X-ray Crystal Structures and Conformational Analysis of Bicyclo[5.3.1]undec-1(11)-enes: Twisting versus Pyramidalization in Anti-Bredt Olefins

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The synthesis of several 9,11,11-trihalo[5.3.1]propellanes and their 4-dimethylsila analogues is described. They solvolyze under formation of the corresponding isomeric 7,9,11- trihalobicyclo-[5.3.l]undec-1(11)-enes which are "anti-Bredt" olefins with a strained trans double bond in a bridged eight-membered ring; in the presence of nucleophiles such as water or ethanol, the corresponding 7-hydroxy or 7-ethoxy derivatives, respectively, are obtained. On the basis of the X-ray crystal structures of four of these compounds (**1a**, **9a**, **15**, **17b**), the effect of strain and of the substitution pattern on the degree of twisting and pyramidalization of the double bond is discussed.

Introduction

Strain in organic molecules has been an intriguing topic in chemistry since the end of the previous century. In this context, strained double bonds have received much attention, the classical examples being the bridgehead olefins.[1−9] In 1924, Bredt formulated his famous rules which "prohibited" the existence of bridgehead double bonds.[10] The synthesis of such molecules, which later became known as anti-Bredt compounds, has been a challenging goal in organic chemistry. Ever more strained derivatives were prepared, and thus the rules kept needing new adjustments. Meanwhile, a large number of highly strained derivatives have been synthesized which illustrates the continuing interest in this field.[6,9,11−13]

However, strain entails increased reactivity, and therefore it has been difficult to obtain experimental structural information on such compounds. The strained olefin can be stabilized by complexation to a metal center, and X-ray crystal structures of such complexes are known, but those of uncomplexed strained anti-Bredt compounds are rare.[9,11−17] In 1992, we reported the synthesis of the strained bicyclo[5.3.1]undec-l(11)-ene derivative **1a**, which was formed on solvolysis of the 11,11-dibromo-*endo*-9-chloro[5.3.1]propellane (**2**) in ethanol (Scheme 1).[12] An X-ray crystal structure analysis revealed that **1a** had a strongly distorted double bond with several remarkable features.

We therefore decided to investigate some closely related derivatives, which were also accessible from halo-[5.3.l]propellanes. It is worth mentioning that in a related context, such propellanes are of interest for the synthesis of small strained [*n*]metacyclophanes.[2,18−21] In this paper, we report the synthesis and structural analysis of several new anti-Bredt compounds. First, we will describe the synthesis of the anti-Bredt compounds **1**, **9**, and **12**, followed by a short description of the synthesis of the 4-sila-anti-Bredt compounds **15** and **17**. Next, the results

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(1) Keese, R.; Luef, W. In *Topics in Stereochemistry*; Eliel, E. L.; Wilen, S. H., Ed.; J. Wiley & Sons: New York, 1991; Vol. 20, pp 231−318.
(2) Warner, P. M. *Chem. Rev.* **1989**, *89*, 1067.
(3) Michl, J.; Radziszewski, J. G.; Downing, J. W.; Kopecky, P.; Miller, R. D. *Pure Appl. Chem.* **1987**, *59*, 1613.
(4) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683.
(5) Buchanan, G. L. *Chem. Soc. Rev.* **1974**, *3*, 41.
(6) Keese, R. *Angew. Chem.* **1975**, *87*, 568.
(7) Buchanan, G. L.; Jamieson, G. *Tetrahedron* **1972**, *28*, 1129.
(8) Buchanan, G. L.; Jamieson, G. *Tetrahedron* **1972**, *28*, 1123.
(9) Lease, T. G.; Shea, K. J. In *Advances in Theoretically Interesting Molecules*; JAI Press Inc.: Greenwich, CT, 1992; Vol. 2, pp 79−112.
(10) Bredt, J.; Thouet, H.; Schmitz, J. *Justus Liebigs Ann. Chem.* **1924**, *437*, 1.
(11) Shea, K. J.; Lease, T. G.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 8627.
(12) (a) Wijsman, G. W.; de Wolf, W. H.; Bickelhaupt, F.; Kooijman, H.; Spek, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 9191. (b) Wijsman, G. W., Thesis, Vrije Universiteit, 1994.
(13) Grimme, W.; Bertsch, A.; Flock, H.; Noack, T.; Krauthiuser, S. *Synlett* **1998**, 1175.
(14) Kumar, A.; Lichtenhan, J. D.; Critchlow, S. C.; Eichinger, B. E.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 5633.
(15) Bly, R. S.; Bly, R. K.; Hossain, M. H.; Lebioda, L.; Raja, M. *J. Am. Chem. Soc.* **1988**, *110*, 7723.
(16) Godleski, S. A.; Gundlach, K. B.; Valpey, R. S. *Organometallics* **1985**, *4*, 296.
(17) Bly, R. S.; Hossain, M. M.; Lebioda, L. *J. Am. Chem. Soc.* **1985**, *107*, 5549.
(18) Kraakman, P. A.; Valk, J. M.; Niederlinder, H. A. G.; Brouwer, D. B. E.; Bickelhaupt, F. M.; de Wolf, W. H.; Bickelhaupt, F.; Stam, C. H. *J. Am. Chem. Soc.* **1990**, *112*, 6638.
(19) Jenneskens, L. W.; de Boer, H. J. R.; de Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1990**, *112*, 8941.
(20) Bickelhaupt, F. *Pure Appl. Chem.* **1990**, *62*, 373.
(21) (a) Bickelhaupt, F.; de Wolf, W. H. *Recl. Trav. Chim. Pays-Bas* **1988,** *107*, 459. (b) Bickelhaupt, F.; de Wolf, W. H. In *Advances in strain in organic chemistry*; Halton, B. Ed.; JAI Press Ltd: Greenwich, CT, 1993; Vol. 3, pp 185−227. (c) Bickelhaupt, F.; de Wolf, W. H. *J. Phys. Org. Chem.* **1998**, *11*, 362−376.

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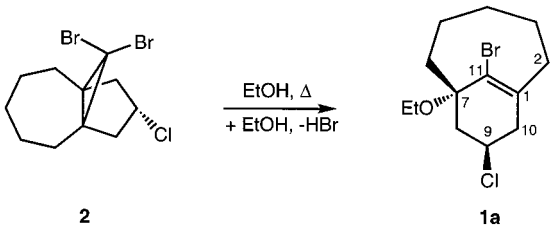
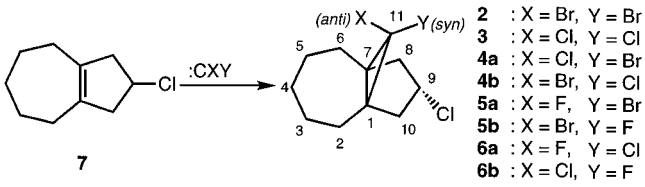
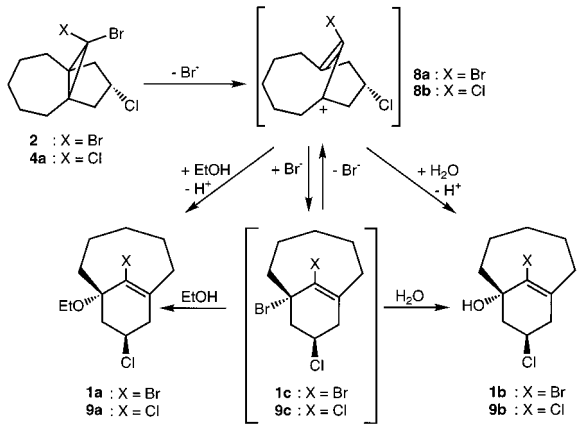
Scheme 1



Scheme 2



Scheme 3



of the X-ray crystal structure determinations and the analysis of the geometries will be presented.

Synthesis and Mechanistic Aspects

Bicyclo[5.3.1]undec-1(11)-enes. Anti-Bredt compounds with the bicyclo[5.3.1]undec-1(11)-ene skeleton can be prepared by solvolysis of the corresponding halo-[5.3.l]propellanes such as **2**, **4**, **5**, and **6**. The synthesis of these precursors is outlined in Scheme 2.

Dibromocarbene addition by the method of Skattebøl[22] (t-BuOK/$CHBr_3$/benzene) to **7**[23] gave the unstable **2** in about 70% yield;[12,13] the *exo*-9-isomer was also formed (7%). Due to the instability of **2**, it could not be purified satisfactorily. Column chromatography (silica/pentane) yielded small amounts of **2** (about 16%), but most of the material was transformed on the column to **1b** (Scheme 3), the hydroxy analogue of the ethoxy bridgehead olefin **1a**; **1b** was also obtained by the reaction of **2** with water. However, for the synthesis of **1a**, it was not necessary to use purified **2**, as **1a** could readily be obtained by heating crude **2** in ethanol, followed by column chromatography and recrystallizations from ethanol. The formation of **1** may be rationalized by invoking ionization and electrocyclic ring opening of **2** to furnish the intermediate bridgehead allylic cation **8a** which is intercepted by the bromide ion to yield **1c**; **1c** may react (via **8a**) with ethanol or water to yield **1a**[12] or **1b**, respectively (Scheme 3). More likely, **8a** is directly intercepted by the solvent. This type of solvolysis of propellanes has ample precedent.[2]

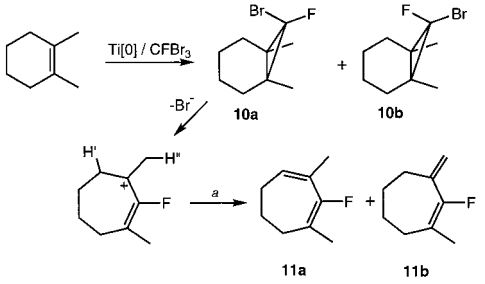
The cyclopropane ring opening is symmetry controlled and obeys the Woodward−Hoffmann−de Puy rules.[24] This implies that ionization of the halogen *syn* to the five-membered ring gives a *trans*-cyclooctene derivative. Ionization of the *anti* halogen does not occur because a *trans*-cyclohexene ring would result, which is too strained to be formed under ordinary conditions. (Note that for reasons of clarity, we designate the halogens at the cyclopropane ring (position 11) as *syn* and *anti* with respect to the five-membered ring, while the chlorine at the five-membered ring (position 9) is indicated as *exo* and *endo* in line with the usual definition (Scheme 2)).

The synthesis of **9**, the 11-chloro analogue of **1**, was slightly more difficult. It could not be achieved by solvolysis of **3**, the trichloropropellane analogue of **2**; previous studies had shown that **3** can be recrystallized from ethanol without decomposition.[23] Apparently, ionization and electrocyclic ring opening requires at least a *syn*-bromine substituent as leaving group (as in **2**). Thus, to obtain **9**, we needed the 11-bromo-11-chloropropellane **4a**. A 1:1 mixture of **4a** and **4b** was obtained by addition of bromochlorocarbene (from $CHClBr_2$, Skattebøl conditions[22]) to **7** (along with very small amounts of the corresponding *exo*-isomers). Purification was achieved by recrystallization from ethanol at −20 °C.

A solution of **4a**,**b** in $CDCl_3$ became intensely gray-brown on standing for several days at room temperature. According to the NMR spectrum, one isomer of **4** had partly been converted to a new compound. In an attempt to separate the various products by column chromatography, elution with pentane yielded one isomer of **4**. Subsequently, elution with diethyl ether yielded a compound which was identified as the hydroxy bridgehead olefin **9b**. At room temperature, **4a**, with the *syn*-bromine function, slowly rearranged to an anti-Bredt compound **9** which was too unstable for full characterization; the ^1H and ^{13}C NMR spectra and several 2D-NMR techniques revealed that the new compound had the same skeleton and geometry as **9b**, but carried a different substituent at C7, so that transformation of **4a** to **9c** is the most plausible rationalization (Scheme 3). The unreacted propellane isomer must by exclusion be assigned to the structure of **4b** with the chlorine in *syn* position. This is supported by the chemical shifts of the carbons and protons in the five-membered ring; they show a very close resemblance with those of **3**:[25] The resonances C8/10 appear at $\delta = 47.1$ (**4b**) and 47.0 ppm (**3**), those of C9 at $\delta = 58.6$ (**4b**) and 58.5 ppm (**3**); the proton signals are also very similar: for **4b**, the A_2B_2C-system is observed at $\delta = 4.25$, 2.86, and 2.46 ppm ($^2J = -16.0$ Hz, $^3J = 8.1$ Hz, $^3J = 4.1$ Hz), and for **3** at $\delta = 4.28$, 2.84, and 2.49 ppm ($^2J = -15.9$ Hz, $^3J = 8.1$ Hz, $^3J = 4.3$ Hz). Further confirmation of the structure assignment of **9c** came from its reactions: with water it gave **9b**, and with ethanol it yielded the desired 7-ethoxy derivative **9a**. These reactions proceed presumably via **8b**. Finally, a mixture of **4b** and **9a**, prepared from **4a**,**b** by a special procedure (see Experimental Section), was obtained by crystallization.

