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Reaction of 1-(Halomethyl)bicyclo[1.1.1]pentanes with Strong Bases: Evidence for a Carbene–Bridgehead Olefin–Carbene Rearrangement

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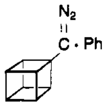
Abstract: The reaction of 1-(dichloromethyl)bicyclo[1.1.1]pentane (**10a**) with MeLi afforded 1-chloro-2-methylbicyclo[2.1.1]hexane (**14**) and 1,2-dichloro-2-methylbicyclo[2.1.1]hexane (**15**) in yields of 15 and 11%. 1-(Trichloromethyl)bicyclo[1.1.1]pentane (**10b**) and MeLi led to a 62% yield of **15**. [^{12}C]-Labeling of the trichloromethyl group (**10e**) showed that the label was exclusively found in the C-1 position of **15**, indicating an overall two CC bond breaking and two CC bond forming process. Treatment of **10b**, **10c**, and **10d** with MeLi or $NaN(SiMe_3)_2$ in the presence of 2,5-dimethylfuran, cyclohexene, and tetramethylethylene, respectively, gave rise to spiroadducts **24a**, **25**, and **27**, respectively, in yields of 29, 10, and 10%. The last two reactions were accompanied by the formation of trihalides **26** (16%) and **28** (25%). **10d**, $NaN(SiMe_3)_2$, and triethylsilane produced a 34% yield of silane **29**. The results are interpreted on the basis of a carbene (**19**) → bridgehead olefin (**20**) → carbene (**21**) rearrangement.

Introduction

Carbene centers attached to the bridgehead of a bicyclic or polycyclic framework tend to stabilize by ring enlargement to give bridgehead olefins.[1] In a few cases, the bridgehead olefin is sufficiently reactive to undergo a subsequent rearrangement to afford a carbene.[2] A prominent example has been reported by Eaton and his co-workers: carbene **2**, generated from diazoalkane **1**, converted to homocubylidene **4b** via homocubene **3b**. Bridgehead olefin **3b** and carbene **4b** were trapped by the solvent.[3] Further significant results were obtained by Jones and his group, who, in a series of elegant experiments, were able to prove the existence of an equilibrium between **3a** and **4a**.[4] Carbene **6**, structurally related to **2** and generated from diazoalkane **5**, rearranged in part to olefin **7**. Both **6** and **7** were trapped by ethanol to afford the ethyl ethers **8** and **9**.[5] Kirmse and his co-workers, however, have shown recently that skeletal rearrangement of diazoalkanes or diazirines under photolysis in protic solvents may proceed via carbenium ions generated by protonation of the corresponding carbenes.[6] Although the consequences of these results concerning the mechanistic interpretation of reactions of this type are not clear at present, reexaminations of the mechanisms in some cases might become necessary.



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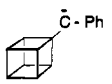

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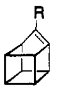

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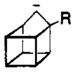
3, 4:
a: R = H
b: R = Ph



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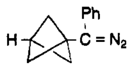

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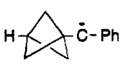

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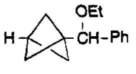

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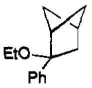

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Stimulated by the findings of Wiberg[5] and by the ready access to a series of halides of type **10**, we studied their treatment with strong bases to generate carbenoids of type **11**. These might be in equilibrium with carbenes **12** or form these carbenes irreversibly. Product studies should reveal if carbenes **12** show a propensity to rearrange in nonprotic solvents.

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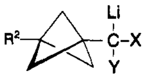

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12

13

Synthesis of 1-(Halomethyl)bicyclo[1.1.1]pentanes (10)

The synthesis of halides **10** was achieved by radical chain addition of halomethanes HCXYZ to [1.1.1]propellane (**13**) under photolytic or thermal conditions. The reaction of **13** with chloroform has been reported by Wiberg,[5] and the addition of bromoform to **13** affording **10c** by Michl and his group.[7] Our results are given in Table 1. The last two reactions of Table 1 were carried out to obtain "carbon-labeled" starting material which should be useful to confine mechanistic pathways concerning the formation of products. $D^{12}CCl_3$ was commercially obtained from Merck AG, Germany, and its ^{13}C carbon content was reduced to at least 5% of natural abundance. $H^{12}CCl_2I$ was synthesized from $D^{12}CCl_3$ by reaction of aqueous NaOH/NaI in the presence of benzyltriethylammonium chloride following the procedure of Dehmlow and Stütten.[8]

Reaction of 10a, b, and e with Methyllithium

The mixture of **10a** with approximately 2.0 equiv of MeLi in ether was slowly warmed from −78 to −18 °C. Above −25 °C evolution of a gas from the reaction mixture was observed. Aqueous workup followed by distillation of the organic residue

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[⊗] Abstract published in *Advance ACS Abstracts*, July 1, 1994.

