Preparation, Characterization and Stereochemistry of 2-Methyl-2-silabicyclo[2.2.1]heptane Derivatives[1)]

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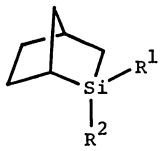
A new class of bicyclic compounds containing a single silicon atom at the bridge, 2-exo- and endo-substituted 2-methyl-2-silabicyclo[2.2.1]heptanes, have been prepared from the corresponding 3-cyclopentenylmethylhydrosilane by the intramolecular hydrosilylation catalyzed by chloroplatinic acid, and their structures were unquivocally assigned by ^1H and ^{13}C NMR spectra. Dramatic crossover from inversion to retention was found in the phenylation of chlorosilanes with phenyllithium and phenylmagnesium bromide in ether. Regio- and stereoselective insertion of dichlorocarbene generated from phenyl(bromodichloromethyl)mercury, or from chloroform and sodium hydroxide in the presence of a phase transfer catalyst, into $C_{(6)}$-$H_{(exo)}$ bond of 2-silanorbornanes has been observed.

In spite of a large number of publications relating to silacycloalkanes, little attention has been paid to a class of bicyclic organosilicon compounds, except for bridgehead silicon compounds. We have prepared 2-silabicyclo[2.2.1]heptanes (**1**—**5**) by the intramolecular hydrosilylation of (3-cyclopentenylmethyl)hydrosilanes. Very recently Cremer and Blankenship have also reported the preparation of 2-silanorbornanes (**2** and **5**).[2)] Now we report our own results with respect to their characterizations by spectroscopic methods, some interesting stereochemical behaviors on the silicon atom and a remarkably regio- and stereoselective insertion of dichlorocarbene into the $C_{(6)}$ carbon–hydrogen bond.



1 , $R^1=R^2=CH_3$
2a, $R^1=CH_3$, $R^2=H$: **2b**, $R^1=H$, $R^2=CH_3$
3a, $R^1=CH_3$, $R^2=C_6H_5$: **3b**, $R^1=C_6H_5$, $R^2=CH_3$
4a, $R^1=CH_3$, $R^2=i\text{-PrO}$: **4b**, $R^1=i\text{-PrO}$, $R^2=CH_3$
5a, $R^1=CH_3$, $R^2=Cl$: **5b**, $R^1=Cl$, $R^2=CH_3$

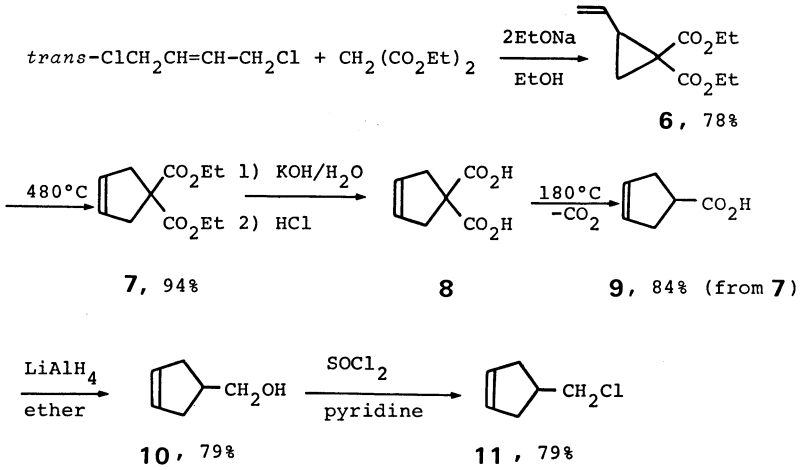
Hitherto optically active silicon compounds have been used almost exclusively in order to investigate the stereochemical behavior of reactions on a silicon atom.[4)] We have felt frequently, however, that these compounds give rise to rather limitations for exploring the stereochemistry of some reactions, *e.g.*, arylations or dearylations, since substituents in the case of optically active silicon compounds are mostly restricted in their kinds. After desiring to produce a quite new system involving geometrical isomers in organosilicon chemistry for several years,[3)] we recently realized this vision by means of the synthesis of 4-*t*-butylsilacyclohexane derivatives.[5)]

The present system possesses a similar molecular structure to the parent norbornane which shows a lot of unique reactivities in ionic[6)] and free radical process,[7)] and at the same time indicates practically the following merits to investigate the stereochemistry: (a) preparation of objective compounds is easily attained in good yield if we use the intramolecular hydrosilylation catalyzed by a transition metal, the procedure of which was already established;[9,10)] (b) resolution of exo and endo isomers is easy by GLC; (c) two isomers are determined by ^1H NMR because the chemical shift of Si–CH_3 protons is characteristic for each isomer; (d) hence it is possible to discuss the stereochemistry of reactions by using both of the geometrical isomers without optical resolution; (e) accordingly a small amount of substrate is sufficient to study the stereochemical behavior by NMR spectroscopy.

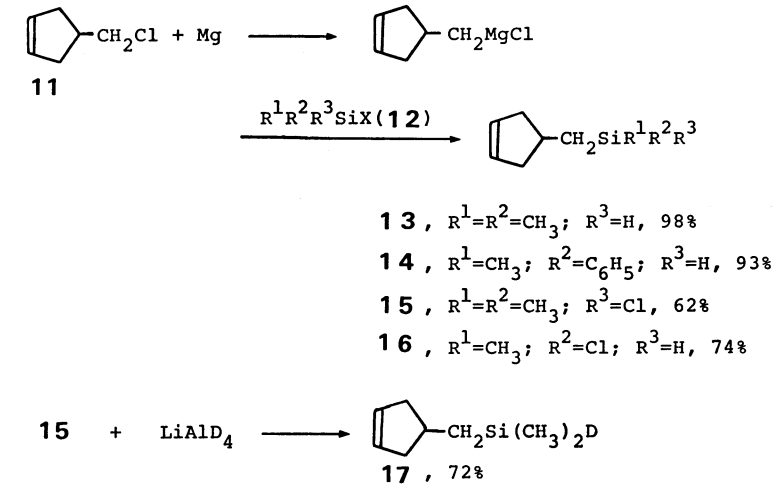
Results and Discussion

Preparation and Characterization. First 3-cyclopentenylmethyl chloride(**11**), the starting alkyl chloride, was prepared from *trans*-1,4-dichloro-2-butene and diethyl malonate in the presence of two equivalents of sodium ethoxide by a six-step synthesis through diethyl 2-vinyl-1,1-cyclopropanedicarboxylate (**6**), diethyl 3-cyclopentene-1,1-dicarboxylate (**7**), 3-cyclopentene-1,1-dicarboxylic acid (**8**), 3-cyclopentenecarboxylic acid (**9**), 3-cyclopentenylmethanol (**10**), as follows (Scheme 1).