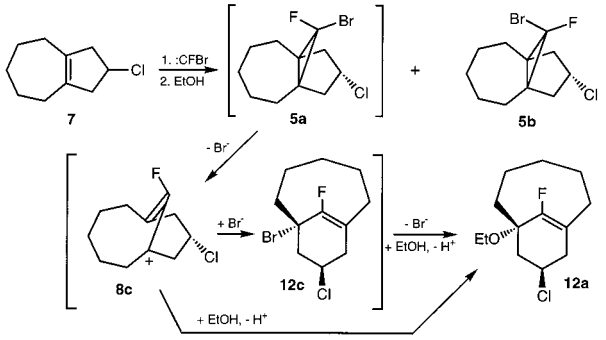
(22) Skattebol, L. *J. Org. Chem.* **1964**, *29*, 2951.
(23) Jenneskens, L. W.; Turkenburg, L. A. M.; de Wolf, W. H.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 184.
(24) Hoffmann, R.; Woodward, R. B. *Acc. Chem. Res.* **1968**, *1*, 17.
(25) Jenneskens, L. W. Thesis, Vrije Universiteit Amsterdam, 1986.

Scheme 4



[a] − H′ or − H″, respectively.

Scheme 5

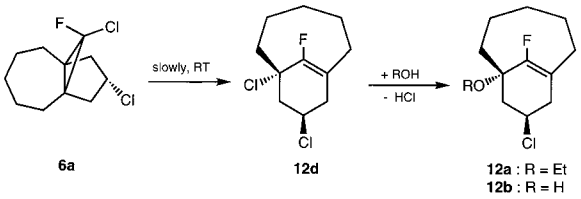


In view of the results obtained by the X-ray crystal structure determination of **9a** (vide infra), it was desirable to synthesize an 11-fluoro analogue in order to study the influence of the size of the various halogens at position 11 on the geometry of the molecule. In analogy with the successful preparation of **1** and **9** (Schemes 2 and 3), the reaction of **7** with bromofluorocarbene to form **5** and rearrangement of the latter seemed attractive.

For the generation of chlorofluorocarbene, Dolbier has reported an elegant method which involves a reduction of $CFCl_3$ with low-valent titanium (Ti[0]).[26] We modified the procedure slightly by adding the Ti[0] suspension to the solution of $CFCl_3$ and the alkene, which turned out to be more convenient for our halogenated olefins. The same approach was successful in the generation of bromofluorocarbene from $CFBr_3$. This was tested with 1,2-dimethylcyclohexene (Scheme 4); it yielded the two isomers **10** in good yield, which had previously been synthesized by Anke et al. with a different carbene source.[27] One of the isomers was very unstable and rapidly rearranged to a mixture of **11a** and **11b**. The formation of **11** can be rationalized by ionization and electrocyclic ring opening of the cyclopropane ring, forming an allyl cation which loses a proton to form a diene system. In accordance with the Woodward−Hoffmann−De Puy rules, only the *syn*- bromo isomer **10a** is capable of doing so, because it leads to an allylic cation comprising a *cis*-cycloheptene unit. The *anti*-bromo isomer **10b** would lead to a *trans*-cycloheptene intermediate, which is energetically inaccessible.[27]

In an analogous fashion, **5** was synthesized (Scheme 5). Instead of trying to isolate pure **5** which (in analogy to **2** and **10)** could be problematic due to rearrangement reactions, we poured the reaction mixture into ethanol

Scheme 6



and allowed the *syn*-bromo isomer **5a** to form the anti-Bredt compound **12a**. Here again, one must assume that the allylic cation **8c** is formed as an intermediate which either directly or via **12c** solvolyzes to furnish **12a** (Scheme 5).

As **5b** and **12a** could not be separated, we investigated an alternative approach to **12a** via **6**. Although this route seemed attractive because it involved the cheaper $CFCl_3$ instead of $CFBr_3$ (Scheme 2), it was not a priori clear whether the 11-chlorine in **6** would be sufficiently reactive to serve as leaving group in the electrocyclic ring opening to form **8c**, especially in view of the behavior of **3** and **4b** (vide supra). A 1:1 mixture of **6a** and **6b** (Schemes2 and 6) was obtained from **7** and $CFCl_3$ in excellent yield (>95%) by the method of Dolbier.[26] Indeed, on heating **6** for 4 h in ethanol, **6a** was only partially converted to **12a** in sharp contrast to **2**, which immediately and quantitatively rearranged to **1a**; analogously, **12b** was formed from **6** and water. Compound **12d** was slowly formed when **6** was stored at room temperature; reaction of **12d** with ethanol yielded **12a**. Again, **6a** must be the precursor for the rearrangements (Scheme 6); **6b** remained unreacted.

Unfortunately, crystals of **12a** (mp 15 °C) suitable for X-ray analysis could not be obtained. However, a comparison between a fluoro- and bromo-substituted anti-Bredt olefin was achieved in the analogous 4-sila series, the synthesis of which will be described in the next section.

4,4-Dimethyl-4-si1abicyclo[5.3.1]undec-1(11)-enes. The desired sila-anti-Bredt olefins were obtained by the procedure developed for the all-carbon analogues (Schemes 2 and 3), starting from **13** as a key intermediate.[12b,28] Dibromocarbene addition to **13** gave crude **14** which without purification was directly dissolved in ethanol and stirred for 30 min at 50 °C to yield **15** (Scheme 7). Recrystallization from ethanol gave crystals suitable for an X-ray structure determination.

Chlorofluorocarbene addition[26] to **13** yielded the propellanes **16a** and **16b** in good yield. Preparative GLC gave two products, the propellane isomer **16b** and the anti-Bredt compound **17b**. Apparently, the *syn*-chloro isomer **16a** rearranged thermally to **17b** in the injector. In analogy to other 7-halo anti-Bredt olefins (**1c**, **9c**, **12d**), **17b** reacted with ethanol to yield the 7-ethoxy derivative **17a**. Unfortunately, like **12a**, **17a** was not crystalline, in contrast to **17b**. It was, however, not easy to obtain crystals of **17b** which were suitable for X-ray structure determination. Finally, recrystallization from 2-propanol was successful; obviously, the solvolytic power of 2-propanol is sufficiently lower than that of ethanol to prevent (or retard) ionization and nucleophilic allylic substitutions.

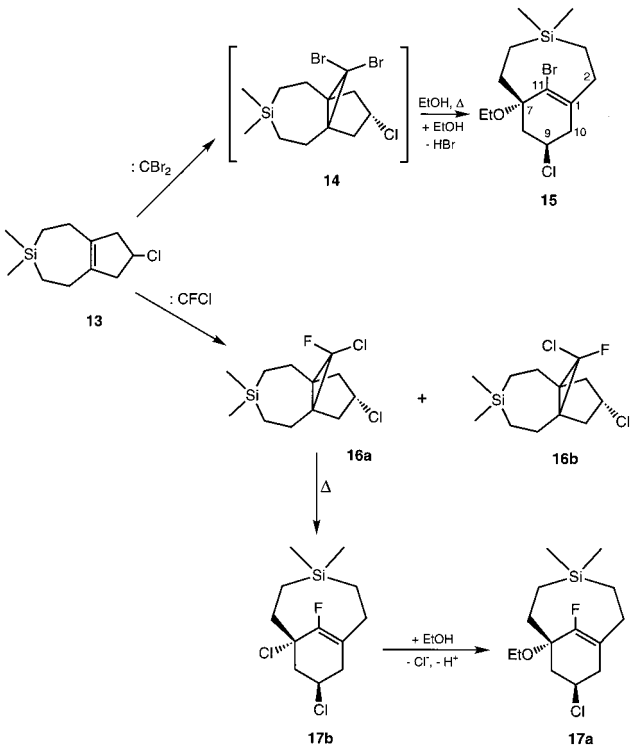
With four crystal structures (**1a**, **9a**, **15**, and **17b**) available, an attempt was undertaken to identify the

(26) Dolbier, W. R., Jr.; Burkholder, C. R. *J. Org. Chem.* **1990**, *55*, 589.

(27) Anke, L.; Reinhard, D.; Weyerstahl, P. *Justus Liebigs Ann. Chem.* **1981**, 591.

(28) Baldew, A. U., Thesis, Vrije Universiteit, 1993.

Scheme 7



factors which determine the geometry of the strained double bond.

Structural Analysis

General Considerations. One of the most fascinating aspects of strained alkenes is the geometry of the double bond, and more in particular the question how the normally planar olefin responds to imposed geometric restrictions.

First, one has to consider that there are two different types of distortions, the *out of plane* (oop) *bending* and the *in plane bending*. The latter is the major distortion observed in small cyclic alkenes (e.g., cyclopropene).[29,30] In anti-Bredt compounds, the oop bending is much more important, due to the three-dimensional nature of the distortions. In this respect, anti-Bredt compounds and *trans*-cycloalkenes are closely related, as pointed out by Wiseman[31] (vide infra).

In *trans*-cycloalkenes two *trans* positions of an olefin are connected by a chain of atoms (usually carbon atoms). If the chain is short, the olefin must bend and will be distorted by oop, bending in order to achieve the *trans* connection. The degree of deformation of the olefin depends mainly on the ring size, but to some extent also on intramolecular steric repulsion between the π-orbitals of the double bond and the methylene groups in the middle of the carbon bridge which are located on top of the π-cloud. The bending can be expressed by the absolute values of the 8 dihedral or torsion angle θ_1 of the two bonds from the olefinic carbon atoms to their adjacent (carbon) atoms in the bridge (Figure 1).

In the oop bending, two major modes of distortion can be distinguished: *twisting* and *pyramidalization*.[4,9,29,31]

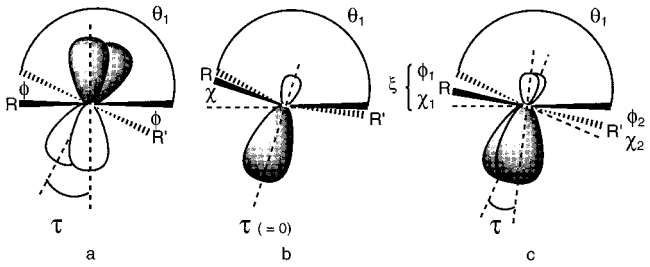


Figure 1. Modes of distortion of strained olefins.

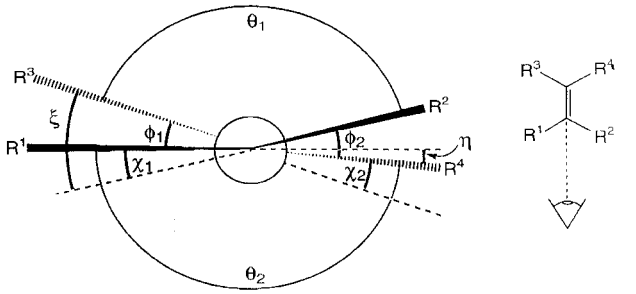


Figure 2. Definition of angles around a distorted C=C bond.

One extreme case is the pure twisting (Figure 1a); the two olefinic carbon atoms stay fully sp^2 hybridized and thus planar. As a consequence, the two p_z-orbitals are misaligned, which weakens the π-component of the double bond. This is visualized by the twisting angle τ which is defined as the dihedral angle between the two p_z-orbitals. The dihedral angle between the *cis*-substituents is ϕ; for planar sp^2 hybridized carbon atoms, $\tau = \phi$.

In the other extreme situation, the *symmetric* pyramidalization (Figure lb), the carbon atoms are rehybridized by admixture of additional p character into the original sp^2 σ-bonds; this makes the geometry around the carbon nonplanar. Now the π-bond is formed from two p_z-orbitals with some s-character added; the alignment between the two orbitals is optimal ($\tau = 0$), but their orientation in the π-plane is no longer parallel, and for this reason, the distance between them increases and the net overlap is smaller, too. The pyramidalization angle χ, the dihedral angle between the planes through C=C−R^1 and C=C−R^2 (see also Figure 2) defines the extent of oop bending; it is equal at both sp^n centers. Another form of pyramidalization, in which the π-type sp^n orbitals are oriented toward opposite sides of the double bond, is called *asymmetric* pyramidalization; it plays a minor role in anti-Bredt compounds and will not be discussed here.[32]

The situation usually encountered in anti-Bredt compounds and *trans*-cycloalkenes is intermediate: twisting and pyramidalization occur simultaneously (Figure 1c). As a rule, the molecules have a different set of substituents at both ends of the double bonds; therefore, the deformations at the two olefinic carbon atoms may be different and more angles are needed to describe such systems. The angles χ_1 and χ_2 are the pyramidalization angles of the two olefinic carbon atoms; the average of the pyramidalization angles can be defined as $\chi_{av} = (\chi_1 + \chi_2)/2$. The *cis*-torsion angles ϕ_1 and ϕ_2 are also not equal, and $\theta_1 \neq \theta_2$, where θ_2 is the torsion angle between the

(29) Ermer, O. *Aspekte von Kraftfeldrechnungen*; Bauer: Munchen, 1981.
(30) Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121.
(31) Wiseman, J. R.; Pletcher, W. *A. J. Am. Chem. Soc.* **1970**, *92*, 956.
(32) Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095.