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Table 1. 1-(Halomethyl)bicyclo[1.1.1]pentanes (10) from 13 and HCXYZ

HCXYZ	**10**	R^1	R^2	% yield
H_2CCl_2	**a**	CCl_2H	H	44[a]
$HCCl_3$	**b**	CCl_3	H	81
$HCBr_3$	**c**	$HCBr_2$	Br	93
$HCCl_2I$	**d**	$HCCl_2$	I	96
$D^{12}CCl_3$	**e**	$^{12}CCl_3$	D	13
$H^{12}CCl_2I$	**f**	$H^{12}CCl_2$	I	41

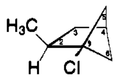
[a] In addition to **10a**, a 4% yield of 3-(dichloromethyl)-1,1′-bisbicyclo[1.1.1]pentane was isolated.

Table 2. $^1J(^{13}C^{13}C)$ Coupling Constants (Hz) of 14 and 15

C atoms	**14** ^1J	**15** ^1J	C atoms	**14** ^1J	**15** ^1J
1, 2	36.7	*a*	2, CH_3	37.9	41.8
1, 5	29.9	28.4	3, 4	31.6	31.5
1, 6	29.1	31.5	4, 5	26.1	25.6
2, 3	32.1	34.6	4, 6	25.0	25.9

[a] This coupling constant could not be determined with certainty from the spectra.

and, in part, separation of the volatile compounds by preparative gas chromatography afforded a 15% yield of chloride **14** and an 11% yield of dichloride **15**. In addition, two further compounds were isolated in trace amounts, the NMR spectra of which are in accordance with structures **16** and **17**. Remarkably, **15** was the main product (yield 62%) of the reaction of **10b** with an excess of MeLi under similar reaction conditions. The structures of **14** and **15** are based on NMR spectroscopy using the 2D INADEQUATE pulse technique. Table 2 shows the $^{13}C^{13}C$ coupling constants of the directly bound carbon atoms of **14** and **15**.



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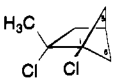

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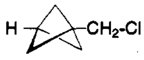

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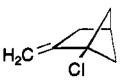

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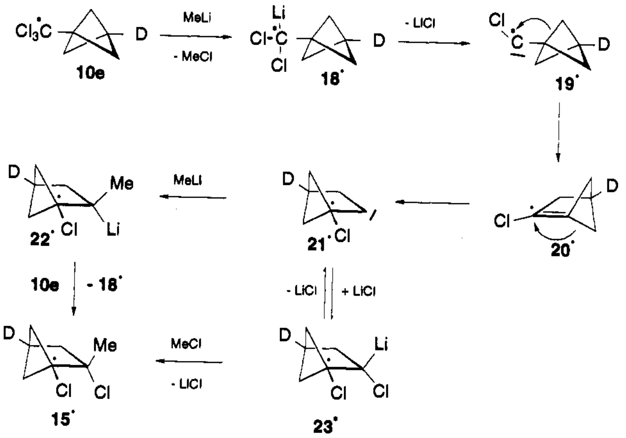
The carbon skeleton of **14** and **15** indicates that substantial rearrangements must have taken place in the course of the reaction. In order to establish the origin of C1 and C2 in **15**, **10e** was treated with an excess of MeLi in ether to afford a 59% yield of [1-^{12}C,4-D]**15** (=**15***). The position of the labels followed unambiguously from the ^{13}C NMR spectrum of **15***. In comparison to the spectrum of **15**, the signal of C1 was completely absent and the signal of C4 appeared as a 1:1:1 triplet of low intensity.

The appearance of the [^{12}C] label at the bridgehead position of **15*** demands that two bond-breaking and two new bond-forming processes had occurred. A mechanism which accounts for this fact is depicted in Scheme 1.

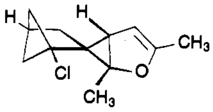
The core of this mechanism is the carbene–bridgehead olefin-carbene rearrangement **19*** → **20*** → **21***. The trapping of **21*** under the reaction conditions could take place in two ways: either carbene **21*** adds the strong nucleophile MeLi to give the *tertiary* alkyllithium base **22***, which subsequently undergoes a chlorine lithium exchange reaction with the starting material **10e**, or **21*** could add lithium chloride, leading to a possible equilibrium between **21*** and the carbenoid **23***, which is alkylated by methyl chloride present in the reaction medium. Both pathways rely on the electrophilic character of the carbene **21***, which is capable of adding a nucleophile. Although, as will be shown later, there exists evidence for the second route, we prefer the first one in this case. The main reason is the formation of **14** in the reaction of **10a** with MeLi, which afforded **14** and **15** as its major products. After metalation of **10a** by MeLi again label-free carbenoid **18** would be formed which would rearrange as indicated in Scheme 1, leading to carbene **21**. After addition of MeLi to afford **22**, this strong base is competitively protonated by **10a** and only to a lesser extent chlorinated by the *gem* dichloride **10a**. The alternative route, addition of LiCl to **21**, would not lead to **14**.