The Grignard reagent from **11** in ether as well as (3-cyclopentenylethyl)magnesium bromide[8)] was quite stable, and did not cause any intramolecular cyclization due to the participation of a carbanionic carbon in the olefinic double bond. The addition of bromodimethylsilane and chloromethylphenylsilane to this solution afforded (3-cyclopentenylmethyl)dimethylsilane (**13**) and (3-cyclopentenylmethyl)methylphenylsilane (**14**), respectively, which were the precursors of 2-silanorbornanes, in good yields. (3-Cyclopentenylmethyl)chloromethylsilane (**16**) was prepared by the inverse addition of the Grignard reagent to excess dichloromethylsilane. Analogously (3-cyclopentenylmethyl)dimethyldeuteriosilane (**17**) was derived by the lithium aluminum deuteride reduction of (3-cyclopentenylmethyl)chlorodimethylsilane (**15**) which was conveniently obtained by the inverse addition of the Grignard reagent to dichloromethylsilane. (Scheme 2)



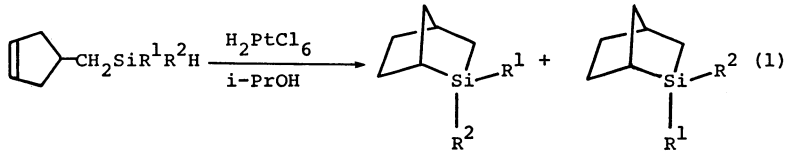
Scheme 1. Synthesis of 3-cyclopentenylmethyl chloride (**11**).



Scheme 2. Synthesis of (3-cyclopentenylmethyl)hydrosilanes (**13**—**17**).

During the investigation of transition metal-[9,10] or free radical-[9]catalyzed hydrosilylation, we[9] and Swicher *et al.*[10] had found that the intramolecular hydrosilylation took place more favorably and easily rather than the intermolecular reaction, provided that a double bond and a silicon–hydrogen bond were separated by three methylene groups, so that this should offer a general and good method to prepare a five or six membered ring compound. Accordingly it will be quite reasonable to consider that the bicyclic compounds involving a silicon atom could be derived intramolecularly from the hydrosilane which involves a cyclic olefin separated by three carbon atoms.

When a neat solution of (3-cyclopentenylmethyl)-dimethylsilane (**13**) was heated in the presence of a catalytic amount of chloroplatinic acid at 130 °C for 100 h in a sealed tube, 2,2-dimethyl-2-silabicyclo[2.2.1]-heptane (**1**) was obtained in 82% yield. Analogously, in the case of R^1=Me and R^2=Ph or Cl, the products **3** and **5** consisting of a mixture of two geometrical isomers at the ratio of *exo*-Me:*endo*-Me=65:35 or 63:37, respectively, were prepared in good yields (Eq. 1). More elevated temperature was required for the cyclization to bicyclic compounds than for that to a monocyclic compound as reported earlier.[9,10] Palladium on charcoal was also effective as a catalyst but free radical initiators not so good.

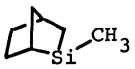
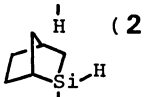
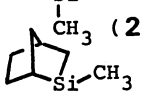
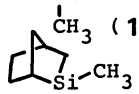
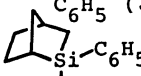
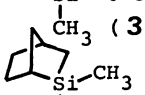
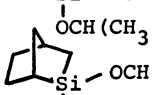


13, $R^1=R^2=CH_3$ **1**, $R^1=R^2=CH_3$

14, $R^1=CH_3$; $R^2=C_6H_5$ **3a**, $R^1=CH_3$; $R^2=C_6H_5$ **3b**, $R^1=CH_3$; $R^2=C_6H_5$

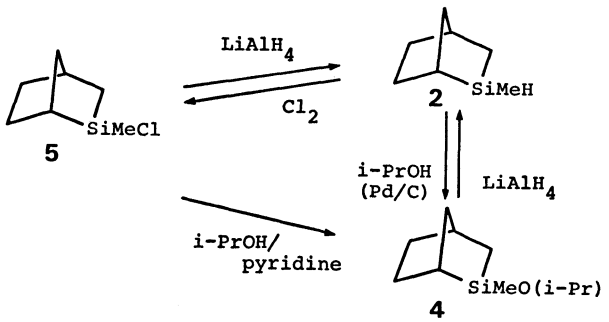
16, $R^1=CH_3$; $R^2=Cl$ **5a**, $R^1=CH_3$; $R^2=Cl$ **5b**, $R^1=CH_3$; $R^2=Cl$

Table 1. ^{13}C NMR chemical shifts[a] of 2-silanorbornanes

	C_1	C_3	C_4	C_5	C_6	C_7	2-*exo*-CH_3	2-*endo*-CH_3
 (2a)	22.0	18.0	35.9	30.5	24.9	37.4	−4.9	
 (2b)	22.0	17.0	36.8	30.9	23.2	38.9		−7.8
 (1)	23.5	21.0	36.5	30.6	23.5	38.1	−2.3	−4.9
 (3a)[b]	24.0	19.0	36.7	30.8	23.4	38.9	−2.8	
 (3b)[c]	23.6	19.9	36.8	30.9	23.6	39.1		−5.2
 (4a)[d]	21.7	19.6	35.9	30.3	23.9	36.6	1.4	
 (4b)[e]	21.7	21.7	34.8	29.7	23.2	37.5		−1.0

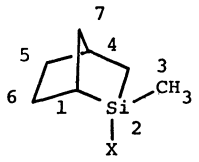
a) δ (ppm), downfield from TMS (0.00 ppm) in $CDCl_3$–$CHCl_3$ (2:1). b) The aromatic carbons resonated at 134.8, 128.0, 129.3 and 137.1 ppm (*o*, *m*, *p*, and *ipso* carbon, respectively). c) The aromatic carbons resonated at 134.1, 127.8, 128.9 and 138.6 ppm (*o*, *m*, *p*, and *ipso* carbon, respectively). d) The methine and methyl carbon of the isopropyl group resonated at 65.6 and 25.0 ppm, respectively. e) 65.3 and 25.0 ppm for the methine and methyl carbon.

Compounds **2** and **4** were mutually prepared from the chlorosilane **5** by the following transformations. (Scheme 3)

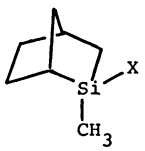


Scheme 3. Mutual transformations between **2**, **4**, and **5**.

Each of stereoisomer of **3** and **4** was readily isolated by fractional distillation and subsequent preparative GLC (Apiezon L, 20% 5 m) collection. In all the compounds investigated in this report the silicon atom has beared at least one methyl group, so that the exo and endo isomers were defined with respect to the methyl group throughout the paper for avoiding confusion. Thus, the exo means that the methyl group orients to exo direction and suffix a is given. Analogously the endo means its geometrical isomer and suffix b is given.