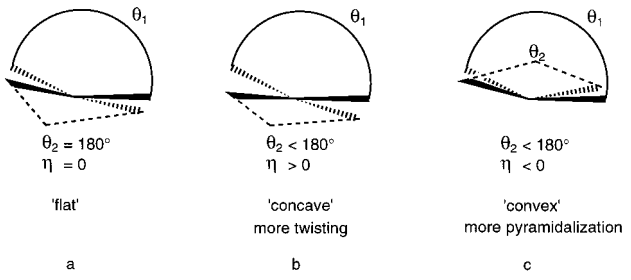


Figure 3. Flat, concave, and convex deformations of a strained olefin.

"free" *trans* substituents R and R′, which are not involved in bridge formation (Figures 1 and 2). The angle τ between the (slightly rehybridized) p_z-orbitals (pure twisting angle) can be shown[29] to be the average of the *cis* torsion angles: $\tau = (\phi_1 + \phi_2)/2$.

For the discussion of geometric distortions, it is convenient to introduce an additional angle $\xi = 180° - \theta_1$, which is the torsion angle between the two *trans* bonds involved in bridging. The value of ξ contains contributions from both twisting (τ) and pyramidalization (χ_{av}) as expressed by eqs 1−3 (see also Figure 2):

$$\xi = 180° - \theta_1 \quad (1)$$

$$\xi = \tau + \chi_{av} \quad (2)$$

$$\xi = \phi_1 + \chi_1 = \phi_2 + \chi_2 \quad (3)$$

Thus, when ξ is forced to have a certain value, which is mainly imposed by ring size and by π-cloud/bridge repulsion, the molecule can achieve this value by adapting either τ or χ. The mode of deformation (twisting or pyramidalization) of the two olefinic carbon atoms is independent of each other, as eq 3 shows. As we will discuss later, ξ mainly depends on the skeleton, and substituents have a minor effect. So the value of ξ can be used to estimate the strain of the olefin in *trans*-cycloalkenes or anti-Bredt compounds.

Another useful angle is η, which is the difference of the twisting τ and pyramidalization χ_{av} (eq 4). While ξ is related to the total *amount* of distortion (twisting *and* pyramidalization; eq 2), η describes *how* the olefin responds to the imposed geometrical restrictions in making a choice between these two modes of deformation.

$$\eta = \tau - \chi_{av} \quad (4)$$

Thus when $\eta = 0$, twisting and pyramidalization are divided equally ($\tau = \chi_{av}$); when η is *negative*, the olefin responds more strongly by pyramidalization ($\chi_{av} > \tau$); and when η is *positive*, it responds more strongly by twisting ($\tau > \chi_{av}$). The angle η may also be defined by $\eta = 180° - \theta_2$, and as such, it describes the "outer", nonbridged side of the double bond, which is influenced by the geometrical restrictions more indirectly. One should note that in practice, θ_2 is usually defined as the *smallest* dihedral angle between the "free" *trans*-substituents, while in reality, three different situations may be encountered (Figure 3, (vide infra)).[33]

In *trans*-cycloalkenes, the "free", nonbridged *trans*-substituents are not subject to the direct restraints imposed by the skeleton and can thus adopt an orientation such as to optimize electronic factors related to optimization of π-overlap and to steric repulsion by the rest of the molecule. They have little influence on ξ, but effect the degree of pyramidalization χ of the carbon atoms (and thus also ϕ according to eq 3). There are three different situations. The olefin looks "flat" when $\eta = 0°$ (Figure 3a). When $\theta_2 < 180°$ and $\eta > 0°$, the olefin looks concave because the two olefinic carbon atoms are surrounded by substituents at both sides of the idealized nodal plane, which is perpendicular to the bisector of the two sp^n-π-orbitals (Figure 3b). When $\theta_2 < 180°$ (or $\theta_2 > 180°$ keeping the sense of rotation constant)[34] and $\eta < 0°$, the olefin looks convex; all the substituents of the olefin are at one side of the average nodal plane, so that the two olefinic carbon atoms are located on the "outer" side of the molecule (Figure 3c).

In an anti-Bredt compound, the bridgehead olefin has three substituents which are part of the bicyclic skeleton. Let us consider that those three substituents have a rigid geometry which make ξ constant. As the three substituents R^2, R^3, and R^4 (Figure 2) are fixed, the movement of the free substituent R^1 can effect χ_{av} and τ. By increasing χ_1, χ_{av} increases, ϕ_1 decreases (ξ = constant, eq 3!), τ decreases and η decreases (eq 4). So the pyramidalization of the olefinic carbon with the free substituent can change the amount of χ versus τ (eq 5).[29]

$$\Delta(\chi_1) = -2\Delta(\tau) \quad (5)$$

Generally, torsion requires more energy per degree of deformation than pyramidalization.[29,30] For this reason, a strained olefin with minor geometrical restrictions (such as *trans*-cycloalkenes) will preferentially respond by increasing pyramidalization rather than torsion. This can be monitored by η (eq 4).

Another method to describe distortions of double bonds is the POAV (Pi-Orbital-Axis-Vector) analysis developed by Haddon;[35,36] it is based on rehybridization of nonplanar olefinic carbon atoms as calculated from their bond and dihedral angles and it is very useful for molecules which have nonplanar conjugated olefins, like bridged annulenes and C_{60}. We have also performed the POAV analysis for **1a**, and it turned out that in our case, the POAV dihedral angle was practically identical with the angle τ.

X-ray Crystal Structures of 1a, 9a, 15, and 17b. The ORTEP structure of **1a** has been published;[12] those of **9a** (Supporting Information), **15** (Figure 4), and **17b** (Figure 5) are presented here. Data relating to **1a**, **9a**, **15**, and **17b** are reported in Tables 1−3. The angles describing the distortion of the double bond are contained in Table 4 and Figure 6.

Discussion. As described in the Introduction, experimental data of distorted double bonds are rare. This is largely due to the instability of these compounds. Surprisingly, our compounds are fairly stable and do not react with oxygen or moisture, in contrast to other

(33) Asymmetric pyramidalization does play a role in dimetallenes (M2R4), see for example: Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomeas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2378.

(34) When defining the new angle $\eta = 180 - \theta_2$, care must be taken when applying θ_2, as it is mostly defined as the smallest angle between the substituents. If one takes into account the sense of rotation for θ_1 and θ_2, then they are at opposite sides of the double bond.

(35) Haddon, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 2837.

(36) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385.

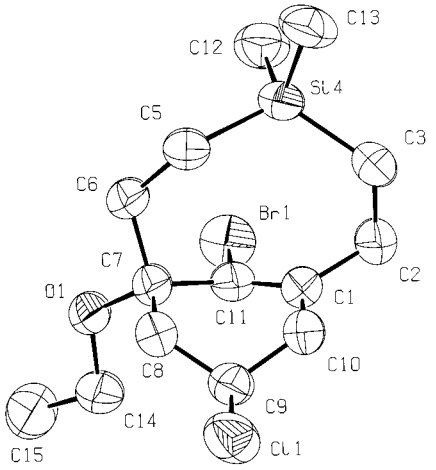


Figure 4. X-ray crystal structure of **15**.

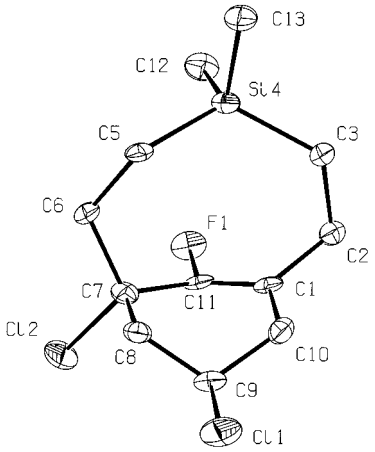


Figure 5. X-ray crystal structure of **17b**.

Table 1. Selected Bond Lengths (Å)

bond	**1a**	**9a**	**15**	**17b**
C_1-C_{11}	1.319 (8)	1.323 (3)	1.331 (4)	1.309 (8)
C_1-C_2	1.502 (9)	1.497 (3)	1.504 (5)	1.505 (7)
C_2-C_3	1.555 (9)	1.544 (3)	1.545 (5)	1.552 (8)
C_3-C_4	1.541 (8)	1.541 (3)	–	–
C_3-Si_4	–	–	1.892 (4)	1.889 (5)
C_4-C_5	1.554 (9)	1.542 (3)	–	–
Si_4-C_5	–	–	1.893 (4)	1.901 (5)
C_5-C_6	1.545 (9)	1.536 (3)	1.545 (5)	1.540 (8)
C_6-C_7	1.554 (9)	1.550 (3)	1.549 (5)	1.540 (7)
C_7-C_{11}	1.502 (8)	1.508 (3)	1.509 (4)	1.482 (7)
C_7-C_8	1.559 (9)	1.551 (3)	1.545 (5)	1.534 (8)
C_8-C_9	1.520 (8)	1.514 (3)	1.505 (5)	1.509 (7)
C_9-C_{10}	1.521(9)	1.509(3)	1.502(5)	1.525 (7)
C_1-C_{10}	1.504 (9)	1.506 (3)	1.509 (5)	1.511 (7)
$C_{11}-X$	1.922 (5)	1.775 (2)	1.911 (3)	1.357 (6)
C_7-Y	1.410 (7)	1.424 (2)	1.423 (4)	1.829 (6)

strained alkenes,[2,9,11] so that we were able to obtain crystals suitable for X-ray analysis. For comparison, the structures of some related compounds will be briefly discussed, too.

Ermer's *trans*-cyclooctene derivative **18** was the first compound of which data of a distorted double bond were experimentally determined (Table 5, Supporting Information).[29,37] The important angle θ_1 is 137.7°; this is the angle "needed" to bend the two *trans* ends of the alkene together by a six-carbon atom chain, and thus the angle

(37) Ermer, O. *Angew. Chem.* **1974**, *86*, 672.

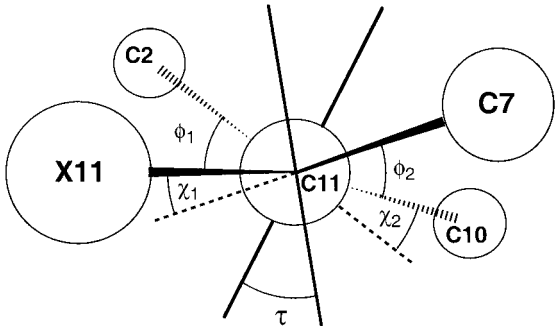


Figure 6. Distortion angles of **1a**, **9a**, **15**, and **17b** as presented in Table 4.

Table 2. Selected Bond Angles (deg)

bond angle	**1a**	**9a**	**15**	**17b**
$C_{11}-C_1-C_2$	123.1 (6)	122.6 (2)	123.8 (3)	121.1 (5)
$C_{11}-C_1-C_{10}$	118.6 (5)	119.1 (2)	118.8 (3)	119.4 (5)
$C_{10}-C_1-C_2$	117.0 (5)	117.2 (2)	116.8 (3)	118.7 (5)
$C_1-C_{11}-X$	121.3 (4)	121.4 (2)	121.4 (2)	119.0 (5)
$C_1-C_{11}-C_7$	122.9 (5)	122.1 (2)	123.3 (3)	125.9 (5)
$C_7-C_{11}-X$	112.9 (4)	113.4 (2)	113.5 (2)	112.2 (4)
$C_1-C_2-C_3$	105.7 (5)	106.4 (2)	106.5 (3)	107.1 (4)
$C_2-C_3-C_4$	116.1 (5)	116.3 (2)	–	–
$C_2-C_3-Si_4$	–	–	121.0 (3)	120.4 (4)
$C_3-C_4-C_5$	117.5 (5)	118.7 (2)	–	–
$C_3-Si_4-C_5$	–	–	117.4 (2)	118.1 (2)
$C_4-C_5-C_6$	119.0 (5)	119.9 (2)	–	–
$Si_4-C_5-C_6$	–	–	125.4 (2)	125.9 (4)
$C_5-C_6-C_7$	117.0 (5)	116.4 (2)	116.8 (1)	113.8 (4)
$C_6-C_7-C_{11}$	105.5 (5)	105.2 (2)	106.9 (3)	106.8 (4)
$C_8-C_7-C_{11}$	111.3 (5)	111.1 (2)	111.1 (3)	111.5 (4)
$C_6-C_7-C_8$	108.6 (5)	110.1 (2)	110.4 (3)	112.9 (4)
$C_7-C_8-C_9$	111.2 (5)	112.0 (2)	112.8 (3)	110.6 (4)
$C_8-C_9-C_{10}$	109.3 (5)	109.9 (2)	110.3 (3)	110.4 (4)
$C_9-C_{10}-C_1$	110.1 (5)	109.7 (2)	109.7 (3)	109.2 (4)