Scheme 1

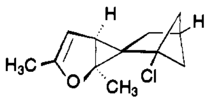


Reaction of 10 with Strong Bases in the Presence of Trapping Reagents

Scheme 1 suggests that the reactive intermediates **20** and **21** could be trapped by cycloadditon reactions. Indeed, an equimolar mixture of **10a** and MeLi in the the presence of an excess of 2,5-dimethylfuran afforded a 29% yield of a 1:1 adduct. NMR analysis showed that carbene **21** had been trapped, giving rise to the spiro compound **24**. Only one of the two stereoisomers **24a** and **b** had been formed, the structure of which is, according to the results given below, most probably **24a**.



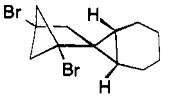
24a



24b

A crystalline carbene adduct of structure **25** was isolated in 10% yield from the reaction of tribromide **10c** with sodium bis(trimethylsilyl)amide ($NaN(SiMe_3)_2$) in the presence of cyclohexene. For this compound, a single-crystal X-ray structure was determined, which confirmed the stereochemistry of the adduct. The same reaction gave rise to an additional 16% yield of 1,2,4-tribromobicyclo[2.1.1]hexane (**26**) as the main product, the structure of which was also determined by single-crystal X-ray spectroscopy.[9]

Tetramethylethylene was used as a trap in the reaction of **10d** with $NaN(SiMe_3)_2$, which led to the isolation of adduct **27** in 10% yield. Again, X-ray crystallographic analysis proved the structure of **27**.[9] In this reaction, trihalide **28** was formed in 25% yield as a second product. It seemed worthwhile to assure that the rearrangement established for the reaction of **10e** → **15*** was also operative in the reaction of **10d** → **28**. Indeed, reaction of **10f** with $NaN(SiMe_3)_2$ in pentane afforded a 20% yield of [1-^{12}C]-1,2-dichloro-4-iodobicyclo[2.1.1]hexane (**28***); again, the position



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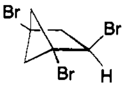

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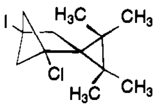

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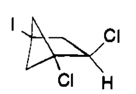

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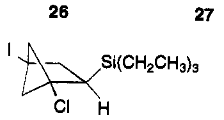

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[9] For details, see supplementary material.

of the label was determined by ^{13}C NMR spectroscopy, showing all of the ^{12}C at the chlorine-carrying bridgehead C1.

Whereas the formation of cycloadducts **24a**, **25**, and **27** does not necessitate a free carbene of type **21** as a reactive intermediate (the corresponding carbenoids of type **23** could also lead to the observed products), carbene insertion into a silicon hydrogen bond is strong evidence for the presence of free carbenes in the above reactions. For this reason, halide **10d** was treated with $NaN(SiMe_3)_2$ in the presence of triethylsilane, which produced besides **28** a 34% yield of 1-chloro-3-(trimethylsilyl)-4-iodobicyclo[2.1.1]hexane (**29**), the structure of which is based on its NMR spectra.

Ab Initio Calculations on Carbene 19, Olefin 20, and Carbene 21

The rearrangement of carbene **19** to carbene **21** via bridgehead olefin **20** can take place only if it is energetically feasible. To gain information about this question, ab initio SCF MO calculations using the GAUSSIAN 90 programs[10] have been carried out for **19**, **20**, and **21** on the MP2/6-31G*//MP2/6-31G* level of theory. Only the singlet states of the reactive intermediates were considered. It was secured that the three compounds are local minima on the corresponding potential surface: vibrational analyses for **19** (6-31G* basis set), **20** (3-21G basis set), and **21** (6-31G* basis set) led to real frequencies only. Table 3 shows the results, which indicate that the energy of **20** is lower by 19.3 kcal/mol than that of **19** and that **21** is lower in energy by 4.0 kcal/mol than **20**. These data suggest that the conversion of **19** → **20** → **21** is energetically possible.

Table 3. Results of ab Initio SCF MO Calculations on the MP2/6-31G*//MP2/6-31G* Level of Theory

	19	20	21
energy (hartrees)	−691.494 829	−691.525 579	−691.531 971
energy difference (kcal/mol)		−19.30	−4.01

Discussion

The present study provides evidence for a carbene–bridgehead olefin–carbene rearrangement under aprotic reaction conditions. In addition, there is a considerable synthetic aspect in this work: to our knowledge, the synthesis of bicyclo[2.1.1]hexanes is not always achieved without difficulty.[11] The reaction sequence of Scheme 1 opens a reasonable access to this carbon framework starting from precursors available with moderate effort. The bicyclo[2.1.1]hexanes obtained here carry at least one halogen at the bridgehead position, which could be used for a wide range of modifications.

