of its ^1H NMR spectrum measured at the respective temperature in $CDCl_3$ solution. This temperature dependence indicates a conformational change with an increasing proportion of a synclinal conformation of the central bicyclopropyl moiety upon decreasing temperature. An analogous behavior was reported for bicyclopropyl itself with $^3J(H,H) = 4.39 \pm 0.02$ Hz (20 °C), as determined for octadeuteriobicyclopropyl.[44] Contrary to this, for octamethylbicyclopropyl (**53**) an increasing proportion of an anticlinal conformation of the central bicyclopropyl moiety upon decreasing temperature was observed ($^3J(H,H) = 8.3 \pm 0.1$ Hz at 20 °C).[44] The corresponding {^{13}C,H} coupling constants are essentially independent of the temperature and equal to 160 ± 1, 152.0 ± 0.5 and 157.76 ± 0.03 Hz for **52**, **53**,[44] and bicyclopropyl,[44] respectively.

Experimental Section

General aspects: ^1H and ^{13}C NMR: Spectra were recorded at 200, 250 (^1H), and 62.9 MHz [^{13}C, additional DEPT (distortionless enhancement by polarization transfer)] on Varian XL 200 and Bruker AM 250 instruments in $CDCl_3$ solution, $CHCl_3/CDCl_3$ as internal reference; δ in ppm, J in Hz. Low-temperature ^1H NMR spectra were recorded at 500 MHz on a Varian INOVA-500 instrument in $CDCl_3$, $CHCl_3/CDCl_3$ as internal reference. IR spectra were recorded on a Perkin–Elmer 298 and Bruker IFS 66 instruments, measured as KBr pellets, oils between KBr plates. Mass spectra were measured at 70 eV with a Finnigan MAT 95 spectrometer (EI). Melting points were determined on a Büchi 510 capillary melting point apparatus and are uncorrected. GC analyses were carried out with a Siemens Sichromat 1-4, 25 m capillary column CP-SIL-5-CB, and GC separations with an Intersmat 130 instrument, 20% SE-30 on Chromaton W-AW-DMCS, 1000×8.2 mm Teflon column. TLC analyses were performed using Macherey-Nagel precoated aluminum plates, 0.25 mm Sil G/UV_{254}, and column chromatography using Merck silica gel, grade 60, 230–400 mesh. Starting materials: Anhydrous diethyl ether and THF were obtained by distillation from sodium/benzophenone, pyridine from CaH_2

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and methylene chloride from P_4O_{10}. Bicyclopropylidene (**1**),[3] 7-cyclopropylidenedispiro[2.0.2.1]heptane (**4**)[3] 1,1-dibromospiropentane (**13**),[13] 7,7-dibromodispiro[2.0.2.1]heptane (**15**),[13d, 14] and 1,1-dibromotetramethylcyclopropane[45] were prepared according to published procedures. All other chemicals were used as commercially available (Merck, Acros, BASF, Bayer, Hoechst, Degussa AG, and Hüls AG). All reactions were performed under argon. Organic extracts were dried with $MgSO_4$.

Crystal structure determinations: Suitable crystals were grown by slow concentration of diluted solutions in pentane [(*E*)-**14**, at 0°C], methanol/diethyl ether (**20**), benzene (**38**), or hexane/diethyl ether mixture (other compounds). The data were collected on a Siemens P3 (**20**) or a Bruker SMART CCD 1 K (other compounds) diffractometer, the latter equipped with a home-built low temperature device, for (*E*)-**14**, **33**, **37**, and **38** it was equipped with an Oxford Cryostream devise, for **20** a Siemens LT-2 unit, $Mo_{K\alpha}$ radiation (graphite monochromator). The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically, all hydrogen atoms were located on the difference Fourier maps and refined isotropically. The parameters of crystal data collections and structure refinements are presented in Table 1.[46]

Table 1. Crystal and data collection parameters for compounds (*E*)-**14**, **17**, **20**, **32**, **33**, **36**–**38**, **51**.

	(*E*)-**14**	**17**	**20**	**32**	**33**
formula	$C_{10}H_{12}$	$C_{30}H_{32}$	$C_{28}H_{32}$	$C_{31}H_{32}Cl_2$	$C_{31}H_{32}BrF$
molecular mass	132.20	392.56	368.54	475.47	503.48
crystals	triclinic	tetragonal	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$I4_1/a$	$P\bar{1}$	$C2/c$	$P2_1/n$
a [Å]	5.0981(4)	23.293(2)	10.599(3)	22.340(2)	7.4062(5)
b [Å]	6.0900(6)		13.098(6)	7.5679(5)	31.471(2)
c [Å]	6.7959(6)	8.8272(5)	15.778(6)	17.3642(14)	11.6954(8)
α [°]	71.890(4)		94.01(4)		
β [°]	77.336(4)		99.98(3)	112.558(1)	105.32(1)
γ [°]	72.645(4)		91.53(3)		
V [Å^3]	189.54(3)	4789.4(6)	2150(1)	2711.1(4)	2629.1(3)
Z	1	8	4	4	4
F(000)	72	1696	800	1008	1048
ρ [g cm^{-3}]	1.158	1.089	1.138	1.165	1.272
μ [mm^{-1}]	0.065	0.061	0.064	0.256	1.587
T [K]	100	143	153	263	120
θ_{max} [°]	29.8	28.41	25.1	28.31	30.49
refl. collected	2271	9384	5486	11502	26051
refl. independent	1016	2321	5091	2918	7363
R_{int}	0.0480	0.0413	0.0416	0.0947	0.0430
w$R_2(F^2)$	0.0895	0.1464	0.1210	0.1426	0.0810
$R(F)$	0.0372	0.0564	0.0530	0.0587	0.0485
no. parameters refined	70	136	697	150	434
GOF	1.100	1.018	1.012	0.81	1.174

	36	**37**	**38**	**51**
formula	$C_{15}H_{24}BrF$	$C_{39}H_{50}$	$C_{31}H_{32}\cdot C_6H_6$	$C_{31}H_{34}$
molecular mass	303.25	518.79	482.67	406.58
crystals	orthorhombic	monoclinic	monoclinic	triclinic
space group	$P2_12_12_1$	$P2_1/c$	$C2/c$	$P\bar{1}$
a [Å]	7.076(1)	7.5471(2)	21.623(1)	8.945(2)
b [Å]	13.374(3)	40.871(1)	10.3065(5)	12.061(2)
c [Å]	16.035(3)	10.8826(4)	13.0931(6)	12.605(3)
α [°]				67.514(4)
β [°]		108.79(1)	101.63(1)	79.915(4)
γ [°]				80.625(4)
V [Å^3]	1517.3(5)	3177.9(2)	2858.0(2)	1230.3(4)
Z	4	4	4	2
F(000)	632	1136	1040	440
ρ [g cm^{-3}]	1.327	1.084	1.122	1.098
μ [mm^{-1}]	2.699	0.060	0.063	0.061
T [K]	120	120	120	203
θ_{max} [°]	30.1	25.50	27.5	28.41
refl. collected	17234	18579	12425	15611
refl. independent	4184	5892	3283	6098
R_{int}	0.0574	0.096	0.113	0.0379
w$R_2(F^2)$	0.0919	0.1876	0.1880	0.1241
$R(F)$	0.0378	0.0847	0.0741	0.0510
no. parameters refined	251	552	244	280
GOF	1.046	1.095	1.049	0.912

