Trapping of 4-Halo-2-chlorobicyclo[2.1.1]hex-1-ene: DFT Calculations on This and Related Molecules[**]

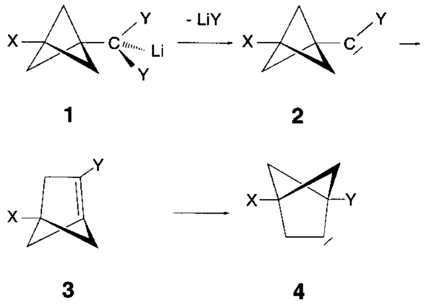
Thomas Ströter, Oliver Jarosch, and Günter Szeimies*

Abstract: The reaction of 1-chloro-3-trichloromethylbicyclo[1.1.1]pentane **5a** with an excess of MeLi leads to 1,3-dichloro-3,4-dimethylbicyclo[2.1.1]hexane (**7a**) as the major product in 33 % yield, as well as to the bicyclo[2.1.1]hexane derivatives **6a** and **8a**. ^{13}C labeling shows that **7a** is formed through two routes, the minor one constituting a trapping reaction of the elusive bicyclo[2.1.1]hex-1-ene (**3**) by MeLi. This bridgehead olefin is also trapped in an ene reaction with α-methylstyrene leading to **18** in 8 % yield. DFT calculations at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) level of theory show that 3-chlorobicyclo[1.1.1]-pent-1-yl-chlorocarbene (**2a**) in its singlet electronic state is local minimum on the corresponding energy hypersurface. It rearranges over a barrier of only 7.9 kcal mol^{-1} to the strongly pyramidalized bridgehead olefin **3a**, which shows a high propensity for a second rearrangement (barrier 8.4 kcal mol^{-1}) to give carbene **4a**. Hydrogen migration of **4a** to afford 1,3-dichlorobicyclo[2.1.1]hex-2-ene (**20a**) needs a somewhat higher barrier of 13.2 kcal mol^{-1} and is not observed under the experimental conditions employed in this work.

Keywords: bridgehead olefins · carbenes · ene reactions · rearrangements

Introduction

The rearrangement cascade carbene →bridgehead olefin →carbene belongs to the fascinating modes of stabilization of reactive intermediates. A prominent reaction sequence has been reported by Eaton et al.,[2] and we have recently added a second example, in which carbenoids of type **1** rearranged, probably after elimination of LiY, via carbenes **2** and bridgehead olefins **3** to give carbenes **4** (see Scheme 1), which were trapped by cycloaddition reactions with olefins, by insertion reaction into the Si–H bond of Et_3SiH, and by addition of organolithium bases and even lithium halides.[3] Furthermore, labeling of the exocyclic C atom in **1** proved that two C–C bonds were broken and two C–C bonds were newly formed in the reaction sequence.[3] Whereas the formation of carbenes **4** in Scheme 1 was experimentally well-established, it is not clear yet, if carbenes **2** are intermediates or if LiY elimination of **1** and ring enlargement to give **3** take place in a concerted process. In addition, efforts of trapping alkenes **3** have not been successful so far in our work.[3]



Scheme 1. Reaction scheme for the formation of **4**.

Herein we report on results that were obtained in extending our investigations on bicyclo[1.1.1]pentanes of type **5** and on a trapping experiment of **3**. Furthermore, some stationary points of the C_6H_6XY potential-energy surface have been calculated by DFT methods, from which information on the structure and energy of **2**, **3**, and **4**, and on the energy barriers separating these molecules could be obtained. In addition, the possibility of the involvement of triplet states of carbenes **2** and **4** and alkenes **3** has been investigated.

Results and Discussion

Reaction of 1-halo-3-trichloromethylbicyclo[1.1.1]pentane with methyllithium: The formation of 1-chloro-3-trichloromethylbicyclo[1.1.1]pentane **5a** by radical chain addition of carbon tetrachloride to [1.1.1]propellane has been reported;[4] the tetrahalide **5a** could be isolated in 50 % yield. The analogous addition of bromotrichloromethane has only been mentioned as an NMR-tube experiment.[4] Working on a

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[**]: See ref. [1].

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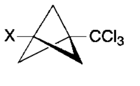
0.1 mole scale, **5b** was obtained in 76% yield; **5a** and **5b** served as the major model compounds for the reaction with MeLi. These reactions were carried out with salt-free MeLi at −78 °C in ether by addition of solutions of **5a/b** to an excess of MeLi (4 equiv).

Aqueous workup afforded a mixture of the products **6**, **7**, and **8**, which could be separated by chromatographic methods.



a: X = Cl
b: X = Br

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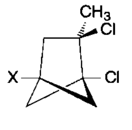

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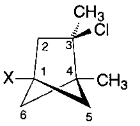

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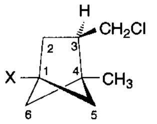

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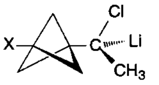
Compound **7** was the major product, but **6** prevailed over **7** when MeLi was added to the solution of **5**. Results are given in Table 1.

Table 1. % Yield of **6**, **7**, and **8** from the reaction of **5** with MeLi.

5	% Yield of **6**	% Yield of **7**	% Yield of **8**
a	7	33	3
b	12	29	4
reversed addition			
a	26	7	2
b	31	5	<1

The structures of **6**, **7**, and **8** followed from their NMR spectra. Whereas the formation of trihalide **6** could be expected from our earlier results,[3] the structures of **7** and **8** were unexpected and need some comment. As it could be excluded that **7** was formed by reaction of **6** with MeLi, the bridgehead methyl group had to be introduced at an earlier stage during the reaction course. There are three ways that this could occur.

1) Nucleophilic exchange of chloride against methyl could take place in carbenoid **1**. Related reactions have been observed with vinylic carbenoids.[5] In detail, carbenoid **1** could either undergo a displacement reaction with exchange of chloride against methyl, or, alternatively, could give carbene **2**, which could add MeLi to afford **9**. After LiCl elimination from **9**, the double rearrangement of carbene **10** would lead via bridgehead alkene **11** to carbene **12**, which could be stabilized by addition of MeLi affording **13**, followed by lithium chlorine exchange with **5a** to give **7**. Alternatively, but less probable, the carbenic carbon in **12** could undergo an insertion reaction into the chloro–carbon bond of chloromethane, present in the reaction mixture, by lithium chlorine exchange of MeLi and **5**, to give **7**.
2) Instead of rearranging, **11** could be trapped by MeLi, which would also lead to **13** and by the same sequence as discussed above would give **7**.
3) Alternatively, MeLi could add to **3** (Y = Cl) affording **14**, which could lose LiCl to **12**, which in turn could be converted into **7** as indicated above.



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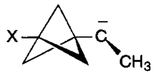

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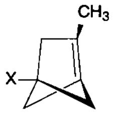

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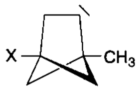

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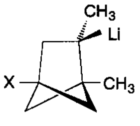

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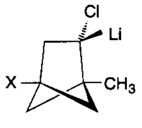

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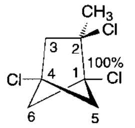
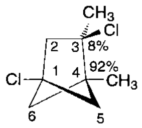
Compound **8** could be generated by a CH insertion reaction of carbene **12** into the methyl group of chloromethane which is generated by lithium chlorine exchange of MeLi with **5**. The processes 2) and 3) are particularly interesting, because they could be regarded as trapping reactions of the elusive bicyclo[2.1.1]hexene system, whose existence has not been fully established so far. Reaction path 1) can be differentiated from 2) and 3) by a labeling experiment: the formation of **7** from path 1) proceeds with two rearrangements, while **7** produced from paths 2) or 3) is formed with only one ring enlargement reaction. Placing a ^{13}C label at the exocyclic carbon of **5a**, path 1) will show the label at C4, path 2) and 3) at C3 of **7a**.