The structures of nearly all substituted bicyclo[2.1.1]hexanes isolated from the base treatment of halides **10** are derived from carbene **21** or from structurally related carbenes. Recently Kirsme has shown that the parent carbene **30** has a singlet ground state and that hydrogen migration to form bicyclo[2.1.1]hex-2-ene (**31**) is a slow process.[6] These findings should also hold for the structurally related carbene **21**. With the exception of dihalocarbenes, nucleophilic addition to carbenic centers is not a particularly well studied topic.[12] There are only a few examples described in the literature where an organometallic species adds to an alkylcarbene.[13] The formation of products **14** and **15** initiated by addition of MeLi to **21** might profit from the enhanced electrophilicity of the carbenic center in **21** compared to the one in **30**, caused by the inductive effect of the bridgehead halide in **21**. This idea is bolstered by the calculated total charge of the carbenic centers (MP2/6-31G*), which amounted to +0.116 for **30** and +0.162 for **21**. Particularly noteworthy and deserving of future attention is the addition of alkali halides to carbenes of type **21** to form carbenoids of type **23**. These, whenever $NaN(SiMe_3)_2$ was used as a base, could be protonated by $HN(SiMe_3)_2$ to give the halides **26** and **28**.


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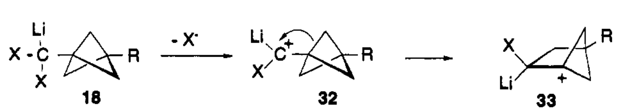
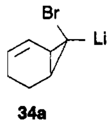
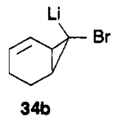




34a



34b

No evidence has been obtained for the intermediacy of halobicyco[1.1.1]pentylcarbenes of type **19**. Probably, the rearrangement of these carbenes to bicyclo[2.1.1]hex-1-enes is much faster than bimolecular trapping reactions. At this point, a remote possibility should be discussed, in which the rearrangement takes place by ionization of the carbenoid leading to **32**, followed by an alkyl shift to give the bridgehead carbenium ion **33**.[14] An example of a cationic rearrangement of a carbenoid has been established by Warner, who found that carbenoids **34a** and **b** led to different product distributions.[15] After loss of the lithium cation, bridgehead olefin **20** would be formed and the reaction sequence would proceed further, as depicted in Scheme 1. With the structure of a bridgehead cation, **33** does not seem to be an energetically favorable intermediate. But it is worth mentioning that ab intio MO SCF calculations (MP2/6-31G*//HF/6-31G* level of theory) put **33** (X = Cl, R = H) 12.6 kcal/mol below **32** (X = Cl, R = H), making the rearrangement **32** → **33** at least energetically feasible.

Conclusion

We have shown that treatment of 1-(halomethyl)bicyclo[1.1.1]pentanes of type **10** with strong bases affords, via two bond-breaking and two bond-forming steps, 2-bicyclo[2.1.1]hexylidenes of type **21**. These carbenes could be trapped either by alkenes giving rise to spiroadducts **24a**, **25**, and **27**, by methyllithium, or even by halides under formation of **26** and **28**. A carbene–bridgehead olefin–carbene rearrangement (**19** → **20** → **21**) accounts best for our experimental results and has precedents in related carbon frameworks. At present, a cationic rearrangement starting from the carbenoid **18** seems less likely but cannot be rigorously excluded.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR 400S at 400 and at 100.6 MHz, respectively. Mass spectra were obtained on a Finnigan MAT 90 instrument. IR spectra were measured on a Bruker IR-IFS 45 instrument. Microanalyses were carried out at the Institute of Organic Chemistry, University of Munich. The photochemically induced addition reactions of halomethanes to [1.1.1]propellane (**13**) were performed in a quartz apparatus using a Philips

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HPK 125 high-pressure lamp. Preparative gas chromatography was carried out on a Varian Aerograph 1400 with a 6 m/1 cm column filled with 20% Carbowax 20 M on kieselguhr.

Syntheses of 1-(Halomethyl)bicyclo[1.1.1]pentanes (10). A. 1-(Dichloromethyl)bicyclo[1.1.1]pentane (10a). A solution of [1.1.1]propellane (**13**)[16] (5.39 g, 81.5 mmol) in 1.2 L of dichloromethane was irradiated for 13 h at room temperature. Monitoring the progress of the reaction by ^{1}H NMR spectroscopy showed that after this time no **13** was present in the reaction mixture. After evaporation of the dichloromethane, the oily residue was distilled in vacuo, affording **10a** (5.41 g, 44%) as a colorless liquid of bp 41 °C/12 Torr and 3-(dichloromethyl)-1,1′-bisbicyclo[1.1.1]pentane (371 mg, 4.2%), bp 25 °C (bath)/0.001 Torr.

(i) 10a. ^{1}H NMR ($CDCl_3$): δ 1.89 (s, 6 H, 2-, 4-, 5-H_2), 2.55 (s, 1 H, 3-H), 5.67 (s, 1 H, $CHCl_2$). ^{13}C NMR ($CDCl_3$): δ 25.99 (CH), 48.23 (CH_2), 48.50 (C), 71.45 (CH). MS (70 eV): *m/e* 115 (2), 113 (1), 101 (4), 88 (6), 91 (100), 77 (36), 67 (30). Anal. Calcd for $C_6H_8Cl_2$: C, 47.72; H, 5.34. Found: C, 48.22; H, 5.43.