Cyclopropylidene(7-dispiro[2.0.2.1]-heptylidene)methane (8): A 1.44 M solution of MeLi in Et_2O (1.46 mL, 2.10 mmol) was added dropwise at 0°C within 1.5 h to a stirred solution of the dibromo[5]triangulane **7** (529 mg, 1.74 mmol) in anhydrous diethyl ether (10 mL). The resulting mixture was allowed to warm to ambient temperature over a period of 0.5 h, poured into ice-cold water (10 mL) and extracted with Et_2O (3×10 mL). The combined organic solutions were washed with H_2O (2×10 mL) and brine (10 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography (20 g silica gel, column 35×2 cm, pentane) to give **8** (210 mg, 84%) as a white powder, $R_f=0.36$. An analytical sample obtained by sublimation at 45°C (0.5 Torr) had a melting point range 84–86°C (decomp). IR: $\tilde{\nu}=3073$, 2993, 2044, 1415, 1146, 1044, 1000, 951, 885, 811, 758 cm^{-1}; ^{1}H NMR (C_6D_6): $\delta=1.33$ (s, 4H), 1.06, 0.77 (m, AA′BB′, 8H); ^{13}C NMR (C_6D_6): $\delta=8.2$ (4CH_2); 7.6 (2CH_2); 21.3 (2C); 172.0, 93.5, 83.6 (C); elemental analysis calcd (%) for $C_{11}H_{12}$ (144.2): C 91.61, H 8.39; found: C 91.90, H 8.72.

7,7′-Bis(dispiro[2.0.2.1]heptylidene) (6), 11-(cyclopropylidene)tetraspiro-[2.0.0.2.0.2.0.1]undecane (9), and heptaspiro[2.0.0.2.0.2.0.0.0.2.0.2.0.0]heptadecane (10): A solution of the allene **8** (251 mg, 1.7 mmol) in anhydrous olefin-free pentane (20 mL) was vigorously stirred with powdered sodium methanolate (2.30 g, 43 mmol) and *N*-nitroso-*N*-cyclopropylurea (370 mg, 2.9 mmol) at 0°C for a period of 8 h. The resulting mixture was poured into a mixture of ice-cold water (20 mL) and pentane (20 mL). The organic solution was washed with H_2O (4×10 mL) and brine (5 mL), dried, and concentrated under reduced pressure. The products were separated by column chromatography (40 g silica gel, column 35×2 cm, pentane) to give starting allene **8** (88 mg, 35%), perspirocyclopropanated bicyclopropylidene **6** (113 mg, 36%), bicyclopropylidene **9** (41 mg, 13%), and triangulane **10** (61 mg, 16%).

Compound 6: $R_f=0.45$; colorless crystals; subl.p. 115°C; Raman (powder): $\tilde{\nu}=1868$, 1487, 1448, 1421, 1301, 1004, 956, 914, 887, 791, 620, 410 cm^{-1}; ^{1}H NMR: $\delta=1.01$, 0.99 (m, AA′BB′, 16H); ^{13}C NMR: $\delta=8.8$ (8CH_2); 16.1 (4C); 115.0 (2C).

Compound 9: $R_f=0.65$; colorless oil; ^{1}H NMR (C_6D_6): $\delta=1.21-1.02$ (m, 8H), 0.94 (m, 4H), 0.75, 0.60 (m, AA′BB′, 4H); ^{13}C NMR (C_6D_6): $\delta=6.3$, 5.1, 3.0 (2CH_2); 2.6, 2.4 (CH_2); 21.0 (2C); 119.1, 104.5, 23.5, 16.0 (C); MS

(CI): *m/z* (%): 368 (100) $[2M]^+$, 219 (40) $[M+NH_3+NH_4]^+$, 218 (48) $[M+2NH_3]^+$, 202 (28) $[M+NH_4]^+$, 201 (100) $[M-H+NH_4]^+$, 170 (20) $[M-CH_2]^+$, 143 (64) $[M-C_3H_5]^+$.

Compound 10: $R_f = 0.78$; colorless powder; m.p. 60°C (subl. at 60°C/0.5 Torr); ^{1}H NMR: $\delta = 0.82-0.69$ (m, 12H), 0.70 (s, 4H; $2CH_2$), 0.56–0.47 (m, 4H); ^{13}C NMR: $\delta = 6.1$, 3.3, ($4CH_2$); 1.3 ($2CH_2$); 17.8 (4C); 25.9 (2C); 16.7 (C); elemental analysis calcd (%) for $C_{17}H_{20}$ (224.3): C 91.01, H 8.99; found: C 90.75, H 8.92.

The structures of the compounds **6** and **10** have been proven by X-ray crystal structure analysis.[7a]

Simmons–Smith cyclopropanation of cyclopropylidene(7-dispiro[2.0.2.1]-heptylidene)methane (8): Diethyl zinc (0.5 mmol, 410 μL of a 1.2 M solution in Et_2O) was added in one portion to a solution of the allene **8** (72 mg, 0.5 mmol) in anhydrous diethyl ether (4 mL). To the resulting mixture, a solution of methylene iodide (200 mg, 60 μL, 0.75 mmol) in Et_2O (2 mL) was added dropwise at 35°C over a period of 2 h. After additional stirring for 1 h at 35°C, the reaction mixture was cooled to ambient temperature, poured into an ice-cold sat. NH_4Cl solution (10 mL), and the aqueous layer was extracted with Et_2O (10 mL). The combined organic phases were washed with H_2O (2 × 10 mL) and brine (5 mL), dried, and concentrated under reduced pressure at 0°C. The residue was purified by column chromatography (40 g silica gel, column 40 × 1 cm, pentane) to give starting allene **8** (7 mg, 10%), 1-(cyclopropylidene)trispiro[2.0.2.0.2.0]nonane (**11**) (28 mg, 35%), pentaspiro[2.0.2.0.0.0.2.1.1.0]tridecane (**12**) (40 mg, 46%), and 7-(spiropentylidene)dispiro[2.0.2.1]heptane (**5**) (4 mg, 5%).

Compound 5: $R_f = 0.39$; colorless oil; ^{1}H NMR: $\delta = 1.25$ (s, 2H), 1.0–0.62 (m, 12H); ^{13}C NMR: $\delta = 5.6$, 4.9, 4.0 ($2CH_2$); 7.1 (CH_2); 22.7 (2C); 117.0, 110.4, 21.6 (C); MS (EI): *m/z* (%): 158 (4) $[M]^+$, 157 (7) $[M-H]^+$, 148 (10), 144 (52) $[M-CH_2]^+$, 131 (100) $[M-C_2H_3]^+$, 117 (45) $[M-C_3H_5]^+$; HRMS: *m/z*: 158.1095; calcd for $C_{12}H_{14}$: 158.1096.