Table 3. Dihedral Angles around the Double Bond (deg)

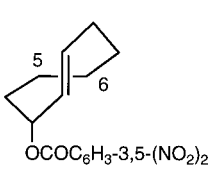
dihedral angles		**1a**	**9a**	**15**	**17b**
$C_2-C_1=C_{11}-C_7$	θ_1	−133.6(6)	−134.2(2)	−143.5(3)	−144.5(5)
$C_{10}-C_1=C_{11}-X$	θ_2	−167.8(4)	−168.2(2)	−169.3(3)	−175.6(4)
$C_2-Cl=C_{11}-X$	ϕ_1	25.6(8)	24.5(3)	20.1(5)	14.8(8)
$C_{10}-C_1=C_{11}-C_7$	ϕ_2	33.0(8)	33.0(3)	27.1(5)	25.0(8)
pyramidalization C_{11}	χ_1	21(1)	21.3(4)	16.4(6)	20.7(9)
pyramidalization C_1	χ_2	13(1)	12.8(4)	9.4(6)	10.5(8)
$(\phi_1+\phi_2)/2$	τ	29(1)	28.8(4)	23.6(7)	20(1)

Table 4. Distortions Angles (deg) of Some Anti-Bredt Compounds

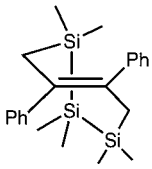
	1a	**9a**	**15**	**17b**	**18**	**19**	**20**
τ	29	28.8	23.6	20	18	19.6	10.8
χ_{av}	17.1	17.1	12.9	15.6	24	13.2	28.5
ξ	46.4	45.8	36.5	35.5	42.3	32.8	39.3
η	12.2	11.7	10.7	4.3	−6	6.4	−17.7

ξ is 42.3° which appears to be the smallest angle required for bending a "normal" *trans*-cyclooctene entity. This is mainly due to two effects. First, there is some *trans*-annular repulsion between the methylene groups of the bridge (especially C5 and C6) and the double bond, and second, there is torsional strain in the bridge, because the bridge is prevented from adapting its most favorable conformation.[29,37] The angle torsion energy of the σ-framework is so high that it will often overrule deformation effects at the double bond. The small hydrogen substituents at the double bond can move without external geometrical restrictions and the angle η is −6°; so the system responds preferentially by pyramidalization (eq 4). The X-ray crystal structure of another *trans*-cy-

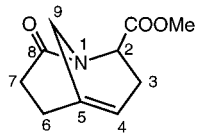
clooctene derivative[38] shows a similar geometry ($\xi = 43.7$, $\tau = 17.7$, $\chi_{av} = 26.1$, $\eta = -8.4$).



18



19



20

Due to the longer Si−C and Si−Si bond lengths, the tris(dimethylsila)-*trans*-cycloheptene derivative **19** is less strained than **18**, as indicated by the values of ξ (32.8°) and η (+6.4°).[39]Apparently, the system responds more by twisting, maybe due to nonbonding interactions of the larger dimethylsilyl and phenyl substituents. This will be illustrated by the following example. In the *trans*-cycloalkene series, the compounds which have two "free" substituents and thus less geometrical restrictions, the angle η depends on steric repulsion between the ring atoms and the substituents. When there are large methyl groups on the ring atoms (i.e., in **19**), the repulsion pushes off the free substituents and pyramidalization becomes more difficult (see Figure 3b). On the other hand, larger substituents at the olefinic carbons increase steric repulsion, too, and force the olefin to respond more by twisting. This is for instance illustrated by the *calculated* values of *trans*,*trans*-1,5-cyclooctadiene ($\xi = 44.2°$ and $\eta = -2.2°$) and its tetramethyl derivative ($\xi = 47.7°$ and $\eta = +22.2°$!!).[29] In this case the carbon bridges are identical; the increasing size of the substituent has a relatively small effect on ξ, but a dramatic one on χ and thus on η.

The first strained anti-Bredt compound of which a crystal structure determination became available was **20**, prepared by Shea in 1990.[11] This aza-derivative of bicyclo-[3.3.1]non-1-ene is highly strained and reactive. Its double bond system is highly pyramidalized: $\xi = 39.3°$ and $\eta = -17.7°$ (Table 5). The angle ξ is smaller than in *trans*-cyclooctene, because the steric repulsion in **20** is reduced by the one-carbon bridge, which connects an olefinic carbon atom with one of the six bridge atoms (in casu nitrogen). This lowers the steric repulsion between bridge and "free" substituent, and the system can be more pyramidalized, which is reflected by the large negative value of η. It thus appears that the size of the ring largely determines the value of ξ, while the substituents have a minor influence only. On the other hand, the substituents determine the value of η, and thus the relative degree of pyramidalization versus twisting.

Returning to our anti-Bredt olefins, the first remarkable feature which can be deduced from Tables 3 and 5 is that the bicyclo[5.3.1]undec-1(11)-ene anti-Bredt compounds have a large twist angle τ; those of **1a** (29°) and **9a** (28.8°) belong to the largest ones experimentally observed so far for distorted C═C double bonds.

The bicyclo[5.3.1]undec-1(11)-ene skeleton of **1a** possesses a *trans*-cyclooctene moiety, and indeed, its angle ξ (46.4°) is close to that of the *trans*-cyclooctene **18** (42.3°). In **1a**, ξ is somewhat larger, due to a large value of η (cf. *trans*,*trans*-cyclooctadiene, vide supra). However, in **20**, which is an anti-Bredt compound, too, ξ is 39.3°, and thus considerably smaller than in **1a**. This can be explained by the position of the double bond. In **20**, there is a direct connection of one olefinic carbon atom to the nitrogen in the bridge, in **1a** this is not the case. On the contrary, the three-atom bridge (C8−C9−C10), connecting C7 with C1, prevents C7 to respond more "freely" to the induced geometric strain of the *trans*-cyclooctene ring and pulls the system into *one* rigid geometry.

A second interesting aspect is that contrary to the situation in **18** and **20**, the system of **1a** responds by twisting more than by pyramidalization: η is strongly positive (**1a**: 12.2°; cf. **18**: −6°; **20**: −17.7°!). From eq 5, it is expected that increasing the pyramidalization of one carbon atom decreases the amount of twisting; why is this not the case in **1a**? The two substituents at the double bond of the *trans*-cyclooctene entity of **1a** (C2 and C7, Figure 6) cannot move freely. C10 is also incorporated into the carbon skeleton and cannot respond freely either, because its displacement causes changes in the geometry of the cyclohexene ring, which goes along with increasing angle strain and steric repulsion, especially between H(5)endo and both H(8)endo (2.183(8) Å) or H(10)endo (2.406(6) Å), respectively. So there are three substituents at the double bond (C2, C7, and C10), which are restricted in their movement. Only the bromine is a "free" substituent; in this case, increasing χ_1 would decrease ϕ_1 and thus decrease η. Nevertheless, this does not happen because it is prevented by the ensuing severe steric repulsion between bromine and parts of the methylene bridge, especially H4exo (2.758 (7) Å); this distance is much smaller than the sum of the van der Waals radii[40] (3.05 Å, $\Delta d = 0.29$ Å). To check this hypothesis, a smaller substituent at position 11 would be desirable, as it would reduce the van der Waals repulsions; as a consequence, this substituent could move closer toward the pentamethylene bridge, and the olefin should respond by adopting a more pyramidalized structure. For this purpose, we compared **1a** and **9a**, the only difference between them being the bromine (**1a**) or chlorine (**9a**) at position 11. However, it turns out that both compounds have almost the same distortion in the olefinic part of the molecule. While η is slightly smaller in the case of **9a** (Table 4), this effect is within the range of experimental error.

Our initial disappointment about this result was removed on a closer look at the data which revealed that the distance between the chlorine substituent and H4exo was smaller (2.673(2) Å), and the geometry of the molecule is almost the same; for example, the distance between C11 and H4exo is almost identical (2.748(8) Å in **1a**, 2.738(3) Å in **9a**). Obviously, the effect of the smaller sphere of chlorine is canceled by the smaller carbon−chlorine bond distance. This is illustrated in Figure S2, Supporting Information.. From the interatomic distances obtained by X-ray crystallography structures (Tables 1 and Table 5 (see Supporting Information)), an angle α can be calculated; $\alpha = 90° -$ angle [H4exo−C11−X]. As the van der Waals contacts in **1a** and **9a** are nearly identical, the difference $\Delta\alpha$ is only 1°. By invoking the same geometry for the fluorine analogue **12a** (of which a crystal structure is *not* available), and keeping the degree of the van der Waals repulsions

(38) Boeckh, D.; Huisgen, R.; Nöth, H. *J. Am. Chem. Soc.* **1987**, *109*, 1248.

(39) Shimizu, T.; Shimizu, K.; Ando, W. *J. Am. Chem. Soc.* **1991**, *113*, 354.

(40) van der Waals radii from: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441: H = 1.20 Å, F = 1.47 Å, Cl = 1.75 Å, Br = 1.85 Å.

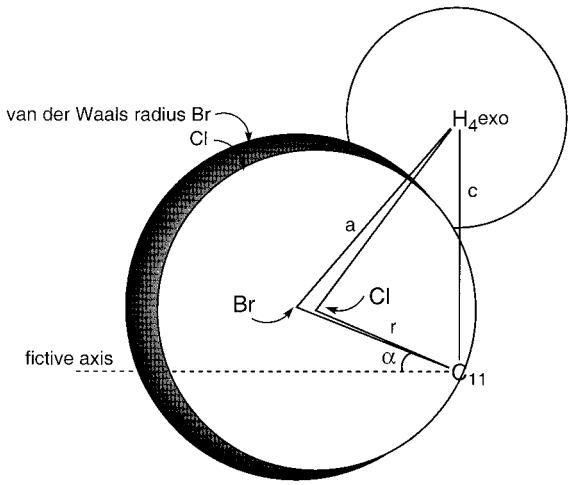


Figure 7. Geometric representation of interatomic distances and van der Waals radii of halogen, C_{11} and H_4exo; $a = d$(Hal−H_4exo) [Å]; $c = d$(C_{11}−H_4exo) [Å]; r = bond distance d(Hal−C_{11}) [Å]; α = fictive angle analogous to χ_1 in Figure 6 [sin α = $(r^2 + c^2 - a^2)$: 2rc]: Hal = Br, $a = 2.76$, $c = 2.75$, $r = 1.92$, α = 20.1°; Hal = Cl, $a = 2.67$, $c = 2.74$, $r = 1.78$, α = 21.3°; Hal = F, $a = 2.42$, $c = 2.73$, $r = 1.36$, α = 28.0°.

constant at (F- - - -H (2.42 Å) in **17b**), one calculates Δα of about 8° relative to **1a**. Apparently, the much smaller fluorine can move closer to H4exo, which allows more pyramidalization at C11. It would be desirable to check this reasoning by a comparison of the crystal structures both for a 15 bromine and a fluorine derivative. Unfortunately, we were not able to obtain crystals of **12a** or a derivative suitable for X-ray analysis, but in the sila anti-Bredt series, this comparison was possible for **15** (bromine derivative) and **17b** (fluorine derivative).

Of course, due to the incorporation of silicon in the bridge, the bridge is longer and the system is less strained (ξ is 36.5° in **15** and 35.5° in **17b**). In **15**, like in **1a** and **9a**, most of the strain in the olefin is released by twisting ($\eta = 10.7$). There is a strong steric repulsion between the halogen and the bridge; in **15**, it is a proton of the one of the methyl groups which causes the most serious interaction (Br···H12a: 2.804(5) Å). As a result, the distortion around the double bond is similar to that in the all-carbon analogues. In this case, the effect of fluorine 11 could be derived from the X-ray crystal structure of **17b**. For comparison, the 7-ethoxy analogue **17a** would have been more desirable, but as it was not crystalline, the 7-chloro derivative **17b** (a slightly unstable compound) was used for the X-ray analysis; we feel that the substituent at position 7 does not influence the geometry significantly. Although expectedly, the system has almost the same ξ value (ξ has a small dependence only on substituents, vide supra), it was gratifying to note that the η value in the 11-fluoro derivative **17b** is significantly lower (**15**: $\eta = 10.7°$, **17b**: $\eta = 4.3°$; Table 4). Also in line with expectation, the free fluorine substituent is pushed toward the methyl group at silicon in the bridge, again far within their van der Waals radii (2.42 Å in **17b**, calculated[40] 2.65 Å, $\Delta d = 0.23$ Å). In line with this structure, the NMR spectrum shows a large fluorine-coupling of this methyl group (J(HF) = 4 Hz and J(CF) = 11.6 Hz); the other methyl group appears as a singlet. This remarkable feature can only be explained by invoking a through-space coupling with fluorine, indicating the close distance between fluorine and one of the methyl groups; through bond coupling (which would imply ^7J(HF) and ^6J(CF)!) can be excluded. While through-space couplings of fluorine are known,[41] that of **17b** is to our knowledge one of the largest through space J(HF) reported.