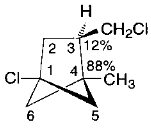
Enriched 1-chloro-3-trichloro[^{13}C]methylbicyclo[1.1.1]pentane (**5a***) was obtained by addition of [^{13}C]Cl$_4$ to [1.1.1]propellane. The enrichment of ^{13}C with respect to natural abundance was 3.295:1.00. When **5a*** was added to an excess of MeLi, the isolated products **6a***, **7a***, and **8a*** showed a label distribution as given in the formulas below. The label distribution was determined by ^{13}NMR spectroscopy using the inverse gated decoupling pulse sequence.[6]



6a*



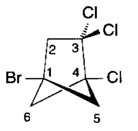
7a*



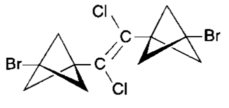
8a*

As already seen in our prior investigation,[3] the full ^{13}C content is retained at C1 of the trichloride **6a***, indicating that two rearrangements have taken place during its formation. In **7a*** and **8a***, most of the label (92% and, respectively, 88%) is retained at C4, which is again in accord with two 1,2-carbon–carbon bond shifts. However, for both compounds there is a second route to product (followed with 8% and, respectively, with 12%), which proceeds with only one rearrangement. This result indicates that formation of **7** proceeds to a minor extent by a trapping reaction of a bicyclo[2.1.1]hex-1-ene derivative with MeLi. The question, if **3a** (X = Y = Cl) or **11** (X = Cl) is involved in the trapping reaction cannot be decided from this experiment; it will be readdressed later (see section on DFT Calculations).

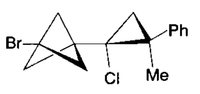
Reaction of 1-halo-3-trichloromethylbicyclo[1.1.1]pentane with methyllithium in the presence of α-methylstyrene: When a solution of halide-free MeLi (1.04 equiv) in ether was added to a solution of **5b** and α-methylstyrene (molar ratio 1:38) in ether at – 78 °C, and the mixture was allowed to warm to room temperature, aqueous workup afforded the products **15**, **16**, **17a**, **17b**, and **18** in yields given in brackets behind the formula numbers (see diagram). Compound **15** was separated by sublimation at 2.0 x 10^{-5} mbar and room temperature, the remaining components were purified by column chromatography with silica gel.



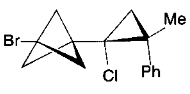
15 *(11%)*



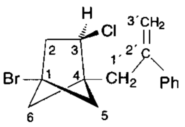
16 *(6%)*



17a *(8%)*



17b *(4%)*



18 *(8%)*

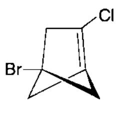
The structures of the products were determined by NMR spectroscopy, with ^{1}H ^{1}H COSY, ^{1}H ^{13}C HETCOR, and for **18** also ^{13}C ^{13}C INADEQUATE techniques. In Table 2, selected ^{1}J ($^{13}C^{13}C$) coupling constants of **18** are given. Looking at the structures of the products, it is evident that **16** and **17a/b** originate from carbenoid **1** (X = Br, Y = Cl). Whereas **17a** and **b** stem from a carbenoid-cycloaddition reaction with α-methylstyrene, the formation of **16** is the outcome of a carbenoid-coupling reaction.[7] Probably for steric reasons, only one of the two diastereomers, presumably the *trans* isomer, was formed.

Table 2. Selected ^{1}J ($^{13}C^{13}C$) [Hz] of **18** obtained from the INADEQUATE spectrum.

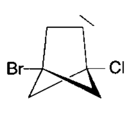
Pair	J [Hz]	Pair	J [Hz]
C1C2	35.8	C3C4[a]	–
C1C5	26.5	C4C5	29.2
C1C6	25.2	C4C6	29.2
C1C1′	39.8	C1′C2′	42.5
C2C3	33.2	C2′C3′	71.7

[a] This value could not be determined with certainty.

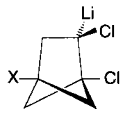
Reaction conditions differ in this experiment from those reported without the presence of α-methylstyrene by a very low MeLi concentration at any time. Therefore, neither bridgehead olefin **3b** nor carbene **4b** is trapped by MeLi. Instead, carbene **4b** adds LiCl to give carbenoid **19**, which in a Li/Cl exchange reaction with **5b** would give rise to the formation of **15**. The addition of lithium halide to a carbene has been reported in the literature.[8] A reasonable alternative for the stabilization of the carbenic center in **4b**, that is, hydrogen migration to afford **20b**, was not observed.



3b



4b



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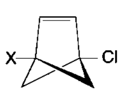

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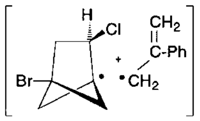
a: X = Cl
b: X = Br

Concerning the outcome of this reaction, alkene **18** is the most significant product of this experiment. The structure of **18** is consistent with an ene reaction of **3b** and α-methylstyrene at the methyl group and C=C double bond. As the double bond in **3b** is strongly twisted, it will have a considerable diradical character. This could lead to three limiting mechanisms:

a) Compound **3b** could abstract a hydrogen from α-methylstyrene, giving rise to the radical pair **21**, which collapses to **18**.
b) Compound **3b** could add to α-methylstyrene, affording diradical **22**, which could be stabilized by hydrogen abstraction.
c) C–C bond formation between **3b** and α-methylstyrene and hydrogen migration could take place in a concerted way as depicted in **23**.



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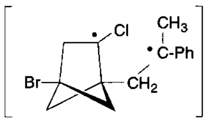

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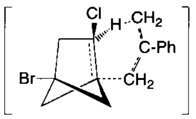
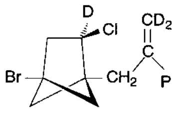


23

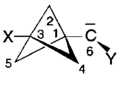
The use of [CD$_3$]-α-methylstyrene as one component for the ene reaction allowed some differentiation between the mechanistic alternatives. In this experiment, [D$_3$]**18** was isolated again in 8% yield. NMR spectroscopy of [D$_3$]**18** revealed that the deuterium distribution was as follows: 1.0 D was found at C-3 of the bicyclo[2.1.1]pentane framework and 2.0 D were at the vinylic carbon of the side chain. This result



[D$_3$]**18**

implies that mechanistic alternative a) assuming the radical pair **21** as an intermediate should be excluded. A decision between **22** and **23** is not possible from this experiment.

DFT calculations on the carbene-bridgehead olefine-carbene rearrangement: Some years ago, ab initio calculations using the GAUSSIAN 90 program package were carried out on **2b**, **3b**, and **4b** at the MP2/6-31G(d)//MP2/6-31G(d) level of theory, which showed that the rearrangements **2b** → **3b** → **4b** are both exothermic.[3] In this paper, we have tried to solve additional problems by computational methods: i) influence of X and Y on the energy of **2**, **3**, and **4** and on the structure of **3**, and ii) for selected models, influence of X and Y on the potential-energy barriers **TS1** and **TS2**, separating **2**, **3**, and **4**. In addition, insight into the energy barrier **TS3** of hydrogen migration leading from **4** to **20** seemed interesting.



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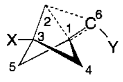
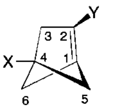


TS1



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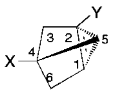

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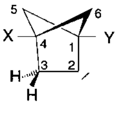

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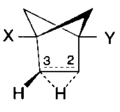

TS3

20

Singlet states: The Gaussian 94 program package[10] was mainly used. Specifically, the density functional theory (DFT)[11] with the Becke3 exchange[12] and the LYP correlation functional,[12] and the 6-31G(d) basis set were applied preferentially in this investigation. For transition states and bridgehead olefins **3** with partial biradical character the spin-unrestricted model seemed appropriate. Identical results were obtained for transition states **TS1**, **TS2**, and **TS3** from the spin-unrestricted and the spin-restricted formalism. For olefins **3**, lower energies were found with the unrestricted formalism. However, the wave functions of the unrestricted formalism are not eigenfunctions of the S^2 operator. For bicyclo[2.1.1]hex-1-enes **3**, $\langle S^2 \rangle$ values as high as 0.94 were calculated, indicating that the electronic states of **3** are mixtures of singlets and higher spin states, preferentially triplets. After spin annihilation, the $\langle S^2 \rangle$ values dropped to 0.05, showing that the projected wave function might be regarded as reasonable for the singlet state of alkenes **3**.[13] For all stationary points, frequency calculations were carried out at the B3LYP/6-31G(d) or UB3LYP/6-31G(d) levels of theory. In all cases, transition structures showed one imaginary frequency. Finally, the energies of the optimized 6-31G(d) structures were recalculated using the B3LYP or UB3LYP formalism and the 6-311G(d,p) basis set. Results are given in Table 3; for alkenes **3**, $\langle S^2 \rangle$ values before and after spin annihilation are also included.

Guided by our experimental results, in which carbenes of type **4** could be trapped in several cases,[3] the carbenes **4** are taken as reference systems. Table 4 gives the relative energies of **2**, **3**, and **20**, and of the barriers **TS1–2**, **TS2–3**, and **TS3–4** with respect to **4**, based on the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) results, including ZPE/6-31G(d) corrections.