Compound 11: $R_f = 0.51$; colorless powder; m.p. 34–36°C (subl. at 30°C/0.1 Torr); ^{1}H NMR: $\delta = 1.40$ (quint, $J = 1.9$ Hz, 2H), 1.19 (ddd, $J = 2$, 4, 6.8 Hz, 4H), 0.89–0.76 (m, 8H); ^{13}C NMR: $\delta = 5.6$, 4.9 ($2CH_2$); 9.0, 3.3, 2.6 (CH_2); 21.7 (2C); 114.7, 108.0, 21.6 (C); elemental analysis calcd (%) for $C_{12}H_{14}$ (158.2): C 91.08, H 8.92; found: C 91.11, H 8.99.

Compound 12: $R_f = 0.64$; colorless oil. Its spectroscopic data were identical with the published ones.[47]

General procedure (GP 1) for the preparation of spirocyclopropanated bicyclopropylidenes 6, 14, and 17: Anhydrous $CuCl_2$ (1.385 g, 10.3 mmol) was added in one portion to a solution of the respective *gem*-dibromotriangulane **13**, **15**, or **16** (103 mmol) in anhydrous THF (150 mL), and the resulting slurry was cooled to −95°C (−110°C for **13**). A 2.60 M solution of *n*BuLi in hexane (47.7 mL, 124 mmol) was added dropwise at this temperature over a period of 1 h. The resulting mixture was stirred for an additional 1 h at this temperature, allowed to warm to room temperature over 1 h, and then poured into an ice-cold mixture of sat. NH_4Cl solution (150 mL) and dichloromethane (pentane for hydrocarbon **14**) (100 mL). The aqueous layer was extracted with the same solvent (2 × 100 mL), the combined organic phases were washed with H_2O (2 × 200 mL), dried, and concentrated under reduced pressure (at 0°C for **14**). The product was purified as described individually below.

7,7′-Bis(dispiro[2.0.2.1]heptylidene) (6): From 7,7-dibromodispiro[2.0.2.1]-heptane (**15**) (26.0 g, 103 mmol), $CuCl_2$ (1.385 g, 10.3 mmol), and *n*BuLi in hexane (124 mmol, 47.7 mL of a 2.60 M solution), hydrocarbon **6** (7.80 g, 82%) was obtained according to GP 1 after column chromatography (100 g silica gel, column 16 × 4.5 cm, hexane) followed by recrystallization from hexane/Et_2O 2:1, as colorless crystals; $R_f = 0.29$; m.p. 134–136°C (sealed capillary). Its spectroscopic data were identical with the published ones.[7]

(*E*)- and (*Z*)-1,1′-Bis(spiropentylidene) (14): The residue obtained from the treatment of dibromospiropentane **13** (21.91 g, 97 mmol) with $CuCl_2$ (1.394 g, 10.4 mmol) and *n*BuLi in hexane (100 mmol, 37.6 mL of a 2.66 M solution) according to GP 1 was distilled under reduced pressure to give **14** (4.30 g, 67%) as a 2:3 mixture of (*E*)- and (*Z*)-isomers, b.p. 40–45°C (1.5 Torr). The diastereomers were separated by preparative GC.

Compound (*E*)-14: colorless crystals; m.p. 43–45°C (pentane); ^{1}H NMR: $\delta = 1.44$ (s, 4H), 1.21–1.05 (m, AA′BB′, 8H); ^{13}C NMR: $\delta = 9.2$ ($4CH_2$); 10.1 ($2CH_2$); 112.5, 10.9 (2C).

Compound (*Z*)-14: colorless oil; ^{1}H NMR: $\delta = 1.54$ (s, 4H), 1.81–1.43, 0.97–0.93 (2m, AA′BB′, 8H); ^{13}C NMR: $\delta = 9.4$ ($4CH_2$); 10.4 ($2CH_2$); 113.0, 11.5 (2C).

15,15′-Bis(hexaspiro[2.0.2.0.0.0.2.0.2.0.1.0]pentadecylidene) (17): The brown oil obtained according to GP 1 from the treatment of dibromotriangulane **16** (2.885 g, 8.10 mmol) with $CuCl_2$ (109 mg, 0.811 mmol) and *n*BuLi in hexane (8.11 mmol, 3.05 mL of a 2.66 M solution) was dissolved in Et_2O (20 mL). The resulting solution was kept at −20°C for 24 h, the precipitate was filtered off and washed with a small quantity of cold diethyl ether to give hydrocarbon **17** (356 mg, 22%). An analytical sample obtained by sublimation at 155°C (0.1 Torr) followed by recrystallization from Et_2O had m.p. 245–246°C (decomp); ^{1}H NMR: $\delta = 0.90-0.73$ (m, 24H), 0.66–0.57 (m, 8H); ^{13}C NMR: $\delta = 7.3$, 4.6 ($8CH_2$); 21.4 (8C); 26.6 (4C); 114.2 (2C); MS (CI): *m/z* (%): 427 (4) $[M+NH_3+NH_4]^+$, 412 (3), 411 (22), 410 (100) $[M+NH_4]^+$; elemental analysis calcd (%) for $C_{30}H_{32}$ (392.6): C 91.78, H 8.22; found: C 91.64, H 8.09.

Octamethylbicyclopropylidene (35): A solution of methyllithium, freshly prepared from Li (0.902 g, 130 mmol) and MeI (8.42 g, 3.70 mL, 59.3 mmol) in Et_2O (65 mL) was added dropwise at −78°C within 10 min to a solution of 1,1-dibromo-2,2,3,3-tetramethylcyclopropane[45] (10.0 g, 39.1 mmol) in Et_2O (130 mL). The resulting mixture was stirred for an additional 20 h at this temperature and allowed to warm to ambient temperature; the reaction was then quenched with water. The organic phase was dried and concentrated under reduced pressure, and the residue was sublimed at 35°C (20 mbar) to give **35** (2.75 g, 73%). Its spectroscopic data were identical with the published ones.[12c]

General procedure (GP 2) for the preparation of dibromotriangulanes 7 and 16: Powdered KOH (8.98 g, 160 mmol) was added in one portion at −10°C to a vigorously stirred solution of the respective bicyclopropylidene (8 mmol), $CHBr_3$ (4.03 g, 1.43 mL, 16.0 mmol), and TEBACl (36.4 mg, 0.16 mmol, 2 mol%) in dichloromethane (15 mL). The exothermal reaction started at 5°C. The temperature of the mixture was maintained at 5–10°C by external cooling for 0.5 h, then the mixture was vigorously stirred at ambient temperature for 5 h, filtered through a 2 cm pad of sea sand, concentrated under reduced pressure and purified as described individually below.