It may thus be concluded from the X-ray crystal structures that in anti-Bredt compounds of the type discussed here, the olefin geometry responds to strain preferentially by pyramidalization. Because the geometry of the rigid skeleton of **15** and **17b** is roughly the same, the main difference is observed in the angles of the free substituent, i.e., the ratio ϕ_1:χ_1 and η (**15**: ϕ_1:$\chi_1 = 1.23$, $\eta = 10.7$; **17b**: ϕ_1:$\chi_1 = 0.71$, $\eta = 4.3$).

Some questions remain unanswered. For example, why are our compounds relatively stable compared to other anti-Bredt compounds?! Admittedly, according to the olefinic strain (OS) as defined by Schleyer, they belong to the group of "isolable" olefins, the borderline being 17 kcal/mol.[42] Thus, by PM3[43] calculations, we found an OS value of 12.2 kcal/mol for the parent hydrocarbon bicyclo-[5.3.1]undec-(11)ene and for its 11-bromo derivative (cf. **1a** without the 7-ethoxy and 9-chloro substituents) a value of 14.6 kcal/mol.[12b] On the other hand, **20** is much more reactive[11] than our compounds. However, as Schleyer pointed out, OS is not the only factor which determines the reactivity and viability of olefins under ordinary conditions. Therefore, although the group of bicyclo[5.3.1]-undec-l(11)enes such as **1a** and the other anti-Bredt olefins discussed here are relatively strained (as reflected by ξ and by OS), they may owe their stability to other factors which affect their tendency to react with themselves or with oxygen.

First, there is a steric factor, also known as kinetic stabilization. Large substituents prevent reactive molecules to approach the olefin. This steric effect is related to the angle η (Figure 3); if η is positive, approach is difficult, if η is negative, approach is rather easy. And as described earlier, larger substituents at the C=C bond tend to increase η. The second factor is the situation around the π-bond. If pyramidalized, the π-cloud becomes more extended toward one side, which makes it more susceptible for attack. This can also be expressed by η (eq 5). Both steric and pyramidalization factors enhance each other (same dependency on η). Thus the newly defined angles ξ and η may serve to predict the reactivity of a strained olefin. We tentatively assume that the reactivity of a distorted olefin depends more strongly on ξ than on η, as expressed in the (somewhat arbitrary) reactivity index RI = $\xi - 0.5\eta$. Though other obvious effects due to charge distribution (polar effects) or radical character of the olefin are neglected, one does indeed obtain a satisfactory qualitative correlation between RI and the reactivity. For instance, our olefins ($\xi = 45$, $\eta = 12$, RI = 39) are more stable than **20** ($\xi = 39.3$, $\eta = -17.7$, RI = 48.2). Also, using calculated values of *trans-trans*-1,5-cyclooctadiene and its tetramethyl analogue, the parent compound is expected to be more reactive (ξ =

(41) (a) Hilton, J.; Sutcliffe, L. H. In *Progress in NMR spectroscopy*; Emsley, J. W., Feeny, J., Sutcliffe, L. H., Eds.; Pergamon Press: Oxford, 1975; Vol. 10, pp 27−39. (b) Kowalski, J. In *Progress in NMR spectroscopy*; Emsley, J. W., Feeny, J., Sutcliffe, L. H., Eds.; Pergamon Press: Oxford, 1975; Vol. 11, pp 1−78. (d) Ernst, L.; Ibrom, K.; Mitchell, R. H.; Bodwell, G. J.; Bushnell, G. W. *Chem. Ber.* **1994**, *127*, 1119.

(42) (a) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891. (b) McEwen, A. B.; Von Ragué Schleyer, P. *J. Am. Chem. Soc.* **1986**, *108*, 3951.

(43) Stewart, J. J. *P. J. Comput. Chem.* **1989**, *10*, 209.

44.2, $\eta = -2.2$, RI = 45.3) than the (more strained!) tetramethyl analogue ($\xi = 47.7$, $\eta = 22.2$, RI = 36.6).

Another unanswered question is why in our anti-Bredt compounds the olefin bond length is so short (Table 1). This is not well understood. One would expect that twisted olefins have a weaker π-bond due to reduced π-orbital overlap, which should result in an increased bond length. Furthermore, a correlation between strain and deformation on one hand and C1=C11 bond length on the other cannot be discerned.

Conclusions

The experimental results from X-ray crystal structure analysis of four related anti-Bredt compounds (**1a**, **9a**, **15**, **17b**) enabled us to study the competition between pyramidalization and twisting in this class of distorted olefins. The twisting in these compounds is among the highest which has been experimentally observed so far. In line with theoretical considerations,[29,30] it turns out that these olefins preferentially respond to out of plane deformation by pyramidalization; this leads to increased reactivity which may be modified by the substitution pattern around the double bond. Two angles have been used to describe the mode of deformation of a distorted olefin: ξ representing the sum of twisting and pyramidalization, and η being a measure of the difference between those two. It has been found that ξ indicates the overall geometric distortion, and η describes by which of the two distortion modes the olefin responds to strain; η is largely determined by substituent effects.

Experimental Section

General. Proton magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker AC-200 or MSL-400 spectrometer as indicated. The observed couplings are given; sometimes spectrum simulations (PANIC)[44] were used to calculate the real couplings. Carbon magnetic resonance spectra (^{13}C NMR) were recorded on a Bruker AC-200 spectrometer operating at a frequency of 50.29 MHz. All NMR samples were measured in $CDCl_3$, and chemical shifts are reported relative to $CHCl_3$ ($\delta = 7.27$ ppm) or $^{13}CDCl_3$ ($\delta = 77.0$ ppm). The assignment of signals is based on several 2D-NMR techniques (CH-correlation, HH-COSY and sometimes NOE experiments). Silicon magnetic resonance spectra (^{29}Si NMR) were recorded on a Bruker MSL-400 spectrometer operating at 79.48 MHz. Chemical shifts are reported as δ (ppm) relative to TMS. Fluorine magnetic resonance spectra (^{19}F NMR) were recorded in $CDCl_3$ on a Bruker MSL-400 spectrometer operating at 376.43 MHz; chemical shifts are reported as δ (ppm) relative to hexafluorobenzene. Preparative gas chromatography was performed on an Intersmat P120 apparatus with a 1.5 m 15% SE-30 on Chromsorb W 60/80 mesh column and H_2 as carrier gas. GCMS spectra were recorded on a HP-5971-MSD; where applicable, the expected isotope patterns were observed. High-resolution mass spectra (HRMS) were measured on a Finnigan MAT 90 spectrometer operating at an ionization potential of 70 eV.

11-Bromo-*endo*-9-chloro-7-ethoxybicyclo[5.3.1]undec-1(11)-ene (1a).[12] Attempted crystallization of **2** from boiling ethanol gave **1a** in quantitative yield as colorless crystals: mp 130 °C; ^{1}H NMR (400 MHz): δ 4.11 (dddd, ^3J = 13.1 Hz, ^3J = 10.3 Hz, ^3J = 5.0, ^3J = 4.9, 1H, H(9)), 3.43 (AB system: δ(A) 3.49 (dq, ^2J = −8.1 Hz, ^3J = 6.9 Hz, 1H), δ(B) 3.37 (dq, ^2J = −8.1 Hz, ^3J = 6.9 Hz, 1H), OCH_2), 3.18 (ddd, ^2J = −12.2 Hz, ^3J = 12.0 Hz, ^3J = 5.7 Hz, 1H, H(2)$_{exo}$), 2.72 (AB system: δ(A) 2.76 (dd, ^2J = −17.3 Hz, ^3J = 10.3 Hz, 1H, H(10)$_{endo}$), δ(B) 2.68 (ddd, ^2J = −17.3 Hz, ^3J = 4.9 Hz, ^4J = 2.8 Hz, 1H, H(10)$_{exo}$)), 2.39 (AB system: δ(A) 2.60 (ddd, ^2J = −14.4 Hz, ^3J = 5.0 Hz, ^4J = 2.8 Hz, 1H, H(8)$_{exo}$), δ(B) 2.18 (dd, ^2J = −14.4 Hz, ^3J = 13.1 Hz, 1H, H(8)$_{endo}$)), 2.04 (AB system: δ(A) 2.28 (dd, ^2J = −13.1 Hz, ^3J = 12.5 Hz, 1H, H(6)$_{exo}$), δ(B) 1.8, H(6)$_{endo}$), 2.14−2.07 (m, 2H, H(2)$_{endo}$/H(3)), 1.91−1.70 (m, 5H, H(3)/H(4)/H(4)/H(5)$_{exo}$/H(6)$_{endo}$), 1.28 (t, ^3J = 6.9 Hz, 3H, Me), 1.03 (ddd, ^2J = −14 Hz, ^3J = 12.1 Hz, ^3J = 7.3 Hz, 1H, H(5)$_{endo}$); ^{13}C NMR (100.6 MHz): δ 15.5 (q, J(CH) = 126 Hz, C(13)), 25.6 (t, J(CH) = 124 Hz, C(5)), 25.9 (t, J(CH) = 124 Hz, C(4)), 36.6 (t, J(CH) = 127 Hz, C(3)), 38.1 (t, J(CH) = 134 Hz, C(2)), 43.3 (t, J(CH) = 135 Hz, C(10)), 43.8 (t, J(CH) = 132 Hz, C(8)), 48.6 (t, J(CH) = 129 Hz, C(6)), 53.4 (d, J(CH) = 141 Hz, C(9)), 59.4 (t, J(CH) = 140 Hz, C(12)), 83.2 (s, C(7)), 128.9 (s, C(11)), 143.7 (s, C(1)); MS *m*/*z* (rel intens): 308 (51, M^+), 273 (46, M − Cl), 265 (54), 237 (100, M − $EtOC_2H_2$), 227 (42, M − Br), 199 (41), 91 (39); HRMS ($C_{13}H_{20}O^{81}Br^{35}Cl$) calcd 308.0364, 19 found 308.031.

11-Bromo-*endo*-9-chloro-7-hydroxybicyclo[5.3.1]undec-1(11)-ene (1b). When crude **2** was subjected to column chromatography (silica), it reacted on the column to give **1b**, which was isolated by elution with diethyl ether (Yield = 70%). It was also obtained when **2** was exposed to water. White waxy solid: ^{1}H NMR (200 MHz): δ 4.17 (dddd, ^3J = 12.5 Hz, ^3J = 10.2 Hz, ^3J = 5.1 Hz, ^3J = 5.0 Hz, 1H, H(9)), 3.04 (m, 1H), 2.85−2.61 (m, 3H), 2.5 (bs, 1H, OH), 2.25−2.10 (m, 4H), 1.9−1.6 (m, 5H), 1.10 (m, 1H); GCMS *m*/*z* (rel intens): 280 (15, $M^{+\bullet}$), 245 (16), 237 (100), 224 (28), 199 (16); HRMS ($C_{11}H_{16}O^{79}Br^{35}Cl$) calcd 278.0073, found 278.008.

11,11-Dibromo-*endo*-9-chlorotricyclo[5.3.1.0]undecane (2).[12] To a solution of **7**[23] (2 mmol, 0.34 g) and $CHBr_3$ (10 mmol, 2.51 g) in dry benzene (20 mL) was added *t*-BuOK (10 mmol, 1.12 g) in small portions at 0 °C under N_2 during 2 h. After stirring at RT for 1 h, the mixture was poured into cold water (5 °C). The workup was performed rapidly and in the cold in order to prevent **2** from reacting with water to give **1b**. The water layer was extracted three times with cold pentane. The combined organic layers were washed twice with water, once with brine, dried over $MgSO_4$, filtered, and concentrated at reduced pressure. The remaining bromoform was evaporated in vacuo at 40 °C. The residue was a brown oil (ca. 0.6 g) which was purified by rapid column chromatography (silica/pentane), yielding 0.11 g of **2** (16%), yellowish crystals, which rapidly colored on standing at room temperature. **2.** ^{1}H NMR (200 MHz): δ 4.28 (tt, ^3J = 8.0 Hz, ^3J = 4.0 Hz, 1H, H(9)), 2.67 (AB system: δ(A) = 2.82 (dd, ^2J = −16.3 Hz, ^3J = 8.0 Hz, 2H, H(8,10)$_{exo}$), δ(B) = 2.52 (dd, ^2J = −16.3 Hz, ^3J = 4.0 Hz, 2H, H(8,10)$_{endo}$)), 2.15−1.55 (m, 9H), 1.22 (m, 1H); ^{13}C NMR (50.3 MHz): 27.0, 32.2, 33.4, 45.0 (C (1.,7), 49.4 (C(8,10), 58.9 (C(9)), signal C(11) missing due to low intensity. MS *m*/*z* (rel intens): 342 (11, $M^{+\bullet}$), 307 (14, M − Cl), 286 (53), 263 (100, M − Br), 145 (53); HRMS ($C_{11}H_{15}{}^{35}Cl^{79}Br_2$) calcd 339.9229, found 339.923. For the material balance, see **1b**.