(ii) **3-(Dichloromethyl)-1,1′-bisbicyclo[1.1.1]pentane.** ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 12 H, 2-, 4-, 5-, 2′-, 4′-, 5′-H_2), 2.39 (s, 1 H, H-3′), 5.69 (s, 1 H, $CHCl_2$). ^{13}C NMR ($CDCl_3$): δ 26.69 (CH), 38.23 (C), 43.43 (C), 44.28 (C), 47.58 (CH_2), 49.19 (CH_2), 72.39 (CH). MS (70 eV): *m/e* 153 (2), 139 (29), 130 (16), 117 (31), 105 (48), 91 (100), 67 (37). Anal. Calcd for $C_{11}H_{14}Cl_2$: C, 60.85; H, 6.50. Found: C, 60.89; H, 6.50.

B. 1-(Trichloromethyl)bicyclo[1.1.1]pentane (10b). 10b was obtained in 81% yield in analogy to **10a** from **13** in ether[16] irradiated for 16 h in chloroform. For spectroscopic characterization of **10b**, see ref 5.

C. 1-(Trichloro[^{12}C]methyl)[3-D]bicyclo[1.1.1]pentane (10e). A solution of **13** (2.01 g, 30.4 mmol, free of solvent, prepared according to ref 17) in 25 mL of [^{12}C]deuteriochloroform (^{13}C content <5% of natural abundance) was irradiated in a quartz reaction vessel for 60 h with a high-pressure mercury lamp. Distillative workup afforded **10e** (720 mg, 13%). ^{1}H NMR ($CDCl_3$): δ 1.99 (s, 6 H, 2-, 4-, 5-H_2).

D. 1-Bromo-3-(dibromomethyl)bicyclo[1.1.1]pentane (10c). 10c was obtained in 93% yield following the procedure of Michl et al.[7]

E. 1-Iodo-3-(dichloromethyl)bicyclo[1.1.1]pentane (10d). A solution of **13** (71.0 mmol) in ether[13] and dichloroiodomethane (21.1 g, 100 mmol) was stirred for 16 h at room temperature. The solvent was removed in vacuo, and the excess $CHICl_2$ at 0 °C (bath)/0.001 Torr. The remaining slightly yellow solid was recrystallized from petrol ether, giving rise to **10d** (18.8 g, 96%) as colorless crystals of mp 71–72 °C. ^{1}H NMR ($CDCl_3$): δ 2.31 (s, 6 H, 2-, 4-, 6-H_2), 5.75 (s, 1 H, $CHCl_2$). ^{13}C NMR ($CDCl_3$): δ 4.44 (C), 51.79 (C), 58.04 (CH_2), 70.31 (CH). Anal. Calcd for $C_6H_7Cl_2I$: C, 26.02; H, 2.55. Found: C, 26.28; H, 2.70.

F. 1-Iodo-3-dichloro[^{12}C]methylbicyclo[1.1.1]pentane (10f). $^{12}CDCl_3$ (10.0 mL, 125 mmol) was treated with 50% aqueous NaOH (10 mL), NaI (50.0 g, 334 mmol, in 22 mL of water), and triethylbenzylammonium chloride (0.50 g, 2.3 mmol), as reported in the literature,[8] affording 2.02 g (8%) of [^{12}C]dichloroiodomethane.

$^{12}CHCl_2I$ (2.02 g, 9.58 mmol) was reacted with 9.50 mmol of **13** in ether, as described above for $CHCl_2I$. The yield of **10f** was 1.08 g (41%).

Reaction of 10 with Methyllithium. A. 10a and Methyllithium. 10a (6.48 g, 42.9 mmol) and MeLi (60 mL of a 1.60 M solution in ether, 96.0 mmol) were mixed at −78 °C and, under stirring, slowly warmed to about −18 °C. Starting at about −25 °C gas evolution was observed which came to an end after 15 min. The solution was stirred for 2 h at room temperature, followed by slow addition of 50 mL of water at −30 °C. The organic layer was separated and dried over $MgSO_4$, the solvent was removed under reduced pressure, and the volatile material of the oily residue was condensed at 20 °C/ 0.1 Torr into a trap cooled in a dry-ice bath, affording 1.84 g of a colorless oil. Further distillation at 20 °C (bath)/0.001 Torr led to the isolation of 1,2-dichloro-2-methylbicyclo[2.1.1]hexane (**15**) (795 mg, 11%) as a waxy material melting at about 25 °C. Preparative gas chromatography of the oily fraction (297 mg) afforded 1-(chloromethyl)bicyclo[1.1.1]pentane (**16**) (22 mg, total yield 2.7%), 1-chloro-2-methylbicyclo[2.1.1]hexane (**14**) (133 mg, total yield 15%), and 26 mg of a compound, the NMR data of which are in accord with 1-chloro-2-methylenebicyclo[2.1.1]hexane (**17**, total yield 2.9%).

In two further experiments **10a** (1.00 g, 6.62 mmol) was reacted with MeLi (32.0 mmol) (a) in ether followed by workup with D_2O and (b) in THF-d_8 followed by aqueous workup. No evidence of deuterium was found in the MS and NMR spectra of **15** isolated by gas chromatography.