Table 4 contains some interesting features. Carbene **2c** is not a local energy minimum and the barrier between carbene **2d** and alkene **3d** is practically nonexistent. The chlorocarbenes **2a** and **2e** are local energy minima separated by a barrier of 7.1–7.9 kcal mol^{-1} from the corresponding bridgehead olefin **3**. Olefins **3** are considerably lower in energy than the corresponding singlet carbenes **2**; the energy differences are $\Delta E = -16.8$ kcal for **3a**/**2a**, $\Delta E = -27.4$ kcal for **3d**/**2d**, $\Delta E = -16.4$ kcal for **3e**/**2e**, $\Delta E = -23.3$ for **3f**/**2f**, and $\Delta E = -23.6$ for **3g**/**2g**. Obviously, a chlorine atom at the carbenic center in **2a** and **e** stabilizes the singlet carbene considerably, but has a smaller effect in stabilizing the bridgehead olefin **3a** and **e**. All bridgehead olefins **3** are less stable than the corresponding carbenes **4**. The barriers **TS2–3** for the rearrangement of **3** → **4** depend slightly on the substituents Y at the bridgehead double bond; the methyl group effects a greater decrease than a chlorine atom. In the rearrangment of **4** → **20**, the substituents Y are not located at the reactive site; consequently the barrier heights of **TS3–4** and the energy differences of **20–4** vary only marginally. The former range from 12.4 to 13.2 kcal mol^{-1}, and the latter from -51.2 to -52.7 kcal mol^{-1}. It is interesting to note that in our low-temperature experiments hydrogen migration from **4** to afford **20** was not observed. Obviously the lifetime of carbenes of type **4** is sufficiently long to favor intermolecular trapping processes.

The rearrangement of homo-1(9)-cubene, which also contains a *trans* cyclopentene substructure, to 9-homocubylidene has been investigated theoretically.[15, 16] Holthausen and Koch have calculated the potential-energy barrier for this process at the CASSCF/DZP level of theory and obtained a value of 23.5 kcal mol^{-1},[16] which is considerably higher than our values of Table 3. In a recent paper Hrovat and Borden revisited this problem and computed a value for this barrier as low as 8 kcal mol^{-1}.[17]

2-Bicyclo[2.1.1]hexylidene (**4c**) has been the subject of a DFT theoretical investigation by Schaefer III et al. who used the BH and HLYP/DZP formalism.[18] In accordance with earlier experimental results[19] they found that the preferred internal stabilization of **4c** is hydrogen migration to afford alkene **20c**. The activation enthalpy for this reaction was calculated to be 16.2 kcal mol^{-1}, which is somewhat higher than our B3LYP/6-311G**//B3LYP/6-31G* barrier of 12.6 kcal mol^{-1}.

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Table 3. Results of B3LYP/6-311G(d,p)//B3LYP/6-31G(d) calculations on **2**, **3**, **4**, and **20** and on **TS1**, **TS2**, and **TS3**.

X	Y		**2** E[a] ZPE[b] E_{total}[c]	**TS1** E[a] ZPE[b] E_{total}[c]	**3** E[a] $\langle S^2\rangle_b/\langle S^2\rangle_a$[d] ZPE[b] E_{total}[c]	**TS2** E[a] ZPE[b] E_{total}[c]	**4** E[a] ZPE[b] E_{total}[c]	**TS3** E[a] ZPE[b] E_{total}[c]	**20** E[a] ZPE[b] E_{total}[c]
Cl	Cl	**a**	– 1152.449079 0.101797 – 1152.461156	– 1152.434781 0.100953 – 1152.448522	– 1152.477261 *0.744/0.029* 0.102564 – 1152.487983	– 1152.458948 0.100900 – 1152.474626	– 1152.477503 0.101509 – 1152.491797	– 1152.452104 0.099162 – 1152.470724	– 1152.562904 0.103899 – 1152.574539
H	H	**c**	– – –	– – –	– 233.269826 *0.932/0.050* 0.120330 – 233.210339	– 233.249042 0.117568 – 233.194766	– 233.279708 0.118634 – 233.223771	– 233.255381 0.116267 – 233.203768	– 233.365006 0.120758 – 233.306708
Cl	H	**d**	-692.827353 0.110122 – 692.806178	– 692.826843 0.110039 – 692.806168	– 692.873618 *0.838/0.041* 0.111080 – 692.849830	– 692.855268 0.110465 – 692.834824	– 692.880311 0.111368 – 692.858177	– 692.855217 0.108969 – 692.837350	– 692.965877 0.113602 – 692.941272
H	Cl	**e**	– 692.846534 0.111278 – 692.822638	– 692.833761 0.110508 – 692.811409	– 692.874185 *0.861/0.037* 0.112107 – 692.848810	– 692.855269 0.110750 – 692.834545	– 692.879255 0.111266 – 692.857348	– 692.855137 0.108850 – 692.837520	– 692.965877 0.113602 – 692.941272
H	Me	**f**	– 272.55262 0.147253 – 272.477410	– 272.541392 0.147477 – 272.467271	– 272.591431 *0.942/0.052* 0.148402 – 272.514465	– 272.576514 0.147697 – 272.503595	– 272.598813 0.148415 – 272.524522	– 272.574494 0.146049 – 272.504308	– 272.683607 0.150752 – 272.606112
Cl	Me	**g**	– 732.155391 0.135082 – 732.117370	– 732.144824 0.135240 – 732.106814	– 732.195702 *0.848/0.043* 0.136142 – 732.154942	– 732.182793 0.135495 – 732.145634	– 732.199631 0.136032 – 732.161537	– 732.174389 0.133709 – 732.140464	– 732.284358 0.138363 – 732.243138

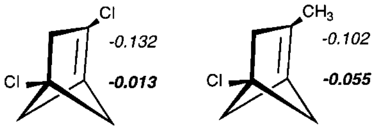
[a] B3LYP/6-31G(d)//B3LYP/6-31G(d) energy in a.u. [b] Zero point energy, obtained from frequency calculations at the B3LYP/6-31G(d) level of theory and scaled by a factor of 0.98040; see ref. [14]. [c] B3LYP/6-311G(d,p)//B3LYP/6-31G(d) energy, ZPE/B3LYP/6-31G(d) corrected. [d] $\langle S^2\rangle$ before/$\langle S^2\rangle$ after spin annihilation.

Table 4. Relative energies (kcal mol^{-1}) of **2**, **3**, **4**, and **20** and the barriers **TS1-2**, **TS2-3**, and **TS3-4**.

X	Y		**2** E_{rel}[a]	**TS1−2** E_{rel}[a]	**3** E_{rel}[a]	**TS2−3** E_{rel}[a]	**4** E_{rel}[a]	**TS3−4** E_{rel}[a]	**20** E_{rel}[a]
Cl	Cl	**a**	19.23	7.93	2.39	8.38	0.00	13.22	– 51.92
H	H	**c**	–	–	8.43	9.77	0.00	12.55	– 52.04
Cl	H	**d**	32.63	0.01	5.24	9.42	0.00	13.07	– 52.14
H	Cl	**e**	21.78	7.05	5.36	8.95	0.00	12.44	– 52.66
H	Me	**f**	29.56	6.36	6.31	6.82	0.00	12.68	– 51.20
Cl	Me	**g**	27.72	6.62	4.14	5.84	0.00	13.22	– 51.21

[a] kcal mol^{-1}.

The results on the calculations of **3a** and **3g** open an answer to a question, which could not be given experimentally: would an excess of MeLi preferentially add to the C=C double bond of **3a** or **3g**? In Figure 1, the total charges of C-1 and C-2 of **3a** and **3g** are depicted. The numbers show that the C=C double bond in **3a** is stronger polarized than the one in **3g**, which might lead to a preferred reaction of **3a** with MeLi in comparison to **3g**.