exo: a



endo: b

The unequivocal assignment of the stereochemistry of 2-silanorbornanes could be achieved on the basis of the ^1H and ^{13}C NMR spectroscopic studies where **2a** and **2b** were used. Although neither isomer of **2** could be isolated by GLC collection, a 200 MHz ^1H NMR spectrum of approximately 1:2 mixture of **2a** and **2b** shows that the characteristic signals due to Si–CH_3 and Si–H appear at δ 0.03 (d, J=4.0 Hz) and 0.12 (d, J=4.0 Hz) (3H as a total), and δ 3.72 (m) and 3.87 (m) (1H as a total), respectively. The signals due to 3-exo and 3-endo protons of **2a** and **2b** appear at δ 0.48 (m) as an unseparable multiplet peak, and at δ 0.07 (m) and 0.80 (m), respectively, in a integral ratio of approximately 4:1:1 (2H as a total). $H_{(1)}$, $H_{(4)}$, and $H_{(5),(6),(7)}$ signals of **2a** and **2b** are obtained as peaks which resonate at δ 1.4 (m), 2.5 (m) and 0.9—1.8 (m), respectively, in a ratio of 1:1:6. Irradiation of the higher field Si–CH_3 signal reveals a quartet of the Si–H proton, since the coupling constants due to three vicinal protons, $H_{(1)}$, $H_{(3exo)}$ and $H_{(3endo)}$, become equal (J=2.5 Hz) fortuitously. Thus, small $J_{(2),(3endo)}$ and $J_{(2),(3exo)}$ suggest that this isomer should be the exo (**2a**). On the other hand

Table 2. Si-CH_3 Proton chemical shifts of 2-silanorbornanes[a]

Compound	*exo*-CH_3	*endo*-CH_3	Δ[b]
1	0.03	0.09	0.06
2	0.03	0.12	0.09
3	0.35	0.40	0.05
4	0.17	0.22	0.05
5	0.50	0.55	0.05

a) δ (ppm) from TMS in CCl_4. b) Difference in exo-endo methyl proton (ppm).

decoupling of Si–H signal in a lower field reveals that $J_{(2),(3exo)}$ is 5.5 Hz. Therefore this compound should be identified as the endo isomer (**2b**).

2-Silanorbornanes have a similar trend, though in a smaller extent, not only in the coupling constants but also in the chemical shifts originating in the exo and endo Si–H protons as is generally observed for the ^1H NMR spectra of norbornane derivatives.[11] The absorption of the 2-exo proton attached to a silicon appeared as a somewhat broad peak at 0.15 ppm lower field than the corresponding endo proton. Clearly it has been found that NMR spectra are most convenient and effective to investigate the stereochemistry in these systems.

These assignments were further supported by the ^{13}C NMR spectra shown in Table 1. The chemical shifts were decided relatively by their comparison with those of the norbornane systems, using both wide-band ^1H decoupled and off-resonance decoupling experiments. The $^{13}C_{(6)}$ carbon chemical shift is distinctly assigned by the complete decoupling of the $C_{(6)}$-deuterium labelled compound.

Depending upon the stereochemistry of a silicon bearing a methyl group, the $C_{(7)}$ carbon in **2a** and the $C_{(6)}$ carbon in **2b** revealed slightly up-field shifts by 1.5 ppm and 1.7 ppm, compared with the corresponding carbons in **2b** and **2a**, respectively. In general, it is well established that both of ^{13}C chemical shifts of two carbons which approach spatially each other cause up-field shift.[12] This phenomenon is called the steric compression shift.[13] Therefore, the upfield shifts associated with $C_{(6)}$- and $C_{(7)}$-carbons in each isomer could be reasonably explained by the steric shift.

The stereochemistry of **3a** and **3b**, and **4a** and **4b** is analgously determined by the results arising from ^{13}C NMR steric shift. Supporting evidence of the assignment with respect to the stereochemistry was further obtained from the results that the methyl group on the silicon atom in all these bicyclic systems exhibited configurationally dependent shieldings[13c] with endo groups more shielded than their exo counterparts (See Table 2). Thus the structures determined by the ^{13}C NMR spectra are in doubtless consistent with those assigned by ^1H NMR spectra. The relationship and some characteristics in ^1H and ^{13}C NMR spectra between 2-silanorbornane and norbornane derivatives[13c] are shown in Table 3.

Throughout these series, the exo isomers have shorter retention times on GLC (Apiezon L and SE 30) than do the endo ones, and in the IR spectra, although only groups of absorption bands characteristic of C–H and Si–CH_3 stretching were observed, any characteristic bands to be attributed to the bicyclic structure did not appear. The IR spectra therefore could not be effectively applied for the structural analysis so much.

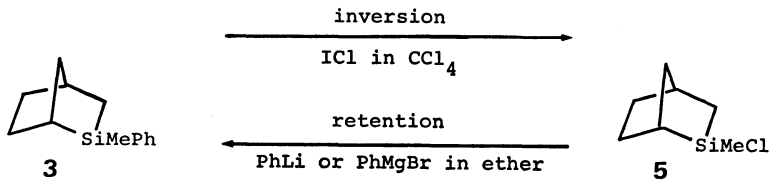
Stereochemistry on a Silicon Atom. There have been extensively systematized studies with respect to the stereochemistry on an asymmetric silicon atom in a number of different chiral organosilane systems.[4] As results, it is known that the predominant stereochemistry depends largely on the nature of leaving groups and entering groups and frequently the solvent but not usually on the nature of substituents, even if the cis and trans geometrical isomers such as a series of 4-*t*-butylsilacyclohexanes were used.[5] However dramatic crossover from inversion to retention has been recently reported on the stereochemistry of some optical and geometrical isomers in which strained carbon-silicon bonds were substantially involved.[14–16]

Our new stereochemical systems may be suitable for the tests of the effect of angle strain at the silicon because of their longer Si–C bond length than C–C bond length in norbornanes.[17]

An interesting example of stereochemical behavior can be found in the case of phenylation of the chlorosilanes with both the Grignard reagent and the lithium reagent in ether. The results are shown in Table 4 along with some other stereochemical reactions (Scheme 4). Thus the result in which the chlorine atom in **5a** and **5b** was displaced in highly retentive way (>92% predominant stereochemistry) with both phen-

Table 3. Relationship and characteristics between 2-silanorbornanes and norbornanes in ^1H and ^{13}C NMR spectra

	2-Silanorbornanes	Norbornanes[11]
Coupling constants	$Si_{(2)}H_{(exo)}$-$C_{(3)}H_{(exo)}$ 5.5 Hz $Si_{(2)}H_{(endo)}$-$C_{(3)}H_{(exo)}$ 2.5 Hz $Si_{(2)}H_{(endo)}$-$C_{(3)}H_{(endo)}$ 2.5 Hz	$C_{(2)}H_{(exo)}$-$C_{(3)}H_{(exo)}$ 9—10 Hz $C_{(2)}H_{(endo)}$-$C_{(3)}H_{(exo)}$ 2.5—5.0 Hz $C_{(2)}H_{(endo)}$-$C_{(3)}H_{(endo)}$ 6.7 Hz
Chemical shift (^1H)	Si-H; endo upfield Si-CH_3; exo upfield	C-H; endo upfield
Chemical shifts (^{13}C)	Si-CH_3; endo upfield	C-CH_3; endo upfield



Scheme 4. Stereochemistry on a silicon atom.