11-Bromo-9,11-dichlorotricyclo[5.3.1.0]undecane (4). To a solution of **7**[23] (5 mmol, 0.85 g) and $CHClBr_2$ (25 mmol, 5.20 g) in dry pentane (50 mL) was added *t*-BuOK (25 mmol, 2.80 g) in small portions at 0 °C under N_2 during 2 h. After stirring at RT for 16 h, the mixture was poured into ice−water. The water layer was extracted three times with pentane. The combined organic layers were washed two times with water, once with brine, dried over $MgSO_4$, filtered, and concentrated at reduced pressure. The remaining $CHClBr_2$ was evaporated in vacuo at 40 °C. The residue was purified by column chromatography (silica/pentane), yielding 0.9 g (about 60%) of a colorless oil, which crystallized on standing. Further purification was achieved by crystallizations from ethanol at −20 °C. The crystals consisted of an almost 1:1 mixture of **4a** and **4b**. The former compound is unstable at RT (see synthesis of **9c**).

***syn*-11-Bromo-*endo*-9-*anti*-11-dichlorotricyclo[5.3.1.0]-undecane (4a).** ^{1}H NMR (200 MHz): δ 4.32 (tt, ^3J = 8.1 Hz, ^3J = 4.1 Hz, 1H, H(9)), 2.68 (AB system: δ(A) = 2.81 (dd, ^2J = −16.5 Hz, ^3J = 8.1 Hz, 2H, H(8,10)$_{exo}$), δ(B) = 2.54 (dd, ^2J = −16.5 Hz, ^3J = 4.1 Hz, 2H, H(8,10)$_{endo}$)), 2.20−1.60 (m, 9H), 1.23 (m, 1H); ^{13}C NMR (50.3 MHz): 26.9 (t), 30.6 (t), 32.4 (t),

(44) Program PANIC, Bruker program Library, a version of the LAOCOON type programs: Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863.

45.5 (s, C(1,7)), 49.5 (t, C(8,10)), 58.8 (d, C(9)), 70.8 (s, C(11)); MS *m*/*z* (rel intens): 296 (5, $M^{+\bullet}$), 261 (16, M − Cl), 240 (96), 217 (100, M − Br), 145 (51); HRMS ($C_{11}H_{15}{}^{35}Cl_2{}^{79}Br$) calcd 295.9734, found 295.973.

***anti*-11-Bromo-*endo*-9-*syn*-11-dichlorotricyclo[5.3.1.0]undecane (4b).** ^{1}H NMR (200 MHz): δ 4.25 (tt, ^3J = 8.1 Hz, ^3J = 4.1 Hz, 1H, H(9)), 2.66 (AB system: δ(A) = 2.86 (dd, ^2J = −16.0 Hz, ^3J = 8.1 Hz, 2H, H(8,10)$_{exo}$), δ(B) = 2.46 (dd, ^2J = −16.0 Hz, ^3J = 4.1 Hz, 2H, H(8,10)$_{endo}$)), 2.15−1.60 (m, 9H), 1.22 (m, 1H). ^{13}C NMR (50.3 MHz): 26.9 (t), 32.4 (t), 33.5 (t), 44.3 (s, C(1,7)), 47.1 (t, C(8,10)), 58.6 (d, C(9)), 69.1 (s, C(11)); MS *m*/*z* (rel intens): 296 (5, $M^{+\bullet}$), 261 (16, M − Cl), 240 (96), 217 (100, M − Br), 145 (51); HRMS ($C_{11}H_{15}{}^{35}Cl_2{}^{79}Br$) calcd 295.9734, found 295.973.

General Procedure for Chlorofluorocarbene Addition.[26] To dry THF (25 mL) cooled to −20 °C under N_2, $TiCl_4$ (14.6 mmol, 2.77 g) was added at such rate that the temperature did not exceed 5 °C. To this bright yellow-colored suspension, $LiAlH_4$ (14.6 mmol, 0.55 g) was added in small portions by means of a solid reactant addition tube at such rate that the temperature did not exceed 10 °C. The mixture turned from green via brownish to bright black. The mixture was stirred for 0.5 h at RT. Then the black suspension was added slowly under nitrogen to a cooled mixture of $CFCl_3$ (14.6 mmol, 2.00 g) and **7** (3.9 mmol, 0.66 g) in dry THF (25 mL) under stirring at such a rate that the temperature did not exceed 0 °C. After stirring for 0.5 h at 0 °C, the mixture was allowed to warm to RT and stirred for 3 h. Then it was poured into 100 mL of ice−water containing 10 mL of concentrated HCl and extracted three times with CH_2Cl_2. The combined, black organic layers were washed with a 7.5% $NaHCO_3$ solution (20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure.

11-Bromo-9-chloro-11-fluorotricyclo[5.3.1.0]undecane (5). Bromofluorocarbene was prepared in analogy to the method of Dolbier described above.[26] To dry THF (30 mL), cooled to −20 °C, was added $TiCl_4$ (21.2 mmol, 4.03 g) at such rate that the temperature did not exceed 5 °C. To the bright yellow-colored suspension thus obtained was added $LiAlH_4$ (21.3 mmol, 0.81 g) in small portions by means of a solid reactant addition tube at such rate that the temperature did not exceed 10 °C. The mixture turned from green via brownish to bright black. The mixture was stirred for 0.5 h at RT. Then the black suspension was added slowly under nitrogen to a cooled mixture of $CFBr_3$ (21.3 mmol, 5.75 g) and of **7**[23] (5.9 mmol, 1.00 g) in dry THF (30 mL) under stirring with such rate that the temperature did not exceed 0 °C. After stirring for 5 h at 0 °C, the mixture was poured into cold dry ethanol (100 mL, −20 °C) and stirred for 1 h. The mixture was concentrated under reduced pressure to 40 mL. Then 100 mL of ice−water containing 10 mL of concentrated HCl was added. The mixture was extracted three times with CH_2Cl_2. The combined, black organic layers were washed with a 7.5% $NaHCO_3$ solution (20 mL), dried on $MgSO_4$, filtered, and concentrated under reduced pressure. The residue (1.66 g) was of a yellow oil, consisting of a 1:2 mixture of **5b** and **12a**. Purification was achieved by preparative GLC (T_{oven} = 200 °C, $T_{inj} = T_{det}$ = 210 °C); however, the retention times were almost identical, so a good separation was not possible.

***anti*-11-Bromo-*endo*-9-chloro-*syn*-11-fluorotricyclo-[5.3.1.0]undecane (5b).** ^{1}H NMR (400 MHz): δ 4.19 (dtt, J(HF) = 4.6 Hz, ^3J = 7.9 Hz, ^3J = 6.2 Hz, 1H, H(9)), 2.55 (AB system: δ(A) = 2.69 (dd, ^2J = −14.6 Hz, ^3J = 7.9 Hz, 2H, H(8,10)$_{exo}$), δ(B) = 2.41 (dd, ^3J = −14.6 Hz, ^3J = 6.2 Hz, 2H, H(8,10)$_{endo}$)), 2.07 (dd, ^2J = −14.5 Hz, ^3J = 5.8 Hz, 2H), 1.94 (m, 1H, H4), 1.76 (m, 2H), 1.7−1.4 (m, 4H), 1.12 (m, 1H, H4); ^{19}F NMR (376.43 MHz): δ 28.2; MS *m*/*z* (rel intens): 280 (2, $M^{+\bullet}$), 245 (9, M − Cl), 224 (42), 201 (100, M − Br), 159 (22); HRMS ($C_{11}H_{15}F^{35}Cl^{79}Br$) calcd 280.0030, found 280.004.

9,11-Dichloro-11-fluorotricyclo[5.3.1.0]undecane (6). This reaction was performed several times as described for **5**; the yield depended on the quality of the $LiAlH_4$, and sometimes, more equivalents of $LiAlH_4$ were needed in order to obtain Ti[0] of good quality. A 4-fold excess of carbene is preferable. In a typical example, 6.04 g (31.8 mmol) of $TiCl_4$, 1.24 g (32.7 mmol) of $LiAlH_4$, 4.23 g (30.8 mmol) of $CFCl_3$, and 1.50 g (8.8 mmol) of **7**[23] were used. The residue (2.18 g) was dark yellow oil, consisting of four isomers of **6**, mainly **6a** and **6b** in a 1:1 ratio. At room temperature, **6a** was slightly unstable and reacted to give **12d**.

endo-9-*syn*-11-Dichloro-*anti*-11-fluorotricyclo[5.3.1.0]undecane (6a). ^{1}H NMR (200 MHz): δ 4.32 (tt, ^3J = 7.8 Hz, ^3J = 5.4 Hz, 1H, H(9)), 2.54 (AB system: δ(A) = 2.67 (dd, ^2J = −18 Hz, ^3J = 7.8 Hz, 2H, H(8,10)$_{exo}$), δ(B) = 2.41 (dd, ^2J = −18 Hz, ^3J = 5.4 Hz, 2H, H(8,10)$_{endo}$)), 2.0−1.4 (m, 9H), 1.12 (m, 1H, H4); ^{13}C NMR (50.3 MHz): 27, 27, 32.6 (t, J(CH) = 125 Hz), 42.4 (d, J(CF) = 9.7 Hz, C(1,7)), 45.4 (dt, J(CF) = 1.1 Hz, J(CH) = 133 Hz, C(8,10)), 57.7 (dd, J(CF) = 3.1 Hz, J(CH)-= 157 Hz, C(9)), 104 (d, ^1J(CF) = 300 Hz, C(11)); ^{19}F NMR (376.43 MHz): δ 21.3; MS *m*/*z* (rel intens): 236 (21, $M^{+\bullet}$), 201 (59, M − Cl), 180 (100), 145 (22), 109 (33); HRMS ($C_{11}H_{15}FCl_2$) calcd 236.0535, found 236.0535 ± 0.0010.

***endo*-9-*anti*-11-Dichloro-*syn*-11-fluorotricyclo[5.3.1.0]undecane (6b).** ^{1}H NMR (200 MHz): δ 4.22 (dtt, J(HF) = 4.5 Hz, ^3J = 7.8 Hz, ^3J = 6.5 Hz, 1H, H(9)), 2.56 (AB system: δ(A) = 2.69 (dd, ^2J = −14.4 Hz, ^3J = 7.8 Hz, 2H, H(8,10)$_{exo}$), δ(B) = 2.43 (dd, ^3J = −14.4 Hz, ^3J = 6.5 Hz, 2H, H(8,10)$_{endo}$)), 2.0−1.4 (m, 9H), 1.12 (m, 1H, H4); ^{13}C NMR (50.3 MHz): 27-(t), 30.2 (dt, J(CF) = 1.8 Hz, J(CH) = 125 Hz), 32.5 (t, J(CH) = 125 Hz), 41.3 (d, J(CF) = 10.2 Hz, C(1,7)), 44.0 (dt, J(CF) = 3.2 Hz, J(CH) = 133 Hz, C(8,10)), 56.6 (dd, J(CF) = 13.1 Hz, J(CH) = 157 Hz, C(9)), 105 (d, ^1J(CF) = 320 Hz, C(11)); ^{19}F NMR (376.43 MHz): δ 22.7; MS *m*/*z* (rel intens): 236 (23, $M^{+\bullet}$), 201 (66, M − Cl), 180 (100), 145 (21), 109 (43); HRMS ($C_{11}H_{15}FCl_2$) calcd 236.0535, found 236.0529 ± 0.0010.