(i) 14. ^{1}H NMR ($CDCl_3$): δ 1.09 (d, $J = 7$ Hz, 3 H, CH_3), 1.22 (dm, $J = 11$ Hz, 1 H, 3-H *cis* to Me), 1.58–1.65 (m, 1 H, *endo* 6-H), 1.68–1.76 (m, 2 H, *exo* 5-H, *exo* 6-H), 1.89 (m, 1 H, *endo* 5-H), 1.97 (dm, $J =$ 11 Hz, 1 H, 3-H *trans* to Me), 2.08–2.18 (m, 1 H, 2-H), 2.44 (narrow m, 1 H, 4-H). ^{13}C NMR ($CDCl_3$): δ 16.28 (CH_3), 32.62 ($J(^{13}C–^{1}H) = 158$ Hz, CH), 36.43 ($J(^{13}C–^{1}H) = 138$ Hz, CH_2), 37.63 ($J(^{13}C–^{1}H) = 132$ Hz, CH), 42.39 ($J(^{13}C–^{1}H) = 146$ Hz, CH_2, C-5), 48.93 ($J(^{13}C–^{1}H) = 142$ Hz, CH_2, C-6), 68.47 (C). MS (70 eV): *m/e* 129 (0.2, M^+), 117 (2), 115 (6), 95 (100), 91 (13), 89 (36), 79 (43). Anal. Calcd for $C_7H_{11}Cl$: C, 64.37; H, 8.49. Found: C, 65.27; H, 8.43. The structure of **14** was confirmed by an INADEQUATE NMR experiment (see Table 2).

(ii) 15. ^{1}H NMR ($CDCl_3$): δ 1.76 (s, 3 H, CH_3), 1.81 (dd, $J = 7.2$ and 10.0 Hz, 1 H, *endo* 6-H), 1.99 (dd, $J = 3.5$ and 7.2 Hz, 1 H, *exo* 6-H), 2.02 (dd, $J = 3.5$ and 6.9 Hz, 1 H, *exo* 5-H), 2.12 (dm, $J = 12.2$ Hz, 1 H, 3-H *trans* to Cl), 2.35–2.43 (m, 2 H, *endo* 5-H, 3-H *cis* to Cl), 2.56 (narrow m, 1 H, 4-H). ^{13}C NMR ($CDCl_3$): δ 27.09 (CH_3), 31.63 (CH), 45.37 (CH_2), 47.49 (CH_2), 46.61 (CH_2), 73.07 (C), 74.17 (C). MS (70 eV): *m/e* 129 (30, $M^+ - Cl$), 123 (13), 109 (79), 93 (100), 79 (56). HRMS: Calcd for $C_7H_{10}Cl$ [$M^+ - Cl$] 129.048, found 129.047. The structure of **15** was confirmed by an INADEQUATE NMR experiment (see Table 2).

(iii) 16. ^{1}H NMR ($CDCl_3$): δ 1.78 (s, 6 H, 2-, 4-, 5-H_2), 2.50 (s, 1 H, 3-H), 3.44 (s, 2 H, CH_2Cl).

(iv) 17. ^{1}H NMR ($CDCl_3$): δ 1.70 (m, 2 H, *exo* 5-H, *exo* 6-H), 2.11 (m, 2 H, *endo* 5-H, *endo* 6-H), 2.36 (m, 2 H, 3-H_2), 2.53 (m, 1 H, 4-H), 4.87 and 5.21 (2 m, 2 H, $H_2C{=}C$). ^{13}C NMR ($CDCl_3$): δ 30.41 (CH), 34.69 (CH_2), 48.98 (CH_2), 70.02 (C), 102.09 (CH_2), 148.41 (C).

B. 10b and Methyllithium. 10b (1.60 g, 8.63 mmol) was dissolved in 30 mL of a 1.6 M solution of MeLi in ether at −78 °C. Under stirring, the mixture was allowed to warm to room temperature. Aqueous workup and distillation of the oily residue of the organic layer. after removal of the ether afforded **15** (883 mg, 62%), bp 25 °C (bath)/0.001 Torr, which solidified in the icebox to a waxy mass.

C. 10e and Methyllithium. 10e (720 mg, 3.90 mmol) was added dropwise under stirring to 13.5 mL of a 1.78 M solution of MeLi in ether, cooled at −78 °C. Warming to room temperature, aqueous workup, and distillation afforded [1-^{12}C,4-D]-1,2-dichloro-2-methylbicyclo[2.1.1]hexane (**15***) (380 mg, 59%) as a colorless oil. ^{13}C NMR ($CDCl_3$): Identical to that of **15** with the exception of the signal at δ 73.07, which is absent in the spectrum of **15***, and the signal at δ 31.63, which is shifted to δ 31.32 and appears as a triplet.