11,11-Dibromotetraspiro[2.0.0.2.0.2.0.1]undecane (7): The residue obtained from the bicyclopropylidene **4** (3.790 g, 28.67 mmol) according to GP 2 was recrystallized from MeOH at −20°C to give **7** (7.00 g, 80%) as a light yellow solid. An analytical sample was obtained by column chromatography (pentane, $R_f = 0.54$) followed by sublimation at 60°C (0.5 Torr). M.p. 71–72°C; IR: $\tilde{\nu} = 3070$, 2994, 1499, 1436, 1419, 1216, 1138, 1115, 1044, 1002, 948, 913, 893, 766, 707 cm^{-1}; ^{1}H NMR: $\delta = 1.43$ (ddd, $J = 3.9$, 5.4, 9.3 Hz, 2H), 1.18, 1.12 (2m, AA′BB′, 4H), 0.86 (ddd, $J = 3.4$, 5.1, 9.6 Hz, 2H), 0.76 (m, 2H), 0.68 (ddd, $J = 3.4$, 5.1, 8.9 Hz, 2H); ^{13}C NMR: $\delta = 9.3$, 3.8, 2.6 ($2CH_2$); 21.9 (2C); 41.4, 32.9, 31.5 (C); elemental analysis calcd (%) for $C_{11}H_{12}Br_2$ (304.0): C 43.45, H 3.98, Br 52.57; found: C 43.40, H 3.87, Br 52.46.

15,15-Dibromohexaspiro[2.0.2.0.0.0.2.0.2.0.1.0]pentadecane (16): The residue obtained from the bicyclopropylidene **6** (1.47 g, 7.98 mmol) according to GP 2 was purified by column chromatography (35 g silica gel, column 10 × 3 cm, hexane) to give **16** (2.37 g, 83%) as a colorless powder. $R_f = 0.39$; m.p. 154°C; ^{1}H NMR: $\delta = 1.46-1.38$ (m, 4H), 0.92–0.85 (m, 4H), 0.82–0.65 (m, 8H); ^{13}C NMR: $\delta = 6.8$, 2.6 (4, CH_2); 22.3 (4C); 35.5 (2C); 43.40 (C); MS (CI): *m/z* (%): 393/391/389 (1/2/1) $[M+NH_3+NH_4]^+$, 376/374/372 (3/6/3) $[M+NH_4]^+$, 278 (100); elemental analysis calcd (%) for $C_{15}H_{16}Br_2$ (356.1): C 50.60, H 4.53, Br 44.88; found: C 50.92, H 4.81, Br 44.70.

9-(Dispiro[2.0.2.1]hept-7‴-ylidene)dispiro{bis(dispiro[2.0.2.1]heptane)-7,7′;8,7″-dispiro[2.0.2.3]nonane} (19): A solution of the hydrocarbon **6** (100 mg, 0.54 mmol) in toluene (1.5 mL) in a sealed Teflon tube was pressurized to 10 kbar and then heated at 130°C for 2 d, cooled, the Teflon tube was carefully opened, and the reaction mixture was concentrated under reduced pressure. Column chromatography of the residue (50 g silica gel, column 20 × 3 cm, pentane) gave **19** (34 mg, 34%) as a colorless oil. $R_f = 0.40$; ^{1}H NMR: $\delta = 1.40$ to −0.08 (m); ^{13}C NMR: $\delta = 10.2$, 9.0, 8.8, 6.4, 6.0, 5.5, 4.2, 3.5 ($2CH_2$); 16.1, 15.0, 13.2 (2C); 135.3, 112.9, 38.9, 36.3, 31.5, 30.4 (C).

2-(Dispiro[2.0.2.1]hept-7′-ylidene)hexaspiro(tricyclo[3.2.2.0^{1,5}]nonane-3,1″-cyclopropane-4,1‴-cyclopropane-6,1⁗-cyclopropane-7,1⁗′-cyclopropane-8,1⁗″-cyclopropane-9,1⁗‴-cyclopropane) (20): A solution of the

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hydrocarbon **6** (200 mg, 1.085 mmol) in toluene (1.5 mL) was heated in a sealed tube at 180°C for 6 d, cooled to room temperature, the ampoule was carefully opened, and the reaction mixture was concentrated under reduced pressure. The product was separated from unreacted **6** (R_f = 0.45, pentane) by column chromatography of the residue (100 g silica gel, column 20 × 4 cm, pentane). Subsequent recrystallization from MeOH furnished **20** (50 mg, 25%) as colorless crystals. R_f = 0.50; m.p. 127–128°C; ^{1}H NMR: δ = 0.88 (m, 4H), 0.75 (m, 2H), 0.60–0.03 (m, 26H); ^{13}C NMR: δ = 11.8, 9.8, 8.3, 6.8, 6.5, 6.3, 6.0, 4.6 (2 CH_2); 29.4, 29.2 (2C); 133.3, 117.3, 50.6, 50.1, 36.2, 31.8, 14.4, 14.2 (C).

Trispiro{9,8‴-(dispiro[2.0.2.2]octane-7‴-one)bis(dispiro[2.0.2.1]heptane)-7,7′;8,7″-dispiro[2.0.2.3]nonane} (23): Hydrocarbon **19** (22 mg, 0.06 mmol) was added at 0°C to a 0.092 M solution of dimethyldioxirane in acetone (2 mL, 0.18 mmol). The resulting solution was stirred at 20°C for 12 h and then concentrated under reduced pressure. Column chromatography of the residue (20 g silica gel, column 20 × 2 cm, pentane/Et_2O 9:1) gave **23** (21 mg, 91%) as a colorless powder. R_f = 0.60; m.p. 70–71°C (from aq. MeOH); ^{1}H NMR: δ = 1.33 to −0.15 (m); ^{13}C NMR: δ = 13.8, 11.8, 8.6, 8.1, 8.0, 6.9, 6.0, 5.5, 5.48, 5.45, 5.4, 5.1, 4.6, 4.2, 4.0, 3.1 (CH_2); 215.7, 75.4, 42.3, 39.7, 37.2, 31.6, 31.2, 27.5, 20.5, 19.0, 18.6, 17.8 (C).

General procedure (GP 3) for the bromination of bicyclopropylidenes 6 and 17: To a stirred solution of the respective bicyclopropylidene (48.9 μmol) in anhydrous olefin-free pentane or hexane (5 mL) in the presence of one drop of pyridine, a solution of Br_2 (0.26 μL, 51 μmol) in the same solvent (0.25 mL) was added at −15°C. The yellow suspension was allowed to warm to 0°C, then poured into sat. Na_2SO_3 solution (20 mL) and extracted with CH_2Cl_2 (20 mL). The combined organic phases were washed with sat. NH_4Cl solution and brine (30 mL each), dried, and concentrated under reduced pressure.

7,7′-Bis(7-bromodispiro[2.0.2.1]heptyl) (25): From the treatment of bicyclopropylidene **6** (2.0 mg, 11 μmol) in pentane (1 mL) with pyridine (0.5 mg) and Br_2 (12 μmol, 17 μL of a 0.71 M solution in pentane) according to GP 3, crude **25** (3.3 mg, 88%) was obtained as a yellow powder; ^{1}H NMR: δ = 1.63, 0.87 (2m, AA′BB′, 16H).