***endo*-9,11-Dichloro-7-ethoxybicyclo[5.3.1]undec-1(11)-ene (9a).** Pure **4a**,**b** (1:1) was dissolved in dry $CHCl_3$, stirred for 5 days, and poured into absolute ethanol. After stirring for 1 h, the solvents were evaporated. Purification by column chromatography (silica prewashed with ethanol, to remove traces of water, and dried in vacuo) with pentane as eluent yielded two inseparable products (**4a** and **9b**). Slow evaporation of the solvent gave two crystalline **23** compounds: needles (**4b**) and plate-shaped crystals (**9a**). Separation of the mixture was achieved by hand-picking. Recrystallization from ethanol gave pure **9a:** mp 117 °C; ^{1}H NMR (400 MHz): δ 4.11 (dddd, ^3J = 13.2 Hz, ^3J = 10.5 Hz, ^3J = 5.0, ^3J = 4.9, 1H, H(9)), 3.43 (AB system: δ(A) = 3.50 (dq, ^2J = −8.2 Hz, ^3J = 7.0 Hz, 1H), δ(B) = 3.35 (dq, ^2J = −8.2 Hz, ^3J = 7.0 Hz, 1H), OCH_2), 3.18 (ddd, ^2J = −12.1 Hz, ^3J = 12.1 Hz, ^3J = 5.7 Hz, 1H, H(2)$_{exo}$), 2.72 (AB system: δ(A) = 2.76 (dd, ^2J = −17.6 Hz, ^3J = 10.5 Hz, 1H, H(10)$_{endo}$), δ(B) = 2.68 (ddd, ^2J = −17.6 Hz, ^3J = 4.9 Hz, ^4J = 2.8 Hz, 1H, H(10)$_{exo}$)), 2.36 (AB system: δ(A) = 2.57 (ddd, ^2J = -14.6 Hz, ^3J = 5.0 Hz, ^4J = 2.8 Hz, 1H, H(8)$_{exo}$), δ(B) = 2.15 (dd, ^2J = −14.6 Hz, ^3J = 13.2 Hz, 1H, H(8)$_{endo}$)), 2.26 (ddd, ^2J = −13.5 Hz, ^3J = 12.5 Hz, ^3J = 1 Hz, 1H, H(6)$_{exo}$), 2.08 (m, 1H, H(3)), 1.99 (ddd, ^2J = −12.1 Hz, ^3J = 4.6 Hz, ^3J = 2.1 Hz, 1H, H(2)$_{endo}$), 1.86−1.66 (m, 5H), 1.28 (t, ^3J = 7.0 Hz, 3H, Me), 0.91 (m, 1H); ^{13}C NMR (50.3 MHz): 15.5 (q, J(CH) = 127 Hz, C(13)), 25.4 (t, J(CH) = 125 Hz, C(5)), 25.6 (t, J(CH) = 125 Hz, C(4)), 35.3 (t, J(CH) = 129 Hz, C(2)), 36.4 (t, J(CH) = 128 Hz, C(3)), 42.5 (t, J(CH) = 130 Hz, C(10)), 44.2 (t, J(CH) = 132 Hz, C(8)), 47.9 (t, J(CH) = 129 Hz, C(6)), 53.1 (d, J(CH) = 153 Hz, C(9)), 59.5 (t, J(CH) = 140 Hz, C(12)), 82.4 (s, C(7)), 132.9 (s, C(11)), 141.0 (s, C(1)); MS *m*/*z* (rel intens): 262 (35, $M^{+\bullet}$), 227 (51, M − Cl), 219 (47), 199 (35, M − Cl − ethene), 191 (100, M − $EtOC_2H_2$), 178 (18); HRMS ($C_{13}H_{20}OCl_2$) calcd 262.0891, found 262.088.

***endo*-9,11-Dichloro-7-hydroxybicyclo[5.3.1]undec-1(11)-ene (9b).** When **9c** reacted with water, **9b** was formed. This happened also on purification of a mixture of **4b** and **9c** by column chromatography (silica). On elution with pentane, **4b** was obtained pure. The unstable **9c** reacted to give **9b** which was obtained by elution with diethyl ether as a waxy solid: ^{1}H NMR (400 MHz): δ 4.16 (dddd, ^3J = 12.9 Hz, ^3J = 10.2 Hz, ^3J = 5.1, ^3J = 5.1, 1H, H(9)), 3.07 (ddd, ^2J = −12.4 Hz, ^3J = 12.1 Hz, ^3J = 5.7 Hz, 1H, H(2)^{exo}), 2.70 (AB system: δ(A) = 2.74 (dd, ^2J = −17.1 Hz, ^3J = 10.2 Hz, 1H, H(10)$_{endo}$), δ(B) = 2.66 (ddd, ^2J = −17.1 Hz, ^3J = 5.1 Hz, ^4J = 2.8 Hz, 1H, H(10)$_{exo}$)), 2.61 (ddd, ^2J = −13.4 Hz, ^3J = 5.1 Hz, ^4J = 2.8 Hz,

1H, H(8)$_{exo}$), 2.51 (bs, 1H, OH), 2.18 (dd, ^2J = −13.4 Hz, ^3J = 12.9 Hz, 1H, H(8)$_{endo}$), 2.14 (dddd, ^2J = −13.6 Hz, ^3J = unres., 1H, H(6)$_{exo}$), 2.09 (m, 1H, H(3)), 2.02 (ddd, ^2J = −12.4 Hz, ^3J = 4.9 Hz, ^3J = 1.9 Hz, 1H, H(2)$_{endo}$), 1.91 (dd, ^2J = −13.6 Hz, ^3J = *5.5* Hz, 1H, 24 H(6)$_{endo}$), 1.85−1.55 (m, 4H), 1.05 (m, 1H, H(5)$_{endo}$); ^{13}C NMR (50.3 MHz): 25.2, 26.0, 35.1, 36.5, 42.6 (C(10), 45.9 (C(8)), 50.5 (C(6)), 51.9 (C(9)), 76.9 (C(7)), 133.0 (s, C(11)), 138.3 (s, C(1)); MS *m*/*z* (rel intens): 234 (14, $M^{+\bullet}$), 199 (31, M − Cl), 191 (100, M − HOC_2H_2), 178 (26), 107 (17); HRMS ($C_{11}H_{16}OC_{12}$) calcd 234.0578, found 234.057.

7-Bromo-*endo*-9,11-dichlorobicyclo[5.3.1]undec-1(11)-ene (9c). On standing at RT, **4a** slowly converted to **9c** which was only stable under an inert atmosphere. The intermediacy of **9c** could only be detected by NMR spectroscopy while **4a** and **4b** still were present, so most proton signals could not assigned unequivocally; however, the carbon signals (with CH correlation) were very informative: ^{1}H NMR (400.1 MHz): δ 4.3 (m, 1H, H(9)), 3.24 (dm, 1H), 3.16 (dt, 1H), 2.9−2.8 (m, 3H), 2.6 (m, 1H), 2.4 (m, 1H), 2.2−1.6 (m, 6H), 1.2 (m, 1H); ^{13}C NMR (50.3 MHz): 24.8 (t, C(4)), 28.0 (t, C(5)), 36.6 (t, C(2)), 37.1 (t, C(3)), 42.2 (t, C(6)), 50.0 (t, C(8 or 10)), 50.6 (d, C(9)), 53.6 (t, C(10 or 8)), 68.5 (s, C(7)), 133.3 (s, C(11)), 140.3 (s, C(1)).

Bromofluorocarbene Addition to 1,2-Dimethylcyclohexene (10/11). The procedure described above was performed with 1,2-dimethylcyclohexene and $CFBr_3$ instead of $CFCl_3$ (0.98 g of $TiCl_4$, 0.21 g of $LiAiH_4$, 1.40 g of $CFBr_3$, and 0.19 g of dimethylcyclohexene). Yield 0.29 of a brown oil, containing **10b** and two isomers of **11**. Separation was achieved by preparative GLC (T_{oven} = 140 °C, T_{inj} = T_{det} = 180 °C); the two isomers of **11** could not be separated.

***anti*-7-Bromo-*syn*-7-fluoro-1,6-dimethylbicyclo-[4.1.0]heptane (10b).**[27] ^{1}H NMR: δ 1.80 (m, 2H), 1.47 (m, 2H), 1.28 (m, 4H), 1.15 (d, 6H, Me); ^{19}F NMR: δ 27.0; HRMS ($C_9H_{14}F^{81}Br$) calcd 222.0243, found 222.024.

2-Fluoro-l-methyl-3-methylenecycloheptene (11a) and 2-fluoro-1,3-dimethyl- cycloheptadi-1,3-ene (11b).[27] **11b.** ^{1}H NMR: δ 5.72 (m, 1H), 2.0 (m, 4H), 1.8 (m, 8H), 1.15 (d, 6H, Me); ^{19}F NMR: δ 50.7; HRMS ($C_9H_{13}F$) calcd 140.1001, found 140.099.

9-Chloro-7-ethoxy- 11-fluorobicyclo[5.3.1]undec-1(11)-ene (12a). After prolonged heating of a 1:1 mixture of **6a**/**b** in ethanol (6 h), more than 50% of **6a** was converted to **12a**, **6b** remained unreacted. Preparative GLC (T_{oven} = 200 °C, T_{inj} = T_{det} = 210 °C) yielded pure **12a** and **6a/6b** in a 1:2 ratio. However, **12a** turned out to be a liquid; on cooling, some crystals were obtained which melted at about 15 °C. Several attempts to obtain good crystals were **25** unsuccessful. **12a.** ^{1}H NMR (400 MHz): δ 4.16 (m, 1H, H(9)), 3.46 (AB system: δ(A) 3.50 (dq, ^2J = −7.2 Hz, ^3J = 7.0 Hz, 1H), δ(B) 3.42 (dq, ^2J = −7.2 Hz, ^3J = 7.0 Hz, 1H), OCH_2), 2.90 (m, 1H), 2.61 (m, 2H, H(10)), 2.28 (AB system: δ(A) 2.45 (m, 1H), δ(B) 2.11 (m, 1H), H(8)), 2.09 (m, 1H)), 2.0−1.6 (m, 6H), 1.32 (m, 1H), 1.23 (t, ^3J = 7.0 Hz, 3H, Me), 0.98 (m, 1H, H(5)$_{endo}$; ^{13}C NMR (50.3 MHz): δ 15.7 (q, J(CH) = 126 Hz, C(13)), 25.4 (dt, J(CF) = 0.8 Hz), 26.0 (dt, J(CF) = 4.5 Hz), 29.7 (dt, J(CF) = 3.2 Hz), 35.1 (dt, J(CF) = 2.0 Hz), 39.0 (dt, ^3J(CF) = 5.3 Hz, J(CH) = 130 Hz, C(8)), 44.2 (dt, J(CF) = 7.0 Hz, J(CH) = 130 Hz), 46.8 (d, J(CH) = 130 Hz), 52.8 (dd, J(CF) = 1.6 Hz, J(CH) = 152 Hz, C(9)), 60.2 (t, J(CH) = 144 Hz, C(12)), 78.5 (d, ^2J(CF) = 25.0 Hz, C(7)), 123.5 (d, ^2J(CF) = 14.0 Hz, C(1)), 155.3 (d, ^1J(CF) = 266 Hz, C(11)); ^{19}F NMR (376.43 MHz): δ 44.5; MS *m*/*z* (rel intens): 246 (27, $M^{+\bullet}$), 211 (22, M − Cl), 203 (46), 175 (100, M − $EtOC_2H_2$), 162 (25); HRMS ($C^{13}H_{20}OFCl$) calcd 246.1187, found 246.1183.

9-Chloro-11-fluoro-7-hydroxybicyclo[5.3.1]undec-1(11)-ene (12b). When a 1:1 mixture of **6a**,**b** was allowed to react with water, **6a** rearranged to **12b**. Purification by column chromatography (silica) gave **6** (eluent pentane) and **12b** (eluent diethyl ether) as a waxy solid. Recrystallizations from pentane and hexane were unsuccessful; good crystals could not be obtained. **12b.** ^{1}H NMR (400 MHz): δ 4.20 (m, 1H, H(9)), 2.86 (m, 1H), 2.59 (m, 2H, H(10)), 2.28 (AB system: δ(A) 2.46 (dt, 1H), δ(B) 2.09 (t, 1H), H(8)), 1.98 (m, 3H)), 1.9−1.7 (m, 3H), 1.62 (m, 1H), 1.30 (m, 1H), 0.98 (m, 1H); ^{13}C NMR (50.3 MHz): δ 25.9 (J(CF) = 4.6 Hz), 26.1 (J(CF) = 1.0 Hz), 29.5 (J(CF) = 2.7 Hz), 35.4 (J(CF) = 2.3 Hz), 39.2 (J(CF) = 5.4 Hz), 45.7 (J(CF) = 6.2 Hz), 49.1, 51.7 (J(CF) = 1.2 Hz, C(9)), 73.3 (d, ^2J(CF) = 27.3 Hz, C(7)), 120.5 (^2J(CF) = 15 Hz, C(1)), 155.9 (d, ^1J(CF) = 262 Hz, C(11)); ^{19}F NMR (376.43 MHz): δ 42.4; MS *m*/*z* (rel intens): 218 (14, $M^{+\bullet}$), 183 (14, M−C1), 175 (100, M − HOC_2H_2), 162 (35); HRMS ($C_{11}H_{16}OFCl$) calcd 218.0874, found 218.0874.