3a **3g**

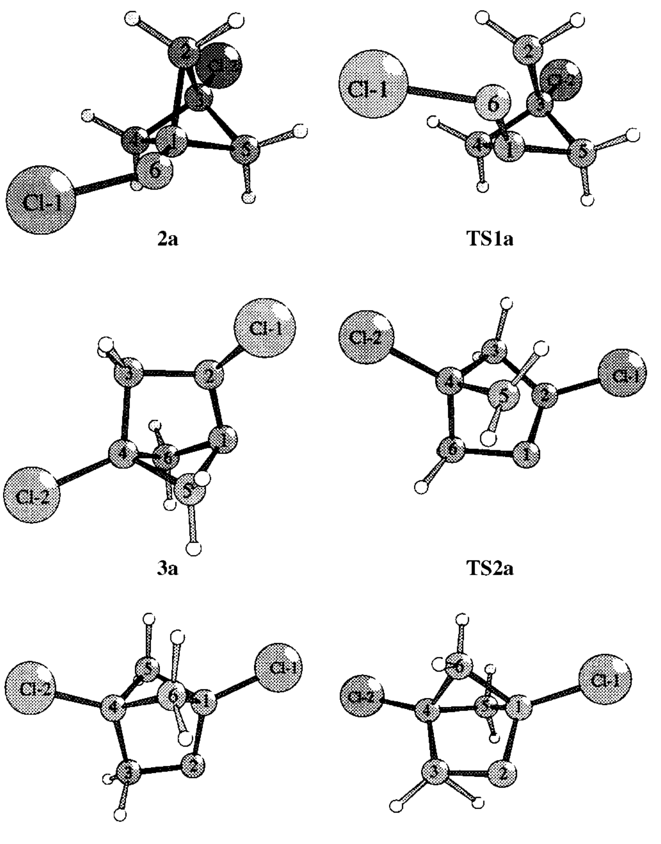
Figure 1. B3LYP/6-311G(d,p) charges of C1 and C2 of **3a** and **g**.

The calculated structures of the stationary points deserve some comment.

1) Carbenes **2**: The structure of **2a** is shown in Figure 2. Common features of the structures of all carbenes **2** are small positive dihedral angles 416Y. In this conformation, the interaction of the empty p orbital of C6 with the strained bond C1−C2 is strong, as indicated by the short bond C6−C1. Therefore C2 will be the migrating C atom, and C1−C2 will be the breaking bond, which is already considerably elongated. This is particularly true for **2d**, which is very close to the transition state **TS1d**. Some selected structural parameters of **2** are given in Table 5.

Table 5. Selected structural parameters of **2**.

X	Y	**2**	C6−C1 [Å]	C1−C2 [Å]	C1−C4 [Å]	C1−C5 [Å]	C2−C3 [Å]	C3−C4 [Å]	C3−C5 [Å]	Y61 [°]	614 [°]	416Y [°]
Cl	Cl	**a**	1.460	1.600	1.568	1.571	1.544	1.544	1.554	109.6	138.3	11.0
Cl	H	**d**	1.421	1.702	1.572	1.556	1.544	1.544	1.541	106.1	138.9	6.7
H	Cl	**e**	1.457	1.601	1.567	1.567	1.554	1.553	1.554	109.4	138.5	12.2
H	Me	**f**	1.445	1.607	1.588	1.563	1.554	1.549	1.552	113.4	137.9	10.2
Cl	Me	**g**	1.447	1.609	1.589	1.565	1.542	1.539	1.542	113.4	137.6	10.1



2a TS1a

3a TS2a

4a TS3a

Figure 2. B3LYP/6-31G(d) structures of **2a**, **3a**, **4a**, **TS1a**, **TS2a**, and **TS3a** (Numbering of **2**, **3**, and **4** according to nomenclature, numbering of **TS1**, **TS2**, and **TS3** as precursor).

2) Bridgehead olefins **3**: Bridgehead olefin **3** contains a *trans*-cyclopentene substructure;[20] the C=C double bond is strongly twisted. To retain some π overlap, **3a–g** adopt a pyramidal configuration at C2, as indicated by the dihedral angle Y214. By necessity, C1 is also pyramidalized. The structure of **3a** is depicted in Figure 2. Significant structural parameters are shown in Table 6. A common structural feature of all alkenes **3** is the long C=C bond, with bond lengths between 1.445 and 1.470 Å. The bond C1–C5 *syn* to Y is slightly longer than the *anti* bond C1–C6. C5 will be the migrating C atom.

An interesting question with respect to the pyramidalization of C2 in alkenes **3** is the inversion barrier, because some insight into the residual π bond energy of the formal C=C double bond C1–C2 might be obtained. Because of the biradical nature of the transition state, it seemed appropriate to calculate this barrier by using the (2,2)CASSCF and include dynamic correlation. We chose the method of Nakano,[21] implemented as MCQDPT procedure in the program Gamess.[22] The potential-energy barrier, with zero-point-energy correction, for the inversion of **3e** was calculated as 7.6 kcal mol^{-1} (MCQDPT/6-31G(d)//CAS(2,2)/6-31G(d): **3e** $E = -691.500720$ a.u.; ZPE = 0.121261 a.u.; transition state $E = -691.487320$ a.u.; ZPE = 0.119966 a.u.).

3) Transition states **TS1**, **TS2**, **TS3**: Transition state **TS1** is reached by further elongating the longest bicyclo[1.1.1]pentyl sidebond C1–C2 and lowering the C2–C6 distance; the bond C1–C6 gains C=C double bond character. The following values are obtained in **TS1**: **a** 1.884/1.938/1.401 Å; **d** 1.799/1.964/1.398 Å; **e** 1.855/1.916/1.400 Å; **f** 1.837/1.888/1.390 Å; **g** 1.855/1.919/1.393 Å.

The structure of **TS2** shows for the breaking C1–C5 and new C2–C5 bonds distances of 1.853/2.033 Å Å for **a**, 1.773/2.056 Å for **c**, 1.801/2.021 Å for **d**, 1.815/2.060 Å for **e**, 1.769/2.067 for **f**, and 1.811/2.028 Å for **g**, whereas the vanishing pyramidalized C=C double bond C1–C2 takes values of 1.398, 1.395, 1.405, 1.389, 1.408, and 1.417 Å, respectively. It should be realized that the migration of C5 to C2 takes place under inversion of configuration at C2, the pyramidalized Y-carrying carbon atom of bridgehead olefin **3**.

Transition state **TS3** is nearly independent of the substituents X and Y. The distance of C3 to the migrating hydrogen is 1.270–1.271 Å, the corresponding distance to C2 1.366–1.368 Å, whereas the new C=C double bond shows a length of 1.410–1.417 Å. In Figure 2 the structures of **TS1a**, **TS2a**, and **TS3a** are also depicted.

Triplet states: In the reaction sequence **2**→**3**→**4**, reactive intermediates are involved in which the triplet state could be the ground state of the molecule. To shed some light on this point, UB3LYP/6-31G(d) calculations were carried out for the triplets of **2**, **3**, and **4**. The results of these calculations are given in Table 7. The last column shows the triplet-singlet energy differences $E_{\text{T-S}}$ in kcal mol^{-1}.

As seen from the data in Table 6, the electronic ground state of carbenes **2c**, **d**, **f**, and **g** is the triplet state. The 1-bicyclo[1.1.1]pentyl chlorocarbenes **2a** and **e** have singlet ground states.[23] Although the ground state for bicyclo[2.1.1]-hexenes **3a–g** are singlets, the triplet–singlet energy difference at <1 kcal mol^{-1} is only marginal for **3c** and **f**, and small for **3d** and **e**. Under these circumstances, triplet reactions of these alkenes are not excluded under our experimental conditions. As our model compounds resemble best the properties of **3a**, for which $\Delta E_{\text{T-S}}$ was calculated to be 4.2 kcal mol^{-1}, triplet reactivity of **3a** is less probable within the framework of our substitution pattern.

Table 6. Selected structural parameters of **3**.

X	Y	**3**	C1–C2 [Å]	C1–C5 [Å]	C1–C6 [Å]	C2–C3 [Å]	C3–C4 [Å]	C4–C5 [Å]	C4–C6 [Å]	1234 [°]	Y214 [°]
Cl	Cl	**a**	1.445	1.557	1.540	1.536	1.562	1.573	1.543	6.0	130.1
H	H	**c**	1.470	1.561	1.544	1.533	1.559	1.574	1.558	3.7	138.7
Cl	H	**d**	1.458	1.558	1.541	1.534	1.558	1.571	1.542	6.7	132.0
H	Cl	**e**	1.457	1.560	1.541	1.537	1.562	1.576	1.558	3.6	132.5
H	Me	**f**	1.477	1.560	1.543	1.537	1.556	1.572	1.558	3.3	141.9
Cl	Me	**g**	1.466	1.558	1.542	1.538	1.555	1.568	1.541	6.3	136.8

Table 7. Results of B3LYP/6-311G(d,p)//B3LYP/6-31G(d) calculations on the triplet states of **2**, **3** and **4**, and the $\Delta E_{T\text{-}S}$, the triplet/singlet energy difference.