15,15′-Bis(15-bromohexaspiro[2.0.2.0.0.0.2.0.2.0.1.0]pentadecyl) (27): From the treatment of the bicyclopropylidene **17** (19.2 mg, 48.9 μmol) in hexane (5 mL) with one drop of pyridine and Br_2 (0.26 μL, 51 μmol) in hexane (0.25 mL) according to GP 3, **27** was obtained as colorless crystals (20.0 mg, 74%). M.p. > 200°C (decomp); ^{1}H NMR: δ = 1.41–1.25 (m, 8H), 0.92–0.71 (m, 16H), 0.65–0.55 (m, 4H), 0.53–0.42 (m, 4H); ^{1}H NMR (C_6D_6): δ = 1.60–1.53 (m, 8H), 1.06–0.99 (m, 4H), 0.93–0.61 (m, 16H), 0.55–0.48 (m, 4H); ^{13}C NMR (C_6D_6): δ = 6.0 (8 CH_2); 7.1, 2.5 (4 CH_2); 32.2, 21.4, 20.6 (4C); the ^{13}C signal of the CBr fragment was not detected under the routine conditions; MS (CI): *m/z* (%): 589/587/585 (4/8/4) $[M+NH_3+NH_4]^+$, 573/572/571/570/569/568 (15/50/30/100/15/50) $[M+NH_4]^+$, 492/490 (5/5) $[M-Br+NH_4]^+$.

Ethyl hexaspiro[2.0.2.0.0.0.2.0.2.0.1.0]pentadecane-15-carboxylate (28) and ethyl (*Z*)-pentaspiro[2.0.2.0.0.2.0.2.0.1.0]tetradec-14-ylideneacetate (29): Ethyl diazoacetate (2.39 g, 2.19 mL, 20.94 mmol) was added at 0°C over a period of 12 h to a stirred solution of bicyclopropylidene **6** (1.93 g, 10.47 mmol) and $[Rh(OAc)_2]_2$ (46 mg, 0.1 mmol, 1 mol%) in anhydrous CH_2Cl_2 (10 mL). After additional stirring at 20°C for 2 h, the mixture was concentrated under reduced pressure, and the residue purified by column chromatography (50 g silica gel, 40 × 2 cm column, pentane/Et_2O 10:1) to give unreacted **6** (745 mg, 39%, R_f = 0.67), **28** (903 mg, 32%), and **29** (258 mg, 9%).

Compound 28: colorless crystals; R_f = 0.42; m.p. 80–82°C; ^{1}H NMR: δ = 4.05 (q, *J* = 7.0 Hz, 2H; OCH_2), 2.09 (s, 1H; CH), 1.22 (t, *J* = 7.0 Hz, 3H; CH_3), 1.0–0.91 (m, 2H), 0.91–0.63 (m, 12H), 0.63–0.52 (m, 2H); ^{13}C NMR: δ = 14.1 (CH_3); 7.0, 6.6, 5.0, 3.5 (2 CH_2); 59.9 (CH_2); 25.6 (CH); 31.6, 18.5, 18.1 (2C); 172.5 (C); elemental analysis calcd (%) for $C_{18}H_{22}O_2$ (270.4): C 79.96, H 8.20; found: C 79.71, H 8.36.

Compound 29: colorless crystals; R_f = 0.33; m.p. 66–68°C; ^{1}H NMR: δ = 5.20 (s, 1H; =CH), 4.11 (q, *J* = 7.1 Hz, 2H; OCH_2), 1.25 (t, *J* = 7.1 Hz, 3H; CH_3), 1.05–0.95 (m, 4H), 0.87–0.75 (m, 4H), 0.73–0.64 (m, 4H), 0.54–0.45 (m, 2H), 0.12–0.05 (m, AB, *J* = 5.0 Hz, 2H); ^{13}C NMR: δ = 14.6 (CH_3); 14.4, 6.2, 4.1, 2.8 (2 CH_2); 59.3 (CH_2); 104.1 (CH); 26.5 (2C); 175.6, 165.3, 39.1, 32.0, 29.6 (C); elemental analysis calcd (%) for $C_{18}H_{22}O_2$ (270.4): C 79.96, H 8.20; found: C 79.91, H 8.27.

General procedure (GP 4) for the preparation of *gem*-dihalotriangulanes 32–34 and 36: A mixture of the respective bicyclopropylidene (0.3–0.8 mmol), $CHCl_3$ (CH_2Cl_2 for **32**, no solvent for **36**) (10 mL), 50% aqueous NaOH solution (10 mL), TEBACl (20 mol%), dibromofluoromethane (1–10 equiv, only for compounds **33**, **36**), and a drop of EtOH was vigorously stirred at ambient temperature for 3 d. After this, the mixture was diluted with water (20 mL), the aqueous phase was extracted with the same organic solvent that was used in the carbene addition (2 × 30 mL), the combined organic phases were washed with water (100 mL) and dried. After concentration of the solution under reduced pressure, the residue was purified by column chromatography (silica gel, hexane).

24,24-Dichlorotetradecaspiro[2.0.2.0.0.0.0.0.2.0.2.0.0.0.2.0.2.0.0.1.0.0.2.0.2.0.0.0]untriacontane (32): From bicyclopropylidene **17** (138 mg, 0.352 mmol), dichloro[15]triangulane **32** (163 mg, 98%) was obtained according to GP 4 after column chromatography (20 g silica gel, column 13 × 2.5 cm) as colorless crystals. R_f = 0.28; m.p. 212°C (decomp); ^{1}H NMR: δ = 1.25–1.15 (m, 4H), 0.94–0.61 (m, 28H); ^{13}C NMR: δ = 7.7, 7.0, 6.8, 5.0 (4 CH_2); 19.0 (8C); 17.9 (4C); 32.5 (2C); 37.7 (C); MS (CI): *m/z* (%): 513/512/511/510/509 (0.5/1/4/2/6) $[M+NH_3+NH_4]^+$, 497/496/495/494/493/492 (3/10/17/64/28/100) $[M+NH_4]^+$, 278 (100); elemental analysis calcd (%) for $C_{31}H_{32}Cl_2$ (475.5): C 78.31, H 6.78, Cl 14.91; found: C 78.20, H 6.75, Cl 14.68.