Table 4. Stereochemistry on silicon atom

Reaction	Substrate	Proedominant Stereochemistry (%)[a]
Chlorodephenylation with ICl in CCl_4 at r.t.	3a	Inversion 86.0
	3b	Inversion 77.5
Phenylation with PhLi in Et_2O at r.t.	5a	Retention 95.6
	5b	Retention 92.9
Phenylation with PhMgBr in Et_2O at r.t.	5a	Retention 97.4
	5b	Retention 96.5
Chlorination with Cl_2 in CCl_4	2a:2b =71:29	Retention 5a:5b=71:29

a) 90% retention means that the product was 90% retained and 10% inverted, if the pure starting material was used.

yllithium and phenylmagnesium bromide might be attributed to the angle strain.[16] In sharp contrast, however, Sommer et al. have observed that the inversive reaction *via* S_N2-Si mechanism took place in the reaction of the asymmetric chlorosilane with both organolithium and Grignard reagents[4,18] and we have also found the similar configuration inversion in 4-*t*-butylsilacyclohexane system,[19] in which the strained angle with the silicon will not be large in size so much.

On the other hand, the phenyl group was displaced by a chlorine atom with configuration inversion in the chlorodephenylation of **3**a and **3**b with iodine monochloride, in a manner analogous to that noted in our previous report.[19]

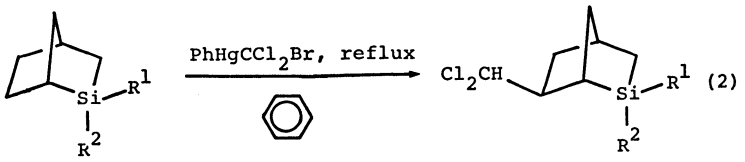
Reduction of **5** (**5**a:**5**b=83:17) with lithium aluminum hydride in ether gave the corresponding hydrosilane **2** (**2**a:**2**b=86:14) in quantitative yield. Interestingly the reduction of **5** (**5**a:**5**b=17:83) which was enriched by **5**b also led to a mixture of the similar composition of **2** (**2**a:**2**b=85:15). Apparently the equilibration to the thermodynamic controlled mixture of **2** occurred during the LAH reduction.[20]

Regio- and Stereoselective Dichlorocarbene Insertion into $C_{(6)}$–$H_{(6exo)}$ Bond of 2-Silabicyclo[2.2.1]heptanes.

The problem of the high exo:endo rate ratio in the solvolysis of 2-norbornyl system is a topic in physical organic chemistry during a few decades.[6,21–23] 2-Silabicyclo[2.2.1]heptanes might be favorable to investigate a hyperconjugating ability of a silicon-carbon bond to an incipient positive charge at $C_{(6)}$-carbon, because they provide not only a polarized but also highly strained carbon-metal σ bonds which could afford significantly large stabilization of neighboring cation.[22]

We have found an interesting dichlorocarbene insertion into 6-carbon–hydrogen exo bond of 2-silanorbornanes (Eq. 2). Important features of this reaction are (a) regiospecific β-CH bond insertion at $C_{(6)}$ position, although there are three kinds of β-CH bond in **1**, (b) the overwhelmingly predominant insertion into the exo CH bond.

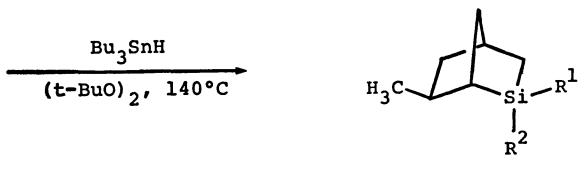
2,2-Dimethyl-2-silabicyclo[2.2.1]heptane (**1**) reacts



(2)

1 , R^1= R^2= CH_3
3a , R^1= CH_3; R^2= C_6H_5
3b , R^1= C_6H_5; R^2= CH_3

18 , R^1= R^2= CH_3
19a , R^1= CH_3; R^2= C_6H_5
19b , R^1= C_6H_5; R^2= CH_3



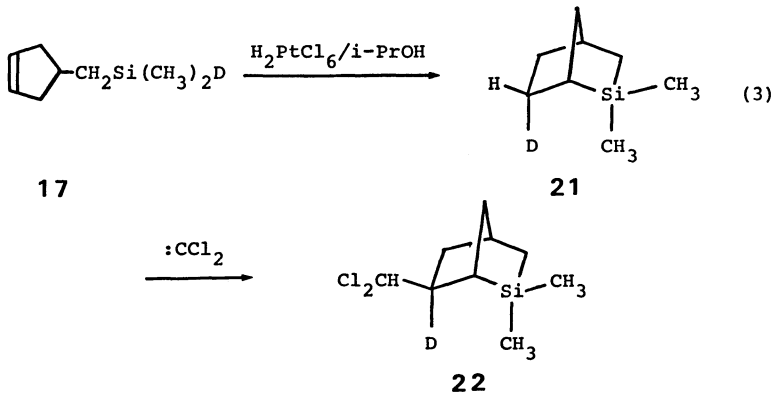
20, R^1= R^2= CH_3

with phenyl(bromodichloromethyl)mercury in benzene at reflux to give a corresponding dichlorocarbene insertion product **18** in 22% yield, along with the recovered **1**. Quite similarly, only **18** was obtained in 71% yield by the reaction of **1** with the dichlorocarbene *in situ* generated from chloroform and sodium hydroxide in benzene-water medium in the presence of benzyltrimethylammonium chloride at room temperature.[24] From the 200 MHz NMR spectrum, the presence of both doublet proton resonance at δ 5.43 (J=9.0 Hz) assigned as the dichloromethyl proton and triply doublet resonance at δ 2.43 (J=9.0 Hz, 9.0 Hz, 6.0 Hz) assigned as the $C_{(6)}$ proton bearing dichloromethyl group clearly led to the suggestion that this compound could be identified as 6-*exo*-dichloromethyl-2,2-dimethyl-2-silabicyclo[2.2.1]heptane (**18**). It was found that the insertion product **18** was derived to 2,2,6-*exo*-trimethyl-2-silabicyclo[2.2.1]heptane (**20**) by the reduction with tributyltin hydride in the presence of free radical initiator (Eq. 2). Analogously 2-*exo*- and 2-*endo*-phenyl derivatives (**3**a and **3**b) afforded exclusively regio- and stereoselective dichlorocarbene insertion products, **19**a and **19**b, respectively, by the reaction with phenyl(bromodichloromethyl)mercury.

The characteristic cracking patterns of the mass spectra have appeared in all of insertion products. Namely the cation in which a dichloromethyl group was removed from the molecular ion peak was strikingly strong, resulting in a base peak.

The stereochemistry and the position at which the insertion of dichlorocarbene occurred were further unambiguously established by the structural analysis of the reaction product when 6-*endo*-deuterium labelled compound (**21**) was utilized as a substrate (Eq. 3).

Thus 6-*endo*-deuterio-2,2-dimethyl-2-silabicyclo[2.2.1]-heptane (**21**), which was derived intramolecularly by the cis addition[25] of (3-cyclopentenylmethyl)-dimethyldeuteriosilane (**17**) catalyzed by chloroplatinic acid, gave exclusively the $C_{(6)}$–H but not $C_{(6)}$–D insertion product (**22**) whose proton NMR spectrum revealed singlet resonance at δ 5.43 and no signals at δ 2.43 in (**18**) (Eq. 3).



(3)

17 **21** **22**

In its mass spectrum, that the cation $[C_6H_{14}DSi]^+$ (m/e=140) appeared as a base peak would reveal the further evidence to demonstrate that the dichlorocarbene insertion was regio- and stereoselective.