Reaction of 10 with Strong Bases in the Presence of Trapping Reagents. A. 10a, Methyllithium, and 2,5-Dimethylfuran. MeLi in ether (18 mL of an 1.8 M solution) was added dropwise under stirring to a solution of **10a** (4.00 g, 26.5 mmol) in 30 mL of 2,5-dimethylfuran at −10 °C. Each drop of MeLi solution caused an immediate gas evolution. After addition of MeLi, the mixture was stirred for 1 h at room temperature. Hydrolytic workup and distillation of the organic part afforded 1,3-dimethyl-2-oxabicyclo[3.1.0]hex-3-ene-6-spiro-2′-(1′-chlorobicyclo[2.1.1]hexane) (**24a**) (1.60 g, 29%) as a colorless semisolid mass of bp 30 °C (bath)/0.001 Torr. IR (KBr): 2990, 2953, 2929, 2875, 1655, 1442, 1380, 1271, 1202, 1060, 960, 946, 849, 741 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.47 (q, $J = 1.3$ Hz, 1 H, 5-H), 1.71 (s, 3 H, CH_3), 1.76 (dd, $J = 1.3$ and 0.7 Hz, 3 H, CH_3), 1.91–1.98 (m, 2 H, *endo* 5′-H, *endo* 6′-H), 2.03–2.13 (m, 2 H, *exo* 5′-H, *exo* 6′-H), 2.14 (narrow m, 2 H, 3′-H_2), 2.57 (narrow m, 1 H, 4′-H), 4.76 (m, 1 H, 4-H). ^{13}C NMR ($CDCl_3$): δ 12.80 (CH_3), 14.44 (CH_3), 29.26 (CH, $J(^{13}C–^{1}H) = 170$ Hz), 30.39 (CH_2, $J(^{13}C–^{1}H) = 133$ Hz), 31.14 (CH, $J(^{13}C–^{1}H) = 160$ Hz), 31.93 (C), 48.70 (CH_2, $J(^{13}C–^{1}H) = 150$ Hz), 50.29 (CH_2, $J(^{13}C–^{1}H) = 150$ Hz), 65.34 (C), 71.20 (C), 98.29 (CH, $J(^{13}C–^{1}H) = 173$ Hz), 154.40 (C). MS (70 eV): *m/e* 210 (16, M^+), 195 (10), 175 (100), 169 (23). HRMS: Calcd for $C_{12}H_{15}ClO$ 210.081, found: 210.080. Anal. Calcd for $C_{12}H_{15}ClO$: C, 68.41; H, 7.18. Found: C, 69.09; H, 7.23.

B. 10c, Sodium Bis(trimethylsilyl)amide, and Cyclohexene. A solution of **10c** (5.90 g, 18.5 mmol) in 10 mL of cyclohexene was added to a suspension of sodium bis(trimethylsilyl)amide (3.76 g, 22.2 mmol) in 100 mL of cyclohexene at room temperature, and the mixture, which turned from colorless to dark brown, was stirred for 16 h. After the reaction was quenched with water, the organic layer was dried over $MgSO_4$, the volatile material was removed under reduced pressure, and the oily residue was flash chromatographed over silica gel (230–400 mesh) with petrol ether to give bicyclo[4.1.0]heptane-7-spiro-2′-(1′,4′-dibromobicyclo[2.1.1]hexane) (**25**) (570 mg, 10%) as colorless crystals of mp 62–65 °C, followed by 1,2,4-tribromobicyclo[2.1.1]hexane (**26**) (920 mg, 16%) as colorless crystals of mp 37–40 °C.

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[17] Alber, F.; Szeimies, G. *Chem. Ber.* **1992**, *125*, 757–758.

(i) 25. IR (KBr): 3008, 2931, 2851, 1446, 1260, 1251, 1196, 892 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.60 (m, 4 H, 3-, 4-H$_2$), 1.24 and 1.41 (2 m, each 2 H, 2-, 5-H$_2$ in unknown order), 1.92 (m, 2 H, 1-, 6-H), 2.00 (narrow m, 2 H, 3′-H$_2$), 2.39–2.46 (m, 4 H, 5′-, 6′-H$_2$). ^{13}C NMR (CDCl$_3$): δ 12.18 (2 CH), 19.91 (2 CH$_2$), 21.56 (2 CH$_2$), 36.46 (C), 38.55 (CH$_2$), 47.30 (C), 56.65 (C), 57.64 (2 CH$_2$). Anal. Calcd for $C_{12}H_{16}Br_2$: C, 45.03; H, 5.04. Found: C, 45.42; H, 4.91. The structure of **25** has been established by X-ray analysis.

(ii) 26. ^{1}H NMR (CDCl$_3$): δ 2.25 (m, 1 H, *endo* 6-H), 2.40 (m, 1 H, 3-H *trans* to Br), 2.49 (m, 2 H, *exo* 5-H, *exo* 6-H), 2.75 (m, 1 H, *endo*-5-H), 2.85 (m, 1 H, 3-H, *cis* to Br), 4.45 (m, 1 H, 2-H). ^{13}C NMR (CDCl$_3$): δ 45.31 (C), 48.79 (CH$_2$), 52.72 (C), 53.49 (CH$_2$), 54.73 (CH$_2$), 54.91 (CH). Anal. Calcd for $C_6H_7Br_3$: C, 22.60; H, 2.21. Found: C, 23.21; H, 2.27. The structure of **26** has been established by X-ray analysis.