24-Bromo-24-fluorotetradecaspiro[2.0.2.0.0.0.0.0.2.0.2.0.0.0.2.0.2.0.0.1.0.0.2.0.2.0.0.0]untriacontane (33): From bicyclopropylidene **17** (296 mg, 0.754 mmol) and $CHBr_2F$ (1.456 g, 0.60 mL, 7.59 mmol), bromofluoro[15]-triangulane **33** (356 mg, 94%) was obtained according to GP 4 after column chromatography (10 g silica gel, column 7 × 2.5 cm) as colorless crystals; R_f = 0.24; m.p. 223–225°C (decomp); ^{1}H NMR: δ = 1.42–1.34 (m, 2H), 1.00–0.61 (m, 30H); ^{13}C NMR: δ = 7.5, 7.0, 6.9, 6.8, 6.6, 5.0, 4.9 (2 CH_2); 6.5 (d, ^5J(C,F) = 3.8 Hz, 2 CH_2); 32.5, 19.0, 18.1, 17.6 (2C); 34.1 (d, ^2J(C,F) = 10.6 Hz, 2C); 31.9 (d, ^3J(C,F) = 1.8 Hz, 2C); 18.6 (d, ^4J(C,F) = 3.1 Hz, 2C); 90.6 (d, ^1J(C,F) = 320.7 Hz, C); MS (CI): *m/z* (%): 540/539/538/537 (2/7/2/7) $[M+NH_3+NH_4]^+$, 523/522/521/520 (30/100/30/99) $[M+NH_4]^+$, 441 (36) $[M-Br+NH_4]^+$; elemental analysis calcd (%) for $C_{31}H_{32}BrF$ (503.5): C 73.95, H 6.41, Br 15.87; found: C 73.84, H 6.38, Br 15.64.

7,7-Dichloro-1,1,2,2,5,5,6,6-octamethyldispiro[2.0.2.1]heptane (34): From bicyclopropylidene **35** (310 mg, 1.61 mmol), dichloro[3]triangulane **34** (201 mg, 45%) was obtained according to GP 4 after column chromatography (30 g silica gel, column 30 × 2 cm) as a colorless powder. R_f = 0.54; m.p. 138–140°C; ^{1}H NMR: δ = 1.36 (s, 12H; 4 CH_3), 1.11 (s, 12H; 4 CH_3); ^{13}C NMR: δ = 21.9 (4 CH_3, 4C); 19.6 (4 CH_3); 28.3 (2C); 41.5 (C); MS (EI): *m/z* (%): 278/276/274 (0.1/0.6/0.9) $[M]^+$, 263/261/259 (2/12/18) $[M-CH_3]^+$, 241/239 (13/40) $[M-Cl]^+$, 197 (40), 183 (32), 175 (50), 157/155 (32/100), 135 (35), 119 (46), 105 (26), 91 (30), 84 (32), 69 (35), 57 (55), 41 (42); elemental analysis calcd (%) for $C_{15}H_{24}Cl_2$ (275.3): C 65.45, H 8.79, Cl 25.76; found: C 61.35, H 8.77, Cl 25.85.

7-Bromo-7-fluoro-1,1,2,2,5,5,6,6-octamethyldispiro[2.0.2.1]heptane (36): From bicyclopropylidene **35** (1.114 g, 5.79 mmol), 50% aqueous NaOH solution (5 mL), and $CHBr_2F$ (5 mL), bromofluorotriangulane **36** (250 mg, 14%) was obtained according to GP 4 after column chromatography (35 g silica gel, column 35 × 2 cm) as colorless crystals. R_f = 0.50. An analytical sample was sublimed at 60°C (0.5 mbar); m.p. 67–68°C; ^{1}H NMR: δ = 1.32 (s, 6H; 2 CH_3), 1.25 (s, 6H; 2 CH_3), 1.14 (s, 6H; 2 CH_3), 1.11 (s, 6H; 2 CH_3); ^{13}C NMR: δ = 21.9, 21.7 (d, ^4J(C,F) = 3.8 Hz), 20.0, 19.1 (2 CH_3); 39.3 (d, ^2J(C,F) = 8.8 Hz), 29.0, 27.6 (2C); 94.5 (d, ^1J(C,F) = 398 Hz, C); MS (EI): *m/z* (%): 304/302 (2/2) $[M]^+$, 389/387 (5/5) $[M-CH_3]^+$, 261/259 (5/5), 247/245 (8/8), 223 (50) $[M-Br]^+$, 163 (36), 139 (100), 121 (37), 81 (35), 69 (42), 57 (82); elemental analysis calcd (%) for $C_{15}H_{24}BrF$ (303.3): C 59.41, H 7.89, Br 26.35; found: C 59.16, H 7.88, Br 26.28.

***cis*-1,4-Di-*n*-butyl-2-(hexaspiro[2.0.2.0.0.0.2.0.2.0.1]pentadec-15‴′-ylidene)-trispiro{dispiro[2.0.2.1]heptane-7′,3-bicyclo[2.2.0]hexane-5,1″-cyclopropane-6,1‴-cyclopropane} (37) and 15,15′-bis(hexaspiro[2.0.2.0.0.0.2.0.2.0.1.0]pentadecylidene)methane (38)**: A 1.65 M solution of *n*BuLi in hexane (0.79 mL, 1.31 mmol) was added dropwise at −10 to −5°C to a stirred solution of bromofluorotriangulane **33** (132 mg, 0.262 mmol) in anhydrous THF (20 mL). The resulting mixture was stirred for an additional 0.5 h at this temperature, poured into ice-cold water (50 mL), and the mixture extracted with CH_2Cl_2 (3 × 50 mL). The combined organic solutions were concentrated under reduced pressure, and the residue was purified by column chromatography (20 g silica gel, column 13 × 2.5 cm,

hexane was used to elute **37** and then hexane/Et_2O 20:1 to elute **38**) to give **37** (74 mg, 55%) and **38** (22.3 mg, 21%).

Compound 37: colorless crystals; $R_f = 0.32$; m.p. 91–92°C (benzene/Et_2O 2:1); ^{1}H NMR (C_6D_6): $\delta = 1.88-1.27$ (m, 13H), 1.04 (t, $J = 7.3$ Hz, 3H; CH_3), 0.94 (t, $J = 7.4$ Hz, 3H; CH_3), 1.23–0.43 (m, 27H), 0.29–0.06 (m, 4H); ^{13}C NMR (C_6D_6): $\delta = 14.3$, 14.2 (CH_3); 8.8, 8.3, 8.0, 7.8, 7.7, 7.5, 7.4, 7.1, 6.7, 6.5, 6.2, 6.1, 5.9, 5.7, 4.7, 4.5 (Cpr-CH_2); 30.7, 30.4, 27.7, 27.2, 24.2, 24.1 (Bu-CH_2); 138.9, 112.0, 58.5, 55.6, 42.2, 31.5, 25.7, 24.1, 23.1, 22.3, 22.0, 21.4, 21.3 (C); MS (CI): *m/z* (%): 521/520/519 (10/42/100) $[M+H]^+$.

Compound 38: colorless crystals; $R_f = 0.01$; m.p. > 210°C (decomp) (Et_2O); ^{1}H NMR (C_6D_6): $\delta = 1.03-0.89$ (m, 16H), 0.83–0.73 (m, 8H), 0.66–0.59 (m, 8H); ^{13}C NMR (C_6D_6): $\delta = 7.5$, 5.8 (8CH_2); 21.4 (8C); 32.2 (4C); 91.9 (2C); 195.0 (C); MS (CI): *m/z* (%): 439 (100) $[M+NH_3+NH_4]^+$.