Although the mechanism of insertion of the dichlorocarbene generated from phenyl(bromodichloromethyl)-mercury into C–H bonds has been investigated in details,[26] two distinct and important features should be instructive to discuss the present results. One is that the dichlorocarbene insertion takes place with retention with respect to the carbon configuration,[27] and the other is that only the activated C–H bonds such as α–CH bond of ethers,[28] β–CH bond of organometallic compounds[29] or tertiary CH bond,[30] show the enhanced reactivity due to the mildly electrophilic nature of free dichlorocarbene.[31] It is worth to note that, in our cases, the insertion of CCl_2 not only into the bridgehead tertiary C–H bond at $C_{(4)}$ but also into bridge methylene C–H bonds at $C_{(7)}$ could not compete at all with the insertion at $C_{(6)}$ position, although all of them were also located in β-position from the metal.

We suggest that the regio- and stereoselectivity in the present system, therefore, may be best understood in terms of the stabilization of the partial positive charge in exo direction in the transition state due to σ-π hyperconjugation using the strained carbon$_{(1)}$–silicon$_{(2)}$ σ bond. This represents a remarkably interesting example in which the existence of the stereoelectronic effect in σ-π hyperconjugation[32] was clearly demonstrated in chemical reactivity. The steric origin, leading to the high stereoselectivity, of course, should be appreciably considered, although it is hard to estimate precisely the steric effect in its extent. Studies on kinetics as well as products of hydride abstraction by trityl cation are presently in progress.

Experimental

General. All reactions were carried out under nitrogen. ^{1}H NMR spectra were recorded with Varian Associates T-60, HA-100 and XL-200 spectrometers. ^{13}C NMR spectra were taken with a Hitachi Perkin-Elmer R-26 spectrometer. GLC was used extensively in the analysis of reaction mixtures and for the isolation of products. Hitachi 063 for the analysis and Varian 90-P gas chromatographs for the collection were used. The columns packed with SE-30 silicone rubber gum or Apiezon L grease on Celite 545 were used. Mass spectra were taken with Hitachi RMU-6D and JEOL JMS-300D Mass spectrometers. Thin layer chromatography (TLC) was used to monitor the organomercurial reactions and to isolate the insertion products. Boiling points are uncorrected.

Bromodimethylsilane. According to the procedure of the S_H2 reaction of organodisilane with 1,2-dibromoethane,[33a] 1,2-dibromoethane (52.6 g, 0.28 mol) was added slowly to 1,1,2,2-tetramethyldisilane (33 g, 0.28 mol) in the presence a catalytic amount of dibenzoyl peroxide. During the addition, ethylene was evolved vigorously. The reaction mixture was distilled to give pure bromodimethylsilane[33b] (52.9 g, 68% yield). Bp 58 °C; NMR (CCl_4) δ 0.59 (6H, d, J=3.5 Hz, Si-CH_3), 4.80 (1H, septet, J=3.5 Hz, Si-H).

*Synthesis of Diethyl 2-Vinyl-1,1-cyclopropanedicarboxylate (**6**).* According to the procedure described in the literature,[34] the ester (**6**) (165 g) was obtained from sodium ethoxide (2.1 mol), diethyl malonate (160 g, 1.0 mol), and *trans*-1,4-dichloro-2-butene (125 g, 1.0 mol) in ethanol (1.5 l) in 78% yield. Bp 85 °C (2 mm) (lit,[34] 116—119 °C (16 mm)); NMR (CCl_4) δ 1.13 (3H, t, J=7.5 Hz, CH_3), 1.15 (3H, t, 7.5 Hz, CH_3), 1.33—1.59 (2H, m, cyclopropane-CH_2), 2.15—2.56 (1H, m, cyclopropane-CH), 4.07 (2H, q, J=7.5 Hz, CH_2), 4.08 (2H, q, J=7.5 Hz, CH_2), 4.85—5.47 (3H, m, CH=CH_2); IR (TF) 3100 (w), 2990 (s), 2850 (m), 1730 (s), 1640 (m), 1450 (m), 1375 (m), 1320 (m), 1275 (s), 1200 (s), 1130 (s), 1030 (m), 990 (w), 960 (w), 920 (m), 865 (s), 855 (m) cm^{-1}.

*Synthesis of 3-Cyclopentenecarboxylic Acid (**9**).*[34] The ester (**6**) (130 g, 0.61 mol) was pyrolyzed through a quartz tube at 480 °C to give diethyl 3-cyclopentene-1,1-dicarboxylate (**7**) (122 g, 94% yield). NMR (CCl_4) δ 1.21 (6H, t, J=7.5 Hz, CH_3), 2.91 (4H, s, cyclopentene-CH_2), 4.12 (4H, q, J=7.5 Hz, CH_2), 5.52 (2H, s, CH=). For the saponification, **7** (121 g, 0.57 mol), thus obtained, was heated with stirring with potassium hydroxide (100 g, 1.7 mol) in 80% ethanol (1 l) for 6 h. After evaporation of ethanol and water, the mixture was acidified with 6 M (1 M= 1 mmol dm^{-3}) hydrochloric acid and extracted with ether. The solvent was evaporated, and the residue was decarboxylated by heating at 180 °C and distilled to give pure 3-cyclopentenecarboxylic acid (**9**) 37.8 g (0.34 mol) in 84% yield. Bp 110 °C (22 mm) (lit,[34] 118—121 °C (20 mm)); NMR (CCl_4) δ 2.53—3.20 (5H, m, CH, CH_2), 5.61 (2H, s, CH=), 11.77 (1H, s, CO_2H); IR (TF) 3200 (s), 3050 (s), 2940 (s), 2850 (m), 1700 (s), 1640 (w), 1420 (m), 1340 (w), 1300 (m), 1230 (m), 1180 (m), 950 (m), 930 (m) cm^{-1}.

*Synthesis of 3-Cyclopentenylmethanol (**10**).*[35] The alcohol (**10**) (25 g, 0.255 mol) was obtained by the reduction of the carboxylic acid (**9**) (36.3 g, 0.324 mol) with lithium aluminum hydride (13.3 g, 0.35 mol) in ether (150 ml) in 79% yield. Bp 90 °C (50 mm) (lit,[35] 98—99 °C (57 mm)); NMR (CCl_4) δ 1.49—2.63 (5H, m), 3.39 (2H, d, J=6 Hz), 4.22 (1H, s), 5.57 (2H, s); IR (TF) 3400 (s), 3050 (m), 2930 (s), 2850 (m), 1650 (m), 1080 (m), 1040 (s), 950 (m), 940 (w), 900 (w) cm^{-1}.

*3-Cyclopentenylmethyl Chloride (**11**).* The alcohol (**10**) (31.9 g, 0.33 mol) was treated with thionyl chloride (42.9 g, 0.36 mol) in pyridine (28.2 g, 0.36 mol) under ice-cooling. After the mixture was heated moderately for an hour, the oily material was separated and immediately distilled under reduced pressure to give **11** (30.1 g, 79% yield). Bp 70 °C (94 mm); n_D^{20} 1.4698; NMR (CCl_4) δ 1.91—2.84 (5H, m, -CH_2-CH(CH_2Cl)CH_2-) 3.47 (2H, d, J=6 Hz, -CH_2Cl), 5.65 (2H, s, =CH-); IR (TF) 3075 (m), 2950 (s), 2850 (s), 1620 (w), 1580 (w) 1440 (s), 1340 (m), 1290 (m), 1210 (m), 1130 (m), 1060 (w), 1040 (w) cm^{-1}. Calcd for C_6H_9Cl: C, 61.81; H, 7.78%. Found: C, 61.98; H, 7.62%.