X	Y		**2** E(T)[a] ZPE[b] E_{total} (T)[c] $\Delta E_{T\text{-}S}$[d]	**3** E(T)[a] ZPE[b] E_{total} (T)[c] $\Delta E_{T\text{-}S}$[d]	**4** E(T)[a] ZPE[b] E_{total} (T)[c] $\Delta E_{T\text{-}S}$[d]
Cl	Cl	**a**	– 1152.339835	– 1152.370477	– 1152.360358
			0.100005	0.100521	0.100795
			– 1152.450131	– 1152.481317	– 1152.471737
			6.92	*4.18*	*12.59*
H	H	**c**	– 233.114811	– 233.150997	– 232.144738
			0.116141	0.117525	0.119606
			– 233.173474	– 233.209257	– 233.202331
			–	*0.68*	*13.45*
Cl	H	**d**	– 692.727255	– 692.762379	– 692.756397
			0.106924	0.108272	0.110279
			– 692.812566	– 692.847643	– 692.841115
			– 4.01	*1.37*	*10.7*
H	Cl	**e**	– 692.728550	– 692.766303	– 692.751859
			0.109359	0.109882	0.110202
			– 692.811806	– 692.844784	– 692.836456
			6.80	*2.53*	*13.11*
H	Me	**f**	– 272.556178	– 272.590296	– 272.583589
			0.144451	0.145468	0.146775
			– 272.480097	– 272.513131	– 272.505024
			– 1.69	*0.84*	*12.24*
Cl	Me	**g**	– 732.159815	– 732.192865	– 732.185933
			0.135158	0.136122	0.137432
			– 732.119745	– 732.144827	– 732.143679
			– 0.70	*6.35*	*11.58*

[a] B3LYP/6-31G(d)//B3LYP/6-31G(d) triplet energy in a.u. [b] Zero point energy, obtained from frequency calculations at the B3LYP/6-31G(d) level of theory and scaled by a factor of 0.9804. [c] B3LYP/6-311G(d,p)//B3LYP/6-31G(d) triplet energy, ZPE/B3LYP/6-31G(d) corrected. [d] E_{total}(T)-E_{total} (of Table 2) in kcal mol^{-1}.

The structures of triplet carbenes **2** as well as triplet olefins **3** deserve some attention. Selected structural parameters are given in Table 8 and 9. A pronounced structural difference between singlet and triplet of carbenes **2** is the dihedral angle 416Y, which is close to 60° for the triplets. This leads, for the triplets, to a bisected structure with a dihedral angle 261Y of close to 180° and (as no symmetry restrictions were used for the calculations) nearly identical values for C1−C4/C1−C5 and C3−C4/C3−C5. As expected, the carbene angle Y61 is wider for the triplets (128.9 – 135.5°) than for the singlets (106.1 – 116.4°).

The triplet bridgehead olefins **3** share with the singlets a long C=C double bond C1−C2. With the exception of **3g**, in all triplets **3** both carbon atoms of the C=C double bond, C1 and C2, are pyramidalized, as indicated by the dihedral angle Y214. However, compared with the singlets, the extent of pyramidalization is smaller.

Conclusion

Our DFT calculations have shown that bicyclo[1.1.1]pentyl carbenes of type **2** with Y = H are not local minima on the corresponding energy hypersurface. For Y = Cl, an energy barrier of 7 – 8 kcal mol^{-1} separates these carbenes from the bridgehead olefins **3**, which are more stable than carbenes **2** by at least 15 kcal mol^{-1}. The bridgehead olefins are fleeting intermediates, separated from a bridgehead olefin-carbene rearrangement leading to **4** by a potential-energy barrier of 8 – 10 kcal mol^{-1}. Under these circumstances, only efficient traps will be able to react with **3** in intermolecular processes. The 1,2-hydrogen shift of carbenes **4** proceeds over a potential-energy barrier of 12 – 13 kcal mol^{-1}, which enables external traps to react with **4**. Formation of alkenes **20** should be observed at elevated temperatures in the absence of appropriate trapping reagents. The triplet state is the ground state of bicyclo[1.1.1]pentyl carbenes **2d**, **f**, and **g**, whereas the chlorocarbenes **2a** and **e** have a singlet ground state and a triplet/singlet energy separation of close to 7 kcal mol^{-1}. All bridgehead olefins **3** have a singlet ground state, but only **3a** and **g** shows a significant triplet/singlet energy separation to assure that the singlet state will react in trapping processes for these short-lived intermediates. The overall picture of our theoretical investigation compares favorably with the experimental results.

Table 8. Selected structural parameters of triplets **2**.

X	Y	**2**	C6−C1 [Å]	C1−C2 [Å]	C1−C4 [Å]	C1−C5 [Å]	C2−C3 [Å]	C3−C4 [Å]	C3−C5 [Å]	Y61 [°]	614 [°]	416Y [°]
Cl	Cl	**a**	1.447	1.566	1.584	1.584	1.545	1.542	1.543	129.0	128.3	61.2
H	H	**c**	1.436	1.569	1.588	1.588	1.553	1.550	1.550	134.6	128.4	60.0
Cl	H	**d**	1.433	1.571	1.592	1.591	1.544	1.540	1.540	134.3	127.8	59.7
H	Cl	**e**	1.451	1.562	1.582	1.581	1.555	1.552	1.552	128.9	128.7	61.2
H	Me	**f**	1.440	1.567	1.590	1.590	1.553	1.550	1.549	135.5	128.6	61.6
Cl	Me	**g**	1.438	1.570	1.593	1.593	1.542	1.539	1.539	135.5	128.3	61.7

Table 9. Selected structural parameters of triplets **3**.

X	Y	**3**	C1−C2 [Å]	C1−C5 [Å]	C1−C6 [Å]	C2−C3 [Å]	C3−C4 [Å]	C4−C5 [Å]	C4−C6 [Å]	1234 [°]	Y214 [°]
Cl	Cl	**a**	1.497	1.552	1.545	1.529	1.553	1.554	1.556	– 2.3	144.1
H	H	**c**	1.497	1.556	1.551	1.523	1.556	1.564	1.566	– 0.9	160.5
Cl	H	**d**	1.486	1.555	1.550	1.524	1.553	1.552	1.554	– 0.9	161.0
H	Cl	**e**	1.498	1.552	1.546	1.527	1.555	1.565	1.567	– 2.2	143.5
H	Me	**f**	1.491	1.555	1.548	1.529	1.554	1.564	1.565	– 1.1	156.2
Cl	Me	**g**	1.493	1.555	1.547	1.531	1.551	1.552	1.553	– 1.1	156.2

Experimental Section

General: ^{1}H and ^{13}C NMR spectra including ^{1}H^{1}H COSY, ^{1}H^{13}C HETCOR and ^{13}C^{13}C INADEQUATE measurements were recorded on a Bruker AM300, Bruker DPX300, Bruker AMX600, and on a Varian 400S spectrometer with TMS as an internal standard. Infrared spectra were obtained on a Perkin–Elmer 881, mass spectra on a Finnigan MAT90. Melting points were determined on a Büchi 530 and are uncorrected. Microanalyses were carried out at the Humboldt Universität, Institut für Chemie, Microanalytical Laboratory. Reactions were monitored by thin-layer chromatography (TLC) with analytical silica gel 60F$_{254}$ on aluminum foil by Merck (Darmstadt) and visualized with ammonium molybdate solution or by UV light. Preparative column chromatography was carried out on glass columns of different size packed with Merck (Darmstadt) silica gel 60 (230–400 mesh ASTM) or Merck silica gel 40 (35–70 mesh ASTM). Preparative gas chromatography (PGC) was effected with a Siemens RGC202 on a silicon OV-1 column (10%) on chromosorb (diameter 5.33 mm, length 4.0 m).

Materials: *n*-Butyllithium (BuLi) was purchased from Chemetall [Frankfurt/M (Germany)] as a 1.6M solution in hexane. Methyllithium (MeLi) salt-free (<0.4% LiCl; 1.6M in ether) was obtained from Aldrich. [D$_3$]Acetophenone (D$_3$ content 98%) was a commercial product of Cambridge Isotope Laboratories. ^{13}CCl$_4$ (^{13}C content 99%) was obtained from Prochem [Wesel (Germany)].

1-Bromo-3-trichloromethylbicyclo[1.1.1]pentane (5b):[4] In a typical experiment, [1.1.1]propellane (70.0 mmol) in ether[24, 25] was mixed at −78 °C with bromotrichloromethane (40.0 g, 202 mmol) and kept for 48 h at room temperature (RT). After removal of the volatile material in vacuo, the solid residue was crystallized from ether affording **5b** (14.1 g, 76%) as colorless crystals. M.p. 63 °C.