7,7′-Bis(dispiro[2.0.2.1]heptylidene)methane (43) and 15-bromo-15-methylhexaspiro[2.0.2.0.0.0.2.0.2.0.1.0]pentadecane (44): A 1.50 M solution of MeLi/LiI in Et_2O (1.10 mL, 1.65 mmol) was added dropwise at 0°C to a stirred solution of dibromotriangulane **16** (587 mg, 1.648 mmol) in anhydrous Et_2O (5 mL), and the resulting mixture was stirred for an additional 0.5 h at this temperature. Work-up according to GP 1 followed by column chromatography (20 g silica gel, column 13 × 2.5 cm, pentane) furnished **43** (146 mg, 45%) and **44** (22 mg, 4.5%).

Under analogous experimental conditions, but at −78°C, from **16** (615 mg, 1.727 mmol) and a 1.50 M solution of MeLi/LiI in Et_2O (1.15 mL, 1.73 mmol) compounds **43** (44 mg, 13%) and **44** (241 mg, 48%) were obtained.

Compound 43: colorless powder; $R_f = 0.30$; ^{1}H NMR: $\delta = 1.18$, 0.97 (2m, AA′BB′, 16H); ^{13}C NMR: $\delta = 8.4$ (8CH_2); 21.0 (4C); 95.3 (2C); 165.0 (C).

Compound 44: colorless powder; $R_f = 0.42$; m.p. 100–102°C; ^{1}H NMR: $\delta = 1.73$ (s, 3H; CH_3), 1.45–1.34 (m, 2H), 1.11–0.90 (m, 2H), 0.90–0.63 (m, 10H), 0.63–0.52 (m, 2H); ^{13}C NMR: $\delta = 24.7$ (CH_3); 6.6, 6.5, 3.7, 2.3 (2CH_2); 31.8, 21.3, 19.2 (2C); 48.1 (C); elemental analysis calcd (%) for $C_{16}H_{19}Br$ (291.2): C 65.98, H 6.58; found: C 65.70, H 6.38.

Hexaspiro[2.0.2.0.0.0.2.0.2.0.1.0]pentadecane-15-carboxylic acid (45): A solution of NaOH (178 mg, 4.45 mmol) in H_2O (30 mL) was added to a solution of the ester **28** (1.00 g, 3.7 mmol) in MeOH (5 mL). After additional stirring at 100°C for 5 h, the mixture was concentrated under reduced pressure, the residue was taken up with H_2O (10 mL), the mixture washed with Et_2O (2 × 10 mL), then acidified to pH 2 with conc. HCl solution at 0°C and extracted with Et_2O (5 × 10 mL). The combined organic phases were dried and concentrated under reduced pressure to give **45** as a colorless powder (720 mg, 80%). M.p. 204–206°C (decomp); ^{1}H NMR: $\delta = 10.50$ (s, 1H; OH), 2.03 (s, 1H; CH), 1.10–1.01 (m, 2H), 0.93–0.76 (m, 6H), 0.76–0.67 (m, 6H), 0.62–0.53 (m, 2H); ^{13}C NMR: $\delta = 7.0$, 6.7, 5.1, 3.3, (2CH_2); 25.4 (CH); 32.5, 18.7, 18.1 (2C); 179.7 (C); elemental analysis calcd (%) for $C_{16}H_{18}O_2$ (242.3): C 79.31, H 7.49; found: C 79.10, H 7.72.

Hexaspiro[2.0.2.0.0.0.2.0.2.0.1.0]pentadecane-15-carbonyl chloride (46): A solution of the acid **45** (677 mg, 2.794 mmol) in thionyl chloride (6.52 g, 4.0 mL, 54.84 mmol) was heated under reflux for 2 h, then cooled to ambient temperature, and concentrated under reduced pressure to give **46** as a yellow oil (722 mg, 99%); ^{1}H NMR: $\delta = 2.55$ (s, 1H; CH), 1.29–1.12 (m, 4H), 0.79–0.71 (m, 8H), 0.71–0.58 (m, 4H); ^{13}C NMR: $\delta = 7.3$, 6.7, 5.4, 3.4 (2CH_2); 36.1 (CH); 36.3, 19.1, 18.2 (2C); 172.4 (C).

***N*-(Hexaspiro[2.0.2.0.0.0.2.0.2.0.1.0]pentadec-15-yl)urea (47)**: A solution of NaN_3 (246 mg, 3.784 mmol) in H_2O (1 mL) was added dropwise at 0°C to a stirred solution of the acid chloride **46** (722 mg, 2.769 mmol) in acetone (7.5 mL). The reaction mixture was stirred for a period of 2 h at this temperature, poured into ice-cold water (30 mL), the resulting mixture extracted with diethyl ether (5 × 10 mL), and the combined organic phases were dried at 0°C for 24 h. After concentration under reduced pressure at 0°C, the residue was taken up with anhydrous benzene (5 mL), and the solution heated at 80°C for 2 h. After cooling, the reaction mixture was saturated with anhydrous NH_3 at 5°C, the precipitate formed was filtered off and dried under reduced pressure to give **47** as a colorless solid (449 mg, 63%). M.p. 176–178°C (decomp); ^{1}H NMR: $\delta = 4.79$ (s, 2H; NH_2), 4.70 (s, 1H; NH), 2.93 (s, 1H; CH), 1.12–0.60 (m, 16H); ^{13}C NMR: $\delta = 6.8$, 6.6, 4.5, 3.8 (2CH_2); 34.0 (CH); 28.7, 18.7, 17.5 (2C); 160.6 (C).

***N*-(Hexaspiro[2.0.2.0.0.0.2.0.2.0.1.0]pentadec-15-yl)-*N*-nitrosourea (48)**: A solution of dinitrogen tetroxide (1.31 g, 0.5 mL, 14.2 mmol) in Et_2O (5 mL) was added dropwise at 0°C to a stirred suspension of the urea **47** (449 mg, 1.75 mmol) and anhydrous powdered NaOAc (2.0 g, 24.4 mmol) in anhydrous Et_2O (50 mL). The reaction mixture was stirred for a period of 2 h at this temperature, filtered, intensively stirred (3 × 1 min) with a suspensions of $NaHCO_3$ (2 g) in H_2O (0.5 mL) followed by rapid decantation and dried. Evaporation of almost all solvent under reduced pressure and filtration gave **48** as yellow crystals (310 mg, 62%). M.p. 124–125°C (decomp); ^{1}H NMR: $\delta = 5.20$ (s, 2H; NH_2), 3.21 (s, 1H; CH), 1.15–0.55 (m, 16H); ^{13}C NMR: $\delta = 6.7$, 6.6, 6.1, 5.0 (2CH_2); 36.1 (CH); 29.5, 19.3, 18.7 (2C); 165.0 (C).