C. 10d, Sodium Bis(trimethylsilyl)amide, and Tetramethylethylene. In identical fashion, sodium bis(trimethylsilyl)amide (6.61 g, 36.0 mmol) and **10d** (9.00 g, 32.5 mmol) reacted in 50 mL of tetramethylethylene to afford, after flash chromatography, 1-chloro-4-iodobicyclo[2.1.1]hexane-2-spiro-1-(2′,2′,3′,3′-tetramethylcyclopropane) (**27**) (1.09 g, 10%) as colorless crystals of mp 63–64 °C and 1,2-dichloro-4-iodobicyclo[2.1.1]hexane (**28**) (2.15 g, 25%) as semisolid material.

(i) 27. ^{1}H NMR (CDCl$_3$): δ 0.96 (s, 6 H, CH$_3$), 1.31 (s, 6 H, CH$_3$), 2.16 (s, 2 H, 3-H$_2$), 2.43 (s, 4 H, 5-, 6-H$_2$). ^{13}C NMR (CDCl$_3$): δ 15.92 (C), 17.12 (CH$_3$), 21.31 (CH$_3$), 23.89 (C), 40.18 (C), 46.67 (CH$_2$), 60.53 (2 CH$_2$), 64.14 (C). MS (70 eV): *m/e* 326 (0.5), 324 (M$^+$, 1.21), 199 (25), 197 (82), 161 (92), 141 (68), 121 (100), 119 (67), 105 (97). Anal. Calcd for $C_{12}H_{18}ClI$: C, 44.40; H, 5.59. Found: C, 44.52; H, 5.67.

(ii) 28. ^{1}H NMR (CDCl$_3$): δ 2.21 (dd, J = 7.1 and 9.6 Hz, 1 H, *endo* 6-H), 2.32–2.38 (m, 2 H, *exo* 6-H, 3-H *trans* to Cl), 2.46 (dd, J = 7.1 and 3.7 Hz, 1 H, *exo* 5-H), 2.67 (dd, J = 9.6 and 7.1 Hz, 1 H, *endo* 5-H), 2.82 (ddd, J = 12.2, 8.0, and 2.9 Hz, 1 H, 3-H *cis* to Cl), 4.27 (dt, J = 8 and 2 Hz, 1 H, 2-H). ^{13}C NMR (CDCl$_3$): δ 12.56 (C–I), 51.76 (CH$_2$), 53.42 (CH$_2$), 56.20 (CH$_2$), 61.94 (CH), 65.34 (C–Cl). The structure of **27** was further confirmed by a ^{13}C,^{13}C INADEQUATE experiment.

The reaction described above was repeated without tetramethylethylene using **10f** (1.08 g, 3.90 mmol) instead of **10d** and sodium bis(trimethylsilyl)amide (847 mg, 4.62 mmol), leading to **28*** (210 mg, 20%). The ^{13}C NMR spectrum of **28*** was identical to that of **28**; however, the signal at δ 65.34 (C1) was completely absent.

D. 10d, Sodium Bis(trimethylsilyl)amide, and Triethylsilane. A solution of **10d** (2.77 g, 10.0 mmol) in 50 mL of pentane was added dropwise under stirring to a suspension of sodium bis(trimethylsilyl)amide (2.05 g, 11.2 mmol) in 50 mL of pentane and triethylsilane (3.49 g, 30.0 mmol) at 0 °C. The mixture was allowed to warm to room temperature and was then stirred for 16 h. After hydrolysis, the organic layer was dried over MgSO$_4$, the solvent was removed under reduced pressure, and the oily residue was flash chromatographed with petrol ether. The material with the highest R_F value consisted of a mixture of triethylsilane and 1-chloro-2-(triethylsilyl)-4-iodobicyclo[2.1.1]hexane (**29**). Removal of triethylsilane at 25 °C/0.001 Torr afforded **29** (1.20 g, 34%) as a colorless oil. IR (film): 2999, 2954, 2910, 2876, 1465, 1457, 1420, 1267, 1254, 1232, 1205, 1158, 1036, 1010, 987, 880, 734. ^{1}H NMR (CDCl$_3$): δ 0.52–0.66 (m, 6 H, Si–CH$_2$), 0.91 (t, J = 6 Hz, 9 H, CH$_3$), 1.65–1.70 (m, 1 H, 3-H), 2.08–2.14 (m, 4 H), 2.25–2.36 (m, 2 H). ^{13}C NMR (CDCl$_3$): δ 3.27 (CH$_2$), 7.58 (CH$_3$), 17.22 (C), 33.73 (CH), 44.22 (CH$_2$), 55.74 (CH$_2$), 60.98 (CH$_2$), 63.80 (C). Anal. Calcd for $C_{12}H_{22}ClISi$: C, 40.40; H, 6.22. Found: C, 40.52; H, 6.02.

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Supplementary Material Available: X-ray characterization data for **25–27** including ORTEP plots and tables of distances and angles, fractional atomic coordinates, and thermal parameters, and results of ab initio calculations on **19–21**, **32**, and **33** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.