7-*endo*-9-Dichloro-11-fluorobicyclo[5.3.1]undec-1(11)-ene (12d). This compound was slowly formed from **6a** on standing at RT. **12d**. ^{1}H NMR (200 MHz): δ 4.26 (m, 1H, H(9)), 3.1−0.9 (m, 14H); ^{13}C NMR (50.3 MHz): δ 25.5 (J(CF) = 5.2 Hz), 27.0, 30.1 (J(CF) = 2.4 Hz), 35.6 (J(CF) = 2.0 Hz), 38.8 (J(CF) = 4.7 Hz), 48.1 (J(CF) = 4.7 Hz), 26 50.4 (J(CF) unresol), 50.6 (C(9)), 121 (^2J(CF) = 17 ± 3 Hz, C(1)), 154 (d, ^1J(CF) = 257 ± 10 Hz, C(11)), signal of C1 and C11 very low, signal of C7 missing due to very low intensity; ^{19}F NMR (376.43 MHz): δ 52.1; HRMS ($C_{11}H_{15}FCl_2$) calcd 236.0535, found 236.053.

11-Bromo-*endo*-9-chloro-7-ethoxy-4,4-dimethyl-4-silabicyclo[5.3.1]undec- 1(11)-ene (15). To a mixture of $CHBr_3$ (7.0 mmol, 1.77 g) and **13**[13] (1.26 mmol, 0.27 g) in dry benzene (15 mL) was added *t*-BuOK (7.1 mmol, 0.71 g) within 20 min under nitrogen. After stirring for 2 h at RT, the mixture was poured into dry ethanol (30 mL) and then heated to 50 °C for 30 min. After cooling, the mixture was concentrated at reduced pressure to 20 mL, and water and pentane were added. The aqueous layer was extracted four times with pentane. The combined organic layers were washed with water and brine, dried on $MgSO_4$, filtered, and concentrated at reduced pressure. The orange-brown oil was purified by column chromatography (silica, several times prewashed with ethanol) with pentane as eluent. After evaporation of the solvent, a yellow oil remained (0.85 g). Further purification was achieved by preparative GLC (T_{oven} = 215 °C, T_{inj} = T_{det} = 225 °C). Pure **15** was obtained by crystallization from ethanol. **15**. ^{1}H NMR (400 MHz): δ 4.06 (dddd, ^3J = 13.0 Hz, ^3J = 10.7 Hz, ^3J = 5.2 Hz, ^3J = 5.0 Hz, 1H, H(9)), 3.40 (AB system: δ(A) = 3.48 (dq, ^2J = −8.0 Hz, ^3J = 6.9 Hz, 1H), δ(B) = 3.32 (dq, ^2J = −8.0 Hz, ^3J = 6.9 Hz, 1H), OCH_2), 3.10 (m, 1H, H(2)$_{exo}$), 2.56 (AB system: δ(A) = 2.58 (dd, ^2J = −17.0 Hz, ^3J = 10.4 Hz, 1H, H(l0)$_{endo}$), δ(B) = 2.54 (ddd, ^2J = −17.0 Hz, ^3J = 5.2 Hz, ^4J = 2.8 Hz, 1H, H(l0)$_{exo}$)), 2.40 (AB system: δ(A) = 2.53 (ddd, ^2J = −14.3 Hz, ^3J = 5.0 Hz, ^4J = 2.8 Hz, 1H, H(8)$_{exo}$), δ(B) = 2.28 (dd, ^2J = −14.3 Hz, ^3J = 13.0 Hz, 1H, H(8)$_{endo}$)), 2.12 (m, 1H, H(2)$_{endo}$), 2.01 (AB system: δ(A) = 2.22 (ddd, ^2J = −12.5 Hz, ^3J = 11.4 Hz, ^3J = 4.3 Hz, 1H, H(6)exo), δ(B) = 1.79 (ddd, ^2J = −12.5 Hz, ^3J = 6.2 Hz, ^3J = 3.2 Hz, 1H, H(6)$_{endo}$)), 1.24 (t, ^3J = 6.9 Hz, 3H, Me), 1.2 (m, 2H, H(3)), 0.6 (m, 2H, H(5)), 0.29 (s, 3H, Si(Me)$_{exo}$), −0.17 (s, 3H, Si(Me)$_{endo}$); ^{13}C NMR (50.3 MHz): δ −0.5 (q, Si(Me)$_{exo}$), 1.0 (q, Si(Me)$_{endo}$), 15.3 (t, C(5)), 15.4 (q, C(13)), 23.9 (t, C(3)), 33.3 (t), 40.0 (t), 41.9 (t), 42.4 (t), 53.2 (d, C(9)), 59.5 (d, C(12)), 80.8 (s, C(7)), 125.4 (s, C(11)), 147.1 (s, C(1)); ^{29}Si NMR (79.48 MHz): δ −0.10; MS *m*/*z* (rel intens): 352 (48, M^+), 337 (10), 323 (22), 271 (39), 243 (40), 202 (38), 185 (75), 157 (83), 139 (100), 121 (54), 105 (77); HRMS ($C_{14}H_{24}SiO^{79}Br^{35}Cl$) calcd: 350.0467, found: 350.046.

9,11-Dichloro-11-fluoro-4,4-dimethyl-4-silatricyclo-[5.3.1.0]undecane (16). The carbene addition was performed as described above (1.83 g of $TiCl_4$, 0.37 g of $LiAlH_4$, 1,32 g of $CFCl_3$, and 0.36 g (1.68 mmol) of **13**[13]). Yield 0.37 g of a mixture of **16a**, **16b**, and **17b**. Preparative GLC (T_{oven} = 190 °C, T_{inj} = T_{det} = 240 °C) of the mixture yielded **16b** and **17b** as pure compounds; both crystallized on standing.

***endo*-9-anti-11-Dichloro-*syn*-fluoro-4,4-dimethyl-4-silatricyclo[5.3.10]undecane (16b).** ^{1}H NMR (400 MHz): δ 4.31 (ttd, ^3J = 7.1 Hz, ^3J = 4.4 Hz, J(HF) = 2.8, 1H, H(9)), 2.53 (AB system: δ(A) = 2.63 (dd, ^3J = −15.2 Hz, ^3J = 7.1 Hz, 2H, H(8,10)$_{exo}$), δ(B) = 2.42 (ddd, ^2J = −15.2 Hz, ^3J = 4.4 Hz, ^4J(HF) = 2.5 Hz, 2H, H(8,10)$_{endo}$)), 1.81 (AB system: δ(A) = 2.04 (ddd, ^2J = −14.7 Hz, ^3J = 6.7 Hz, ^3J = 2.5 Hz, 2H, H(2,6)$_{endo}$), δ(B) = 1.58 (ddd, ^2J = −14.3 Hz, ^3J = 14.5 Hz, ^3J = 1.5 Hz, 2H, H(2,6)$_{exo}$)), 0.85 (AB system: δ(A) = 1.00 (ddd, ^2J = −14.8 Hz, ^3J = 14.5 Hz, ^3J = 2.5 Hz, 2H, H(3,5)$_{endo}$), δ(B)

= 0.70 (ddddd, ^2J = −14.8 Hz, ^3J = 6.7 Hz, ^3J = 1.5 Hz, ^4J = 1.7 Hz, J(HF) = 1.4 Hz, 2H, H(3,5)$_{exo}$)), 0.03 (s, 3H, SiMe), 0.01 (s, 3H, SiMe); ^{13}C NMR (50.3 MHz): δ −4.6 (q, J(CH) = 111 Hz, SiMe), −2.2 (q, J(CH) = 111 Hz, SiMe), 13.0 (td, J(CH) = 115 Hz, ^4J(CF) = 2.9 Hz, C(3,5)), 21.8 (td, J(CH) = 128 Hz, ^3J(CF) 1.7 Hz, C(2,6)), 42.5 (d, ^2J(CF) = 9.8 Hz, C(1,7)), 43.2 (td, J(CH) = 133 Hz, ^3J(CF) = 4.9 Hz, C(8,10)), 59.1 (dd, J(CH) = 170 Hz, ^4J(CF) = 8.4 Hz, C(9)), 103.8 (d, ^1J(CF) = 300 Hz, C(11));^{19}F NMR (376.43 MHz): δ 21.6; ^{29}Si NMR (79.48 MHz): δ 2.57; MS *m*/*z* (rel intens): 280 (0.5, M^+), 245 (8, M − C1), 153 (10), 139 (11), 133 (43), 105 (88), 77 (100); HRMS ($C_{12}H_{19}{}^{28}SiF^{35}Cl_2$) calcd 280.0617, found 280.062.

***endo*-9-Chloro-7-ethoxy-11-fluoro-4,4-dimethyl-4-silabicyclo[5.3.1]undec-1(11)-ene (17a).** Crystalline **17b** reacted in hot ethanol slowly to give **17a**; after evaporation of the solvent, a viscous colorless oil remained. ^{1}H NMR (200 MHz): δ 4.15 (m, 1H, H(9)), 3.43 (AB system: δ(A) = 3.48 (dq, ^2J = −8.0 Hz, ^3J = 7.0 Hz, 1H), δ(B) = 3.38 (dq, ^2J = −8.0 Hz, ^3J = 7.0 Hz, 1H), OCH_2), 2.85 (m, 1H, H(2)$_{exo}$), 2.51 (m, 2H, H(10)), 2.27 (AB system: δ(A) = 2.36 (m, 1H), δ(B) = 2.18 (m, 1H, H(8))), 1.98 (AB system: δ(A) = 2.10 (m, 1H), δ(B) = 1.85 (m, 1H), H(6)), 1.73 (m, 1H, H(2)$_{endo}$), 1.20 (t, ^3J = 7.0 Hz, 3H, Me), 1.06 (m, 2H, H(3)), 0.58 (m, 2H, H(5)), 0.11 (d, J(HF) = 3.6 Hz, 3H, Si(Me)$_{exo}$), −0.18 (s, 3H, Si(Me)$_{endo}$); ^{13}C NMR (50.3 MHz): δ −4.2 (dq, J(CF) = 11.6 Hz, Si(Me)$_{exo}$), 0.52 (q, Si(Me)$_{endo}$), 13.0 (t), 15.7 (q, C(13)), 23.4 (dt, ^4J(CF) = 2.5 Hz), 23.8 (dt, ^3J(CF) = 6.0 Hz), 37.4 (dt, ^3J(CF) = 2.3 Hz), 38.6 (dt, ^3J(CF) = 4.9 Hz), 43.6 (dt, ^3J(CF) = 6.6 Hz), 52.8 (d, C(9)), 60.4 (d, C(12)), 77.2 (very low intensity, C(7)), 125.1 (d, ^2J(CF) = 14.1 Hz, C(1)), 151.8 (d, ^1J(CF) = 260.5 Hz, C(11)); ^{19}F NMR (376.43 MHz): δ 38.1; ^{29}Si NMR (79.48 MHz): δ 1.13 (J(SiF) = 0.4 Hz); MS *m*/*z* (rel intens): 290 (10, M^+), 261 (9, M − Et), 233 (5), 199 (10), 157 (26), 77 (100); HRMS ($C_{14}H_{24}{}^{28}SiF^{35}ClO$) calcd 290.1269, found 290.1272 ± 0.0006.

***endo*-7,9-Dichloro-11-fluoro-4,4-dimethyl-4-silabicyclo[5.3.1lundec-1(11)-ene (17b).** The crystals were recrystallized from 2-propanol: ^{1}H NMR (200 MHz): δ 4.15 (m, H(9)), 2.83 (m, 1H), 2.7−2.3 (m, 5H), 2.20 (m, 1H), 1.74 (dddd, ^2J = −13.8 Hz, ^3J = 5.0 Hz, ^3J = 5.0 Hz, ^4J(HF) = 4.5 Hz, 1H), 1.06 (m, 2H), 0.62 (m, 2H), 0.14 (d, J(HF) = 4.6 Hz, 3H, Si(Me)$_{exo}$), −0.19 (s, 3H, Si(Me)$_{endo}$); ^{19}F NMR (376.43 MHz): δ 44.4; ^{29}Si NMR (79.48 MHz): δ 0.44 (J(SiF) = 1.7 Hz); HRMS ($C_{12}H_{19}{}^{28}SiF^{35}Cl_2$) calcd 280.0617, found 280.062.

X-ray Structure Determination of 1a, 9a, 15, and 17b. The crystal structure determination of **1a** has previously been reported as a communication.[12] Full details of the X-ray crystal structure determinations are given in the Supporting Information. Figures of merit for the reported compounds are as follows. For **1a**: R = 0.050, R_w = 0.025, based on 3076 unique reflections collected at 298 K and 150 model parameters; for **9a**: R = 0.040, R_w = 0.048, based on 3009 unique reflections (298 K) and 150 parameters; for **15**: R = 0.053, $wR2$ = 0.160, based on 3429 unique reflections (295 K) and 167 parameters; for **17b**: R = 0.077, $wR2$ = 0.170, based on 3007 unique reflections (150 K) and 147 parameters.

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Supporting Information Available: Details of the structure determinations of **9a**, **15**, and **17b** including ORTEP structures of **1a** and **9a**; relevant nonbonded distances of **1a**, **9a**, **15**, and **17b**. This material is available free of charge via the Internet at http://pubs.acs.org. Further details of the structure determination of **1a** are available as Supporting Information to the preliminary report.[12a]

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