*(3-Cyclopentenylmethyl)dimethylsilane (**13**) and (3-Cyclopentenylmethyl)methylphenylsilane (**14**).* To the Grignard reagent prepared from 4.7 g (0.04 mol) of the chloride and 1.2 g (0.05 g-atom) of magnesium in 20 ml of dry ether was added 5.6 g (0.04 mol) of bromodimethylsilane. The mixture was stirred for 10 h and hydrolyzed. After work up as usual, distillation of the organic layer under reduced pressure gave 5.5 g (0.039 mol, 98% yield) of **13**. Bp 76 °C (74 mm); n_D^{20} 1.4504; NMR (CCl_4) δ 0.09 (6H, J=4 Hz, Si-CH_3) 0.71—1.04 (2H, m, Si-CH_2), 1.61—2.94 (5H, m, CH_2-CH-CH_2) 5.61 (2H, s, -HC=CH-); IR (TF) 3050 (m), 2900 (m), 2800 (s), 2100 (s), 1610 (w), 1440 (m), 1350 (m), 1250 (s), 1220 (s), 1110 (m), 1070 (m), 1040 (m), 940 (m), 850 (s) cm^{-1}; Mass *m/e* (rel intensity) 140 (11), 125 (11), 99 (60), 97 (78), 59 (100). Calcd for $C_8H_{16}Si$: C, 68.49; H, 11.50%. Found: C, 68.71; H, 11.50%. **14** (7.5 g, 0.037 mol) was analogously prepared from the Grignard reagent (from **11** (5.3 g) and magnesium (1.22 g)) and chloromethylphenylsilane[36] (6.25 mol, 0.04 mol) in 93% yield. Bp 102 °C (7 mm); n_D^{20} 1.5306; NMR (CCl_4) δ 0.29 (3H, d, J= 3.5 Hz, Si-CH_3), 0.91—1.11 (2H, m, Si-CH_2), 1.61—2.68 (5H, m, CH_2-CH-CH_2), 4.37 (1H, m, J=3.5 Hz, Si-H), 5.51 (2H, s, -HC=CH-), 7.21—7.61 (5H, m, C_6H_5); IR (TF) 3050 (s), 2100 (s), 1950 (w), 1880 (w), 1820 (w), 1760 (w), 1590 (w), 1490 (w), 1430 (s), 1330 (w), 1260 (s), 1120 (s), 880 (s), 840 (s) cm^{-1}. Calcd for $C_{13}H_{18}Si$: C, 77.61; H, 8.97%. Found: C, 77.29; H, 9.34%.

*(3-Cyclopentenylmethyl)dimethylchlorosilane (**15**) and (3-Cyclopentenylmethyl)chloromethylsilane (**16**).* The Grignard reagent prepared from 5.9 g (0.05 mol) of the chloride (**11**) and 1.5 g (0.06 g-atom) of magnesium in dry ether was added to a dilute ether solution of 10.4 g (0.08 mol) of dichlorodimethylsilane and the mixture was stirred for 10 h with refluxing. Filtration and fractionation of the organic layer gave 5.5 g (0.031 mol, 62% yield) of pure **15**. Bp 70 °C (19 mm); n_D^{20} 1.4626; NMR (CCl_4) δ 0.42 (6H, s, Si-CH_3); 1.05 (2H, d, J=6 Hz, Si-CH_2), 1.60—2.85 (5H, m, $(CH_2)_2C$ 1.05 (2H, d, J=6 Hz, Si-CH_2), 1.60—2.85 (5H, m, $(CH_2)_2CH$), 5.65 (2H, s, =CH-); IR (TF) 3020 (s), 2900 (s), 2820 (s), 2115 (s), 1610 (m), 1440 (m), 1345 (m), 1335 (m), 1240 (s), 1195 (m), 1105 (m), 1065 (m), 930 (s), 925 (s), 890 (s), 825 (s), 790 (m), 765 (m) cm^{-1}. Calcd for $C_8H_{15}ClSi$: C, 54.99; H, 8.65%. Found: C, 55.16; H, 8.64%.

From **11** (2.9 g, 0.025 mol), magnesium (0.73 g, 0.03 g-atom), and methyldichlorosilane (5.75 g, 0.050 mol), **16** (3.0 g, 0.019 mol) was obtained in 74% yield. Bp 73 °C (38 mm); NMR (CCl_4) δ 0.45 (3H, d, J=3.5 Hz, Si-CH_3), 0.94—1.24 (2H, m, Si-CH_2), 1.71—2.81 (5H, m, CH_2-CH-CH_2), 4.79 (1H, m J=3.5 Hz, Si-H), 5.62 (2H, s, -HC=CH-); IR (TF) 3050 (m), 2950 (s), 2900 (s), 2850 (s), 2160 (s), 1615 (m), 1440 (m), 1350 (m), 1250 (s), 1210 (m), 1110 (m br), 940 (m) cm^{-1}. Calcd for $C_7H_{13}ClSi$: C, 52.31; H, 8.15%. Found: C, 52.29; H, 8.24%.

*(3-Cyclopentenylmethyl)dimethyldeuteriosilane (**17**).* A 6.0 g (0.034 mol) of **15** was reduced with lithium aluminum deuteride (>99% D) (0.42 g, 0.01 mol) in ether. After work up as usual, distillation gave 3.5 g (0.0248 mol) of **17** in 72% yield. Bp 62 °C (34 mm); n_D^{20} 1.4513. The GLC retention time of the product on Silicone gum SE-30, Apiezon L or PEG 20M column was identical with that of the undeuterated material (**13**). NMR (CCl_4) δ 0.07 (6H, s, Si-CH_3) 0.80 (2H, d, J=6 Hz, Si-CH_2), 1.70—2.78 (5H, m, -CH_2-CH-CH_2), 7.64 (2H, s, =CH-) and no Si-D chemical shift. The infrared spectra showed Si-D band at 1532 cm^{-1} and Si-CH_3 band at 1234 cm^{-1}. IR (TF) 3000 (m), 2930 (s), 2870 (s), 2800 (s), 1610 (w), 1540 (m), 1532 (s), 1440 (w), 1350 (w), 1234 (s), 1190 (w), 1100 (w), 1065 (m), 930 (s), 890 (w), 830 (s), 790 (m) cm^{-1}; MS *m/e* (rel intensity) 141 (M^+, 16.5), 126 (M^+-CH_3, 43.5), 100 (54), 99 (64), 98 (79.5), 97 (64), 60 (100), 59

(55.5). A deuterium analysis by the peak ratio at M^+-15 (126/125) by mass stectrum showed 94% replacement of one hydrogen by deuterium. Calcd for $C_8H_{15}DSi$ (d content 94%): C, 68.03; H (D), 12.09%. Found: C, 67.46; H (D), 11.97%.