1-Chloro-3-trichloromethylbicyclo[1.1.1]pentane (5a):[4] A solution of [1.1.1]propellane (70 mmol) in ether[24, 25] and tetrachloromethane (20 mL) was allowed to react as described for **5b**. Compound **5a** was obtained as colorless crystals (11.2 g, 73%). M.p. 58 °C. For the synthesis of 1-chloro-3-trichloro[^{13}C]methylbicyclo[1.1.1]pentane (**5a***), ^{13}CCl$_4$ (1.00 mL; ^{13}C content 99%) was diluted with CCl$_4$ (49.0 mL), leading to a ^{13}C label content of approximately 3%. [1.1.1]Propellane (35.0 mmol) in ether (70 mL) was added into this solvent, and the mixture kept for 4 d at 20 °C. After removal of the solvent, crystallization of the residue from *n*-pentane afforded **5a*** (5.94 g, 77%). Analysis of the ^{13}C content by ^{13}C NMR spectroscopy showed a ratio of the ^{13}C content of the trichloromethyl group to the average of the four additional C atoms of (3.24:1.00) ± 0.06

Reaction of MeLi with 5a: A solution of **5a** (2.20 g, 10.0 mmol) in ether (20 mL) was added dropwise under nitrogen with stirring to a solution of MeLi (48 mmol, salt-free) in ether (30 mL), which was kept in a dry-ice bath at −78 °C. The mixture was allowed to warm to RT. The excess of MeLi was destroyed by careful addition of water under stirring and immersion of the reaction vessel in an ice bath. Aqueous workup and removal of the ether from the organic layer afforded a yellow oil (1.61 g), whose ^{1}H NMR spectrum indicated the formation of three compounds. Partial separation was effected by column chromatography (silica gel, petroleum ether). The first fraction (730 mg) was a 5:1 mixture of 1,3-dichloro-3,4-dimethylbicyclo[2.1.1]hexane (**7a**, yield 33%) and 1,2,4-trichloro-2-methylbicyclo[2.1.1]hexane (**6a**, yield 6.7%), which was further separated by PGC (150 °C; retention time for **7a** 25.5 min, oily liquid; retention time for **6a** 40.8 min, colorless solid, m.p. 38 °C). The second fraction of the column chromatography was 1-chloro-3-chloromethyl-4-methylbicyclo[2.1.1]hexane (**8a**, 60 mg, 3.4%), which was obtained as a waxy solid.

*Compound **6a***: IR (KBr): $\tilde{\nu} = 3019$, 2985, 1451, 1443, 1382, 1280, 1224, 1214, 1202, 1152, 1143, 1121, 1082, 1001, 963, 956, 917, 911, 855, 795 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.76$ (s, 3H; CH$_3$), 2.26–2.33 (m, 3H; 5-H$_{\text{endo}}$, 6-H$_2$), 2.37 (dd, $^2J = 12.0$ Hz, $^4J = 3.0$ Hz, 1H; 3-H), 2.64 (dm, $^2J = 12.0$ Hz, 1H; 3-H), 2.87 (m, 1H; 5-H$_{\text{exo}}$ [*syn* to C-2-Cl]); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 26.36$ (q, C-7), 52.63, 53.64, 54.37 (3t, C-3, C-5, C-6 in unknown order), 54.89 (s, C-4), 67.25 (s, C-1), 74.50 (s, C-2); MS (70 eV, EI): *m/z* (%): 167 (3), 165 (17), 163 (25) [$M^+ - \text{Cl}$], 130 (3), 129 (32), 128 (9), 127 (100), 125 (17), 123 (21), 91 (62), 89 (11), 87 (23), 77 (14), 65 (17); $C_7H_9Cl_3$ (199.51): calcd C 42.14, H 4.55, Cl 53.31; found C 41.10, H 4.33, Cl 52.99.

*Compound **7a***: IR (film): $\tilde{\nu} = 2968$, 2932, 2901, 2875, 1447, 1379, 1283, 1228, 1216, 1174, 1156, 1131, 1104, 1038, 1003, 945, 779, 698, 616 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.25$ (s, 3H; CH$_3$), 1.66 (s, 3H; CH$_3$), 1.77–1.95 (m, 3H; 5-H$_{\text{endo}}$, 6-H$_2$), 2.27 (dd, $^2J = 12.0$ Hz, $^4J = 3.1$ Hz, 1H; 2-H *cis* to 3-Me), 2.46 (dd, $^2J = 9.9$ Hz, $^4J = 6.8$ Hz, 1H; 5-H$_{\text{exo}}$ [*syn* to C-3-Cl]), 2.58 (dd, $^2J = 12.0$ Hz, $^4J = 3.9$ Hz, 1H; 2-H *cis* to 3-Cl); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 13.29$ (q, Me), 26.63 (q, Me), 49.69, 51.87, 54.41 (3t, C-2, C-5, C-6 in unknown order), 52.42 (s, C-4), 58.27 (s, C-1) [The signal of C3 was covered by the signal of the solvent]; MS (70 eV, EI): *m/z* (%): 145 (13), 143 (34) [$M^+ - \text{Cl}$], 129 (11), 127 (15), 108 (11), 107 (100), 105 (17), 103 (21), 102 (12), 93 (15), 91 (48), 79 (26), 77 (26), 69 (13), 67 (31), 65 (23); $C_8H_{12}Cl_2$ (179.09): calcd C 53.65, H 6.75; found C 53.56, H 7.30.

*Compound **8a***: IR (KBr): $\tilde{\nu} = 3007$, 2978, 2963, 2939, 2922, 2885, 1441, 1295, 1283, 1254, 1223, 1199, 1169, 1155, 1120, 1081, 1025, 1001, 953, 915, 881, 827 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.22$ (s, 3H; Me), 1.62 (m, 1H; 5-H), 1.70–1.82 (m, 4H; 2-H$_2$, 5-H, 6-H), 2.20–2.34 (m, 2H; 3-H, 6-H), 3.33 (t, $^2J = 10.8$ Hz, $^3J = 11.0$ Hz, 1H; C*H*Cl), 3.67 (dd, $^2J = 10.8$ Hz, $^3J = 5.8$ Hz, 1H; C*H*Cl); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 17.23$ (q, Me), 42.39 (t, C-6), 44.84 (s, C-4), 46.12 (t, CH$_2$Cl), 47.10 (d, C-3), 47.18 (t, C-5), 54.35 (t, C-2), 59.97 (s, C-1); MS (70 eV, EI): *m/z* (%): 145 (6), 143 (11) [$M^+ - \text{Cl}$], 131 (13), 129 (38) [$M^+ - \text{CH}_2\text{Cl}$], 122 (16), 115 (22), 107 (31), 105 (50), 93 (60), 91 (58), 89 (13), 88 (14), 79 (33), 77 (83), 75 (27), 73 (25), 71 (20), 68 (14), 67 (39), 65 (35).

The experiment was repeated, but with the mixing of the components carried out in the reversed order by adding a solution of MeLi in ether dropwise to a solution of **5a** in ether, which was cooled in a dry-ice acetone bath. After the workup described above, **6a**, **7a** and **8** were isolated in yields of 26, 7, and 2%, respectively.

Reaction of MeLi with 5a*: Compound **5a*** (2.20 g, 10.0 mmol) in ether (30 mL) was added dropwise to MeLi (1.6M; 32.0 mmol, salt-free) in ether (20 mL), which was kept in −78 °C bath. The workup was carried out as given for **5a** and afforded after column chromatography a 1.5:1 mixture of **7a*** and **6a*** (606 mg; yield of **7a***%, yield of **6a*** 13%) and pure **8a*** (40 mg, 2.2%). The ^{13}C NMR investigation on the label distribution in the products was conducted on the mixture of **7a*/6a*** and on pure **8a***. The NMR measurements were performed using the inverse gated decoupling method[6] and a pulse delay time of 200 seconds. The following label distribution was obtained: **6a***: C1 (100 ± 2)%; **7a***: C4 (91.9 ± 2)%, C3 (8.1 ± 2)%; **8a***: C4 (88.1 ± 2)%, C3 (11.9 ± 2)%.