Nonaspiro[2.0.0.0.2.0.2.0.0.0.2.0.2.0.0.0.2.0]uneicosane (D_{3h}-[10]triangulane) (49) and 7,7′-Bis(dispiro[2.0.2.1]heptylidene)methane (43): A solution of the *N*-nitrosourea **48** (310 mg, 1.09 mmol) in bicyclopropylidene (**1**) (3.42 g, 4.0 mL, 42.7 mmol) was vigorously stirred with sodium methanolate (589 mg, 10.9 mmol) at 0°C for a period of 10 h. The reaction mixture was filtered, the filtrate concentrated under reduced pressure, and the residue purified by column chromatography (20 g silica gel, column 13 × 2.5 cm, pentane) to give **49** (42 mg, 14%) and **43** (58 mg, 27%).

Compound 49: colorless crystals; $R_f = 0.45$; m.p. 200–201°C; ^{1}H NMR: $\delta = 0.75$, 0.69 (m, AA′BB′, 24H); ^{13}C NMR: $\delta = 6.5$ (12CH_2); 18.2 (6C); 28.8 (3C); MS (CI): *m/z* (%): 294 (100) $[M+NH_4]^+$.

Attempted recrystallization of the allene **43** to determine its melting point as well as prolonged storage at 0°C led to the quantitative formation of its "head-to-head" dimer, 15,16-bis(dispiro[2.0.2.1]hept-7-ylidene)hexaspiro[2.0.2.0.0.0.2.0.2.0.2.0]hexadecane (**50**), the structure of which was confirmed by X-ray crystal structure analysis;[40] ^{1}H NMR: $\delta = 1.30-0.30$ (m, 32H); ^{13}C NMR: $\delta = 10.0$, 8.8, 8.4, 5.2 (4CH_2); 22.4 (4C); 128.2, 119.2, 44.7, 16.32, 16.28 (2C).

Tetradecaspiro[2.0.2.0.0.0.0.0.2.0.2.0.0.0.0.2.0.2.0.0.1.0.0.2.0.2.0.0.0]untriacontane (C_{2v}-[15]triangulane) (51): Lithium (19.1 mg, 2.75 mmol) was added to a solution of dichloro-D_{2h}-[15]triangulane **32** (131 mg, 0.275 mmol) in a mixture of anhydrous THF (10 mL) and *tert*-butyl alcohol (205 mg, 0.26 mL, 2.77 mmol). The reaction mixture was stirred for 48 h at ambient temperature, then poured into ice-cold water (50 mL), and the mixture extracted with CH_2Cl_2 (2 × 50 mL). The combined organic phases were concentrated under reduced pressure, and the residue was purified by column chromatography (20 g silica gel, column 13 × 2.5 cm, hexane) to give **51** (46 mg, 41%) as colorless crystals. $R_f = 0.33$; m.p. 191–193°C (hexane/Et_2O 1:1); ^{1}H NMR: $\delta = 0.94$ (s, 2H; 24-CH_2), 0.86–0.63 (m, 24H), 0.60–0.47 (m, 8H); ^{13}C NMR: $\delta = 6.5$, 6.0, 4.6, 3.0 (4CH_2); 5.8 (CH_2); 27.6, 18.5, 18.0 (4C); 22.6 (2C); MS (CI): *m/z* (%): 425/424 (34/100) $[M+NH_4]^+$; elemental analysis calcd (%) for $C_{31}H_{34}$ (406.6): C 91.57, H 8.43; found: C 91.81, H 8.56.

General procedure (GP 5) for the hydrogenolysis of bicyclopropylidenes 6, 52: Under stirring, a suspension of the respective catalyst in an appropriate solvent was prehydrogenated with H_2 under ambient pressure for 15 min. After this, a solution of the starting material was added dropwise, and the mixture was stirred at the respective temperature for the time indicated, monitoring the volume of absorbed hydrogen, filtered through a pad of Celite, diluted with pentane (50 mL), washed with H_2O (2 × 50 mL), sat. $NaHCO_3$ solution (50 mL, only when HOAc was used as a co-solvent), and brine (50 mL), dried, and concentrated under reduced pressure. The product was isolated by column chromatography (silica gel, hexane).

7,7′-Bis(dispiro[2.0.2.1]heptyl) (52): a) According to GP 5 (20°C, 2 h), from bicyclopropylidene **6** (451 mg, 2.45 mmol) dissolved in a mixture of hexane and MeOH (20 mL, 1:1) and Pd(10%)/$BaSO_4$ (52.1 mg, 49.0 μmol, 2 mol%) in MeOH (5 mL), hydrocarbon **52** (299 mg, 65%) was isolated after column chromatography (20 g silica gel, column 13 × 2.5 cm) as colorless crystals. $R_f = 0.56$; m.p. 61–63°C (hexane); ^{1}H NMR: $\delta = 0.94$ (s, 2H), 0.83–0.72 (m, 4H), 0.68–0.59 (m, 8H), 0.54–0.43 (m, 4H); ^{13}C NMR: $\delta = 5.7$, 4.1 (4CH_2); 23.7 (2CH); 18.2 (4C); elemental analysis calcd (%) for $C_{14}H_{18}$ (186.3): C 90.26, H 9.74; found: C 90.17, H 9.55.

b) According to GP 5 (−15°C, 1.5 h), from bicyclopropylidene **6** (80 mg, 0.434 mmol), dissolved in hexane (2 mL) and PtO_2 (84 mg, 0.37 mmol) in a mixture of MeOH and HOAc (10 mL, 1:1), hydrocarbon **52** (66 mg, 82%) was obtained in almost pure form after concentration of the pentane solution.

1,1′-Bis(2,2,3,3-tetramethylcyclopropyl) (53):[44] a) According to GP 5 (20°C, 2.5 h), from bicyclopropylidene **6** (369 mg, 2.0 mmol) dissolved in hexane (2 mL) and PtO_2 (200 mg, 0.88 mmol, 44 mol%) in HOAc (10 mL), hydrocarbon **53** (31 mg, 8%) was isolated by column chromatography (20 g

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silica gel, column 13 × 2.5 cm) and further purified by preparative GCto obtain the title compound as a colorless oil. $R_f = 0.81$; ^{1}H NMR: $\delta = 1.06$ (s, 12H; 4CH_3), 0.93 (s, 12H; 4CH_3), −0.14 (s, 2H; 2CH); ^{13}C NMR: $\delta = 23.7$, 17.9 (4CH_3); 30.1 (2CH); 21.5 (4C); elemental analysis calcd (%) for $C_{14}H_{26}$ (194.4): C 86.52, H 13.48; found: C 86.79, H 13.53.

b) According to GP 5 (−15°C, 6 d), from hydrocarbon **52** (66.0 mg, 0.354 mmol), dissolved in a mixture of hexane and Et_2O (6 mL, 2:1) and PtO_2 (60 mg, 0.264 mmol, 75 mol%) in HOAc/MeOH (15 mL, 2:1), hydrocarbon **53** (70 mg, 75% purity, 76%) was isolated after concentration of the solution. Column chromatography (20 g silica gel, column 13 × 2.5 cm) furnished **53** (45 mg, 49%) without improved purity.

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