*Preparation of 2-Silanorbornanes (**1**, **3**, and **5**) by Intramolecular Hydrosilylation. 2,2-Dimethyl-2-silabicyclo[2.2.1]heptane (**1**)*: **13** (2.5 g, 0.018 mol) was placed together with a catalytic amount of chloroplatinic acid in isopropyl alcohol (10^{-2} M, 2 μl) in a glass tube. The tube was sealed and immerced in an oil bath kept constant temperature at 130 °C for 100 h, and then opened. Distillation gave the product (**1**) (2.2 g, 82% yield). Bp 60 °C (38 mm); n_D^{20} 1.4735; NMR (CCl_4) δ 0.03 (3H, s, Si-$CH_{3(exo)}$), 0.09 (3H, s, Si-$CH_{3(endo)}$), 0.20 (1H, d, $J_{(3exo),(3endo)}=14$ Hz, $H_{(3endo)}$), 0.56 (1H, ddd, $J_{(3exo),(3endo)}=14$ Hz, $J_{(3exo),(4)}=5$ Hz, $J_{(3exo),(5exo)}=2$ Hz, $H_{(3exo)}$), 0.85—1.73 (7H, m, $H_{(1),(5),(6),(7)}$), 2.43 (1H, m, $H_{(4)}$); IR (TF) 2925 (s), 2875 (s), 1440 (w), 1400 (w), 1310 (w), 1250 (s), 1150 (w), 1090 (w), 1050 (m), 1020 (w), 1000 (w), 940 (m), 880 (m), 850 (s), 830 (s), 810 (s), 750 (s), 720 (s), 700 (w) cm^{-1}. Calcd for $C_8H_{16}Si$: C, 68.49; H, 11.50%. Found: C, 68.64; H, 11.66%.

*6-Deuterio-2,2-dimethyl-2-silabicyclo[2.2.1]heptane (**21**).* Analogously, from the deuteriosilane (**17**) (1.5 g, 0.11 mol) was obtained **21** (1.0 g, 67% yield). Bp 64 °C (40 mm); n_D^{20} 1.4738; NMR (CCl_4) δ 0.03 (3H, s, Si-$CH_{3(exo)}$), 0.09 (3H, s, Si-$CH_{3(endo)}$), 0.20 (1H, dm, $J_{(3endo),(3exo)}=14$ Hz, $H_{(3exo)}$), 0.56 (1H, ddm, $J_{(3exo),(3endo)}=14$ Hz, $J_{(3exo),(4)}=5$ Hz, $H_{(3exo)}$), 0.85—1.73 (6H, m, $H_{(1),(5),(6),(7)}$), 2.43 (1H, m, $H_{(4)}$); IR (TF) 2950 (s), 2870 (s), 2185 (m), 1470 (m), 1460 (m), 1410 (w), 1300 (m), 1255 (s), 1190 (m), 1095 (m), 1050 (s), 990 (m), 950 (m), 920 (w), 880 (s), 860 (s), 845 (s), 830 (s), 800 (w), 765 (w), 730 (w), 710 (m) cm^{-1}. IR showed only one C–D band at 2185 cm^{-1}. MS *m/e* (rel intensity) 141 (M^+, 40), 126 (24), 99 (100). A deuterium analysis by M^+-15 peaks of mass spectrum showed 72.5% replacement of one hydrogen by deuterium. Assuming that the addition has proceeded *via* cis stereochemistry,[25] it appears reasonable to conclude that the deuterium is located almost exclusively in the $C_{(6\text{-endo})}$ position, *i.e.*, the product is 2,2-dimethyl-6-endo-deuterio-2-silabicyclo-[2.2.1]heptane (**21**). The retention time on GLC was identical with that of **1**. Calcd for $C_8H_{15}DSi$ (d content 72.5%): C, 68.13; H (D), 11.95%. Found: C, 67.73; H (D), 11.92%.

*2-exo- and endo-Methyl-2-phenyl-2-silabicyclo[2.2.1]heptane (**3a** and **3b**).* According to the procedure described above, a mixture of compounds **3a** and **3b** (**3a**:**3b**=68:32) (4.0 g, 20 mmol) boiling over the range of 106—108 °C (5 mm) was obtained from **14**. (5.5 g, 27 mmol). Total yield of **3a** and **3b** was 73%. Either of isomers was readily isolated by preparative GLC (250 °C) equipped with a column packed with Apiezon L 20% (5m) on Celite 545. The retention time on GLC of the exo (**3a**) was shorter than that of the endo isomer (**3b**). **3a**: n_D^{20} 1.5504; NMR (CCl_4) δ 0.35 (3H, s, Si-$CH_{3(exo)}$), 0.78 (2H, m, $J_{(3exo),(4)}=J_{(3endo),(4)}=3$ Hz, $H_{(3endo),(3exo)}$), 1.30—1.77 (7H, m, $H_{(1),(5),(6),(7)}$), 2.61 (1H, m, $H_{(4)}$), 7.23—7.59 (5H, m, C_6H_5); IR (TF) 3090 (w), 3045 (w), 2940 (s), 2870 (m), 1450 (w), 1425 (m), 1400 (w), 1300 (w), 1255 (m), 1190 (w), 1120 (w), 1050 (m), 1000 (w), 940 (m), 880 (m), 860 (m), 820 (m), 800 (m), 780 (m), 740 (m), 700 (s), 680 (w), 640 (w), 600 (w) cm^{-1}. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97%. Found: C, 77.43; H, 8.92%.

3b: n_D^{20} 1.5512; NMR (CCl_4) δ 0.40 (3H, s, Si-$CH_{3(endo)}$), 0.48 (1H, dm, $J_{(3endo),(3exo)}=14.5$ Hz, $H_{(3endo)}$), 1.08 (1H, dd, $J_{(3endo),(3exo)}=14.5$ Hz, $J_{(3exo),(4)}=6.5$ Hz, $H_{(3exo)}$), 1.22—1.88 (7H, m, $H_{(1)(5)(6)(7)}$), 7.23—7.57 (5H, m, C_6H_5). Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97%. Found: C, 76.90; H, 9.00%.

*2-exo- and endo-Methyl-2-chloro-2-silabicyclo[2.2.1]heptane (**5a** and **5b**).* A mixture of **5a** and **5b** (**5a**:**5b**=63:37) (1.47 g, 9.1 mmol) boiling over the range of 63—65 °C (17 mm) was obtained from **16** (1.61 g, 10 mmol) by the chloroplatinic acid catalyzed hydrosilylation, total yield being 91%. The mixture was used for the following derivatizations without the isolation of each isomer. NMR as a mixture of **5a** and **5b** (63:37) (CCl_4) δ 0.50 (s, Si-$CH_{3(exo)}$), 0.55 (s, Si-$CH_{3(endo)}$), 0.72 (2H, m, $H_{(3)}$), 1.00—1.85 (7H, m, $H_{(1),(5),(6),(7)}$), 2.62 (1H, m, $H_{(4)}$); IR (TF) 2900 (s), 2850 (s), 1454 (m), 1403 (m), 1300 (m), 1253 (s), 1215 (s), 1190 (m), 1140 (w), 1085 (m), 1048 (s), 1022 (w), 1000 (w), 930 (m), 880 (m), 850 (m) cm^{-1}. Calcd for $C_7H_{13}ClSi$: C, 52.31; H, 8.15%. Found: C, 52.59; H, 8.33%.