Reaction of MeLi with 5b: A solution of **5b** (5.28 g, 20.0 mmol) in ether (40 mL) was added dropwise under nitrogen with stirring to a solution of MeLi (100 mmol, salt-free) in ether (60 mL), which was kept in a dry-ice bath at −78 °C. The mixture was allowed to warm to RT. The workup was carried out as described for the reaction of **5a** with MeLi. The residue of the organic layer was subjected to a high-vacuum distillation, affording 3.05 g of a colorless liquid, b.p. 20–25 °C/0.001 mbar. Partial separation was effected by column chromatography (silica gel, petroleum ether), for which 1.00 g of the oily mixture was used. According to ^{1}H NMR analysis, the first fraction (620 mg) was a 2.4:1 mixture of 1-bromo-3-chloro-3,4-dimethylbicyclo[2.1.1]hexane (**7b**, yield 29%) and 1-bromo-3,4-trichloro-3-methylbicyclo[2.1.1]hexane (**6b**, yield 12%), which was further separated by PGC (150 °C; retention time for **7b** 23.7 min, colorless liquid; retention time for **6a** 40.8 min, colorless solid, m.p. 42 °C). The second fraction of the column chromatography was 1-bromo-3-chloromethyl-4-methylbicyclo[2.1.1]hexane (**8b**, 60 mg, 4%), which was obtained as a colorless liquid.

*Compound **6b***: IR (KBr): $\tilde{\nu} = 3014$, 2984, 2956, 1440, 1381, 1281, 1221, 1201, 1149, 1136, 1118, 1076, 996, 946, 931, 905, 852, 793, 683 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.77$ (s, 3H; CH$_3$), 2.37 (m, 3H; 5-H$_{\text{endo}}$, 6-H$_2$), 2.46 (dd, $^2J = 12.0$ Hz, $^4J = 2.9$ Hz, 1H; 2-H *cis* to 3-Me), 2.71 (dm, $^2J = 12.0$ Hz, 1H; 2-H *cis* to 3-Cl), 2.91 (m, 1H; 5-H$_{\text{exo}}$ *syn* to 3-Cl); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 26.26$ (q, CH$_3$), 42.70 (s, C-1), 53.29, 54.83, 55.13 (3t, C-2, C-5, C-6 in unknown order), 68.37 (s, C-4), 74.31 (s, C-3); MS (70 eV, EI): *m/z* (%): 211 (1), 209 (5), 207 (5) [$M^+ - \text{Cl}$], 167 (2), 165 (9), 163 (13) [$M^+ - \text{Br}$], 130 (4), 129 (32), 128 (12), 127 (100), 92 (15), 91 (77), 77 (18), 65 (18); $C_7H_9BrCl_2$ (243.96): calcd C 34.46, H 3.72; found C 34.54, H 3.33.

*Compound **7b***: IR (film): $\tilde{\nu} = 2967$, 2931, 2873, 1445, 1378, 1282, 1224, 1172, 1154, 1130, 1100, 1035, 999, 918, 845, 844, 777, 697, 614, 601 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.26$ (s, 3H; CH$_3$), 1.66 (s, 3H; CH$_3$), 1.93 (m, 3H; 5-H$_{\text{endo}}$, 6-H$_2$), 2.35 (dd, $^2J = 12.5$ Hz, $^4J = 2.8$ Hz, 1H; 2-H *cis* to Me), 2.50 (m, 1H; 5-H$_{\text{exo}}$ *syn* to 3-Cl), 2.66 (dm, $^2J = 12.5$ Hz, 1H; 2-H *cis* to 3-Cl).

The assignment of the signals is based on a ^{1}H ^{13}C HETCOR NMR spectrum of **7b**. ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 13.34$ (q, Me), 26.58 (q, Me), 47.91 (s, C-1), 50.58, 52.87, 55.80 (3t, C-2, C-5, C-6), 54.61 (s, C-4), 76.50 (s, C-3); MS (70 eV, EI): *m/z* (%): 189 (2), 187 (2) [$M^{+} - \mathrm{Cl}$], 145 (3), 143 (10) [$M^{+} - \mathrm{Br}$], 108 (11), 107 (100), 91 (32), 79 (20), 77 (13), 67 (14), 65 (13); $C_8H_{12}BrCl$ (223.54): calcd C 42.99, H 5.41; found C 43.04, H 5.38.

*Compound **8b***: IR (film): $\tilde{\nu} = 2985$, 2957, 2924, 2877, 2870, 1447, 1379, 1307, 1272, 1220, 1186, 1164, 1057, 1044, 1036, 999, 920, 836, 798, 732, 673, 601 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.23$ (s, 3H; CH$_3$), 1.74 (m, 1H; 5-H), 1.79–1.92 (m, 4H; 2-H$_2$, 5-H, 6-H), 2.32 (m, 2H; 3-H, 6-H), 3.34 (t, $^{2}J = 11.0$ Hz, $^{3}J = 11.0$ Hz, 1H; C*H*Cl), 3.68 (dd, $^{2}J = 11.0$ Hz, $^{3}J = 5.2$ Hz, 1H; C*H*Cl); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 17.25$ (q, CH$_3$), 43.92 (t, C-6), 46.03 (t, CH$_2$Cl), 47.07, 50.04 (2s, C-1, C-4), 47.20 (d, C-3), 48.17 (t, C-5), 55.37 (t, C-2); MS (70 eV, EI): *m/z* (%): 175 (7), 173 (7) [$M^{+} - \mathrm{CH_2Cl}$], 145 (19), 143 (54) [$M^{+} - \mathrm{Br}$], 129 (13), 107 (100), 105 (19), 93 (33), 92 (13), 91 (79), 79 (78), 77 (46).

The reaction of **5b** and MeLi was repeated, but carried out by combining the components in reversed order and afforded after the same workup procedure **6b**, **7b** and **8b** in yields of 31, 5, and 0.7%, respectively. In addition, 74 mg (2%) of *E*-1,2-bis(3′-bromobicyc[1.1.1]pent-1-yl)-1,2-dichloroethene (**16**) was isolated as a solid of m.p. 165-168 °C, the properties of which are given below.

3-[D$_3$]-2-Phenylpropene:[26] A solution of [D$_3$]acetophenone (20.0 g, 162.4 mmol) in ether (400 mL) was added dropwise under stirring at −60 °C to a solution of methylenetriphenylphosphorane, prepared from methyltriphenylphosphonium bromide (71.4 g, 200 mmol) and BuLi (200 mmol, 125 mL of a 1.60 M solution in hexane) in ether (400 mL). The mixture was stirred for 12 h at RT, the solid precipitate was removed by filtration, the solution extracted twice with water and the organic phase dried with MgSO$_4$. The solvent was removed in vacuo. The distillation of the liquid residue with a short Vigreux column gave 3-[D$_3$]-2-phenylpropene (12.7 g, 65%) as colorless liquid of b.p. 50 °C/12 mbar.

Reaction of 5b with MeLi in the presence of 2-phenylpropene: A solution of MeLi (10.4 mmol, salt-free, in 100 mL of ether and 25 mL of 2-phenylpropene) was added dropwise under stirring to a solution of **5b** (2.64 g, 9.99 mmol) in ether (200 mL) and 2-phenylpropene (50 mL), cooled in an −78 °C bath,. Stirring was continued for 12 h at RT. After aqueous workup the ether layer was dried with MgSO$_4$, and the solvent and 2-phenylpropene removed in vacuo up to 0.001 mbar/RT. Careful distillation of the oily residue at RT/2.0×10^{-5} mbar afforded 1-bromo-3,3,4-trichlorobicyclo[2.1.1]hexane (**15**, 304 mg), which was resublimed to afford 280 mg (11%) of **15** as colorless crystals , m.p. 82–83 °C. The residual oil of the distillation was further purified by column chromatography (silica gel, petroleum ether) to give (increasing running time) **16** (120 mg, 6%) as colorless crystals, m.p. 165–168 °C (decomp), **17a** (250 mg, 8%) as colorless crystals, m.p. 68 °C, 1-bromo-3-chloro-4-(2-phenyl-3-propenyl)bicyclo[2.1.1]hexane (**18**, 260 mg, 8%), m.p. 55 °C, and **17b** (110 mg, 4%) as a colorless oil.

*Compound **15***: IR (KBr): $\tilde{\nu} = 3024$, 2966, 1441, 1276, 1208, 1166, 1118, 1084, 1047, 1014, 995, 952, 913, 874, 827, 801, 759, 709, 692 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 2.49$ (dq, $^{2}J = 4.9$ Hz, $^{4}J = 1.9$ Hz, 2H; 5-H$_{\mathrm{endo}}$, 6-H$_{\mathrm{endo}}$), 2.72 (dd, $^{2}J = 4.9$ Hz, $^{4}J = 1.9$ Hz, 2H; 5-H$_{\mathrm{exo}}$, 6-H$_{\mathrm{exo}}$), 3.09 (t, $^{4}J = 1.9$ Hz, 2H; 2-H$_2$); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 41.35$ (s, C-1), 54.22 (t, C-5, C-6), 60.18 (t, C-2), 70.95 (s, C-4), 90.19 (s, C-3); MS (70 eV, EI): *m/z* (%): 229 (3), 227 (2) [$M^{+} - \mathrm{Cl}$], 183 (7) [$M^{+} - \mathrm{Br}$], 151(7), 149 (50), 147 (79), 113 (48), 112 (46), 111 (100), 91 (28), 87 (28), 77 (42), 73 (36); $C_6H_6BrCl_3$ (264.38): calcd C 27.26, H 2.29; found C 27.17, H 1.85.

*Compound **16***: IR (KBr): $\tilde{\nu} = 3005$, 2968, 2918, 2881, 1504, 1446, 1292, 1261, 1199, 1188, 1146, 1100, 1045, 1028, 1007, 928, 898, 868, 830, 772, 703 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 2.54$ (s, 12H; 2′-H$_2$, 4′-H$_2$, 5′-H$_2$, 2″-H$_2$, 4″-H$_2$, 5″-H$_2$); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 36.69$ (s, C-3′, C-3″), 44.16 (s, C-1′, C-1″), 60.56 (t, C-2′, C-4′, C-5′, C-2″, C-4″, C-5″), 125.60 (s, C-1, C-2); MS (70 eV, EI): *m/z* (%): 309 (1), 307 (2), 305 (1) [$M^{+} - \mathrm{Br}$], 155 (51), 154 (31), 153 (34), 115 (81), 75 (32); $C_{12}H_{12}Br_2Cl_2$ (386.95): calcd C 37.25, H 3.13; found C 37.35, H 3.31.

*Compound **17a***: IR (KBr): $\tilde{\nu} = 3023$, 2999, 2975, 2968, 2917, 2879, 1600, 1493, 1444, 1427, 1189, 1151, 1080, 1067, 1046, 1031, 959, 877, 861, 779, 761, 734, 700 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.07$ (d, $^{2}J = 6.4$ Hz, 1H; 3′-H), 1.51 (d, $^{2}J = 6.4$ Hz, 1H; 3′-H), 1.58 (dd, $^{2}J = 9.0$ Hz, $^{4}J = 1.1$ Hz, 3H; 2-H, 4-H, 5-H), 1.61 (s, 3H; 4′-H$_3$), 1.94 (dd, $^{2}J = 9.0$ Hz, $^{4}J = 1.1$ Hz, 3H; 2-H, 4-H, 5-H), 7.22 (m, 5H; aromatic H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 23.87$ (t, C-3′), 26.10 (q, C-4′), 33.21 (s, C-2′), 37.41 (s, C-1), 45.36 (s, C-3), 52.12 (s, C-1′), 57.61 (t, C-2, C-4, C-5), 127.13, 128.38 (2d, C-2″, C-3″, C-5″, C-6″), 127.88 (d, C-4″), 141.64 (s, C-1″); MS (70 eV, EI): *m/z* (%): 233 (1), 231 (3) [$M^{+} - \mathrm{Br}$], 165 (33), 115 (40), 105 (70), 103 (33), 91 (100), 78 (35), 77 (84); $C_{15}H_{16}BrCl$ (311.66): calcd C 57.81, H 5.18; found C 57.86, H 5.35.

*Compound **17b***: IR (Film): $\tilde{\nu} = 3024$, 2999, 2972, 2921, 1495, 1445, 1433, 1193, 1147, 1110, 1073, 1026, 877, 863, 766, 700, 618, 601 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.14$ (d, $^{2}J = 6.4$ Hz, 1H; 3′-H), 1.49 (s, 3H; 4′-H$_3$), 1.54 (d, $^{2}J = 6.4$ Hz, 1H; 3′-H), 2.40 (s, 6H; 2-H$_2$, 4-H$_2$, 5-H$_2$), 7.30 (m, 5H; aromatic H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 24.26$ (q, C-4′), 25.92 (t, C-3′), 34.39 (s, C-2′), 36.56 (s, C-1), 45.41 (s, C-3), 50.33 (s, C-1′), 59.12 (t, C-2, C-4, C-5), 126.69 (d, C-4″), 128.17, 128.62 (2d, C-2″, C-3″, C-5″, C-6″), 143.41 (s, C-1″); MS (70 eV, EI): *m/z* (%): 231 (2) [$M^{+} - \mathrm{Br}$], 165 (30), 115 (38), 105 (71), 103 (31), 91 (100), 78 (33), 77 (80); $C_{15}H_{16}BrCl$ (311.66): calcd C 57.81, H 5.18; found C 57.75, H 5.30.

*Compound **18***: IR (KBr): $\tilde{\nu} = 2996$, 2956, 2938, 2926, 1493, 1445, 1433, 1292, 1266, 1244, 1216, 1189, 1165, 1029, 978, 920, 901, 813, 779, 703, 699 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.28$ (dd, $^{2}J = 9.8$ Hz, $^{4}J = 7.5$ Hz, 1H; 5-H), 1.76 (m, 2H; 6-H$_2$), 2.14 (ddd, $^{2}J = 12.1$ Hz, $^{3}J = 2.6$ Hz, $^{4}J = 1.1$ Hz, 1H; 2-H), 2.15 (dd, $^{2}J = 9.8$ Hz, $^{4}J = 7.1$ Hz, 1H; 5-H *syn* to 3-Cl), 2.54 (ddd, $^{2}J = 12.1$ Hz, $^{3}J = 7.9$ Hz, $^{4}J = 2.6$ Hz, 1H; 2-H *cis* to 3-Cl), 2.82 (dd, $^{2}J = 14.3$ Hz, $^{4}J = 1.5$ Hz, 1H; 1′-H), 2.95 (dd, $^{2}J = 14.3$ Hz, $^{4}J = 1.5$ Hz, 1H; 1′-H), 4.10 (dt, $^{3}J = 7.9$ Hz, $^{3}J = 2.6$ Hz, $^{4}J = 2.6$ Hz, 1H; 3-H), 5.12 (tt, $^{2}J = 1.5$ Hz, $^{4}J = 0.75$ Hz, 1H; 3′-H), 5.37 (d, $^{2}J = 1.5$ Hz, 1H; 3′-H), 7.30 (m, 5H; aromatic H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 35.44$ (t, C-1′), 48.68 (s, C-1), 47.76, 49.00, 50.39 (3t, C-2, C-5, C-6), 53.22 (s, C-4), 61.79 (d, C-3), 115.81 (t, C-3′), 126.14, 128.41 (2d, C-2″, C-3″, C-4″, C-5″), 127.74 (d, C-4″), 140.83 (s, C-1″), 144.67 (s, C-2′). The assignment of the NMR data was carried out by use of ^{1}H-^{1}H COSY, ^{1}H-^{13}C HETCOR, and ^{13}C-^{13}C INADEQUATE measurements. See also Table 2. MS (70 eV, EI): *m/z* (%): 312 (1), 310 (1) [M^{+}], 195 (44), 117 (32), 115 (47), 103 (36), 91 (89), 79 (32), 78 (33), 77 (100); $C_{15}H_{16}BrCl$ (311.65): calcd C 57.81, H 5.18; found C 58.06, H 5.41.

Reaction of 5b with MeLi in the presence of 3-[D$_3$]-2-phenylpropene: Compound **5b** (4.75 g, 18.0 mmol) and 3-[D$_3$]-2-phenylpropene (12.7 g, 105 mmol) in ether (50 mL) were treated with MeLi (18.4 mmol, salt-free, 1.6 M in ether) as described above. Column chromatographic purification of the crude reaction products afforded **[D$_3$]18** in 8% yield. ^{1}H NMR (300 MHz, CDCl$_3$): The spectrum shows identical chemical shifts as the one of **18**; the signals at $\delta = 4.10$, 5.12 and 5.37 are absent; ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 35.28$ (t, C-1′), 48.68 (s, C-1), 47.76, 48.85, 50.34 (3t, C-2, C-5, C-6), 53.18 (s, C-4), 61.42 (dt, $^{1}J_{\mathrm{CD}} = 24.4$ Hz, C-3), 115.26 (tqi, $^{1}J_{\mathrm{CD}} = 24.2$ Hz, C-3′), 126.13, 128.41 (2d, C-2″, C-3″, C-4″, C-5″), 127.74 (d, C-4″), 140.75 (s, C-1″), 144.43 (s, C-2′).

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