*Preparation of 2-Silanorbornanes (**2**, **3**, **4**, **5**) by Mutual Transformations. 2-exo- and endo-Methyl-2-silabicyclo[2.2.1]heptane (**2a** and **2b**)*: A mixture (1.29 g, 8.0 mmol) of **5a** and **5b** (**5a**:**5b**=63:37) was reduced with lithium aluminum hydride (LAH) (0.15 g) in dry ether (10 ml). Hydrolysis of the reaction mixture and drying and distillation of the organic layer gave **2** (1.02 g, 98% yield), as an isomeric mixture of **2a**:**2b**=74:26. Bp 142 °C; n_D^{20} 1.4796.

A mixture of **2a** and **2b** (**2a**:**2b**=70:30) was also derived from a mixture of **4a** and **4b** (**4a**:**4b**=70:30) by LAH reduction. NMR (200 MHz) as a mixture of **2a** and **2b** (CCl_4) δ 0.03 (3H, d, $J_{(CH_3),(2endo)}=4.0$ Hz, *exo*-CH_3), 0.48 (2H, m, $J_{(2endo),(3exo)}=J_{(2endo),(3endo)}=2.5$ Hz, $H_{(3exo)}$ and $H_{(3endo)}$), and 3.72 (1H, m, $J_{(2endo),(CH_3)}=4.0$ Hz, $J_{(2endo),(1)}=J_{(2endo),(3exo)}=J_{(2endo),(3endo)}=2.5$ Hz, $H_{(2endo)}$) which are attributed to **2a**, and δ 0.07 (1H, m, $J_{(3exo),(3endo)}=15.5$ Hz, $H_{(3endo)}$), 0.12 (3H, d, $J_{(CH_3),(2exo)}=4.0$ Hz, *endo*-CH_3), 0.80 (1H, m, $J_{(3exo),(3endo)}=15.5$ Hz, $J_{(3exo),(4)}=J_{(3exo),(2exo)}=5.5$ Hz, 3.87 (1H, m, $J_{(2exo),(3exo)}=5.5$ Hz, $J_{(2exo),(CH_3)}=4.0$ Hz, $H_{(2exo)}$) which belong to **2b**. Besides, the following complex multiplet signals are obtained from a mixture of **2a** and **2b**: δ 1.4 (1H, m, $H_{(1)}$), 2.5 (1H, m, $H_{(4)}$), 0.9—1.8 (6H, m, $H_{(5)}$, $H_{(6)}$ and $H_{(7)}$). IR (TF) 2910 (s), 2850 (s), 2130 (s), 1455 (w), 1410 (w), 1300 (w), 1250 (m), 1215 (s), 1188 (m), 1140 (w), 1087 (w), 1050 (m), 1028 (w), 1000 (w), 938 (s), 890 (s, br) cm^{-1}. Calcd for $C_7H_{14}Si$: C, 66.58; H, 11.18%. Found: C, 65.92; H, 10.93%.

*2-exo- and endo-Methyl-2-isopropoxy-2-silabicyclo[2.2.1]heptane (**4a** and **4b**).* A mixture of **5** (exo:endo=60:40) (3.2 g, 0.02 mol), isopropyl alcohol (1.8 g, 0.03 mol) and pyridine (2.4 g, 0.03 mol) was heated with stirring for 20 h in dry ether. After filtration of the salt and evaporation of the solvent, ditillation gave 3.1 g (0.017 mol, 84% yield) of the isopropoxy derivative (**4**), as an isomeric mixture of the ratio of **4a**:**4b**=82:18, boiling over the range of 72—76 °C (16 mm).

Alternatively 0.42 g (33% yield) of the compound **4**, as an isomeric mixture of **4a**:**4b**=53:47, boiling over the range of 72—14°/17 mm, was obtained from 0.91 g (7 mmol) **2** (**2a**:**2b**=74:26) and isopropyl alcohol (1 ml) in the presence of Pd–C (10%) (25 mg) in petroleum ether (10 ml) according to the procedure described previously.[37] Either of isomers was readily isolated by preparative GLC (220 °C) using a column packed with Apiezon L 20% (5 m) on Celite 545. The retention time of GLC of **4a** was shorter than that of the endo isomer (**4b**).

4a: n_D^{20} 1.4579; NMR (CCl_4) δ 0.17 (3H, s, Si-$CH_{3(exo)}$), 0.28 (1H, dd, $J_{(3endo),(3exo)}=14.6$ Hz, $J_{(3endo),(4)}=2.1$ Hz, $H_{(3endo)}$), 0.53 (1H, dd, $J_{(3exo),(3endo)}=14.6$ Hz, $J_{(3exo),(4)}=$

5.7 Hz, $H_{(3exo)}$), 1.16 (6H, d, J=6.3 Hz, -CH-$(CH_3)_2$), 1.25—1.90 (7H, m, $H_{(1),(5),(6),(7)}$), 2.43 (1H, m, $H_{(4)}$), 3.96 (1H, septet, J=6.3 Hz, OCH).

4b: n_D^{20} 1.4586; NMR (CCl_4) δ 0.22 (3H, s, Si-$CH_{3(endo)}$), 0.27 (1H, dd, $J_{(3endo),(3exo)}$=14.8 Hz, $J_{(3endo),(4)}$=2.1 Hz, $H_{(endo)}$), 0.72 (1H, dd, $J_{(3exo),(3endo)}$=14.8 Hz, $J_{(3exo),(4)}$= 5.0 Hz, $H_{(3exo)}$), 1.13 (6H, d, J=5.9 Hz, -CH-$(CH_3)_2$), 0.97—1.80 (7H, m, $H_{(1),(5),(6),(7)}$), 2.54 (1H, m, $H_{(4)}$), 3.96 (1H, sept, J=5.9 Hz, OCH). Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.93%. Found: C, 65.15; H, 11.16%.

Chlorination of Compound **2**. Into a carbon tetrachloride solution of **2** (**2a**:**2b**=71:29) dry chlorine gas was passed through until the yellowish color was left in nmr tube. The yield of the chloride **5** was almost quantitative by GLC determination. The ratio of **5a**:**5b** was 71:29 by nmr determination.

Chlorodephenylation of **3** *and Phenylation of* **5**. The exo isomer **3a** (0.1 g), freshly isolated, was treated with iodine monochloride in carbon tetrachloride. Predominant formation of endo isomer **5b** (**5a**:**5b**=14.0:86.0) was observed by NMR determination. After carbon tetrachloride was substituted for dry ether, the mixture was treated with phenyllithium or phenylmagnesium bromide at ether refluxing temperature. After work up, the phenylated compound **3** as an isomeric mixture of **3a**:**3b**=19.5:80.5 or 19.4:80.6, respectively, was isolated by GLC in the pure state. In repeated runs, essentially the same result was obtained.

Analogously, the compound **3b** was chlorodephenylated, resulting in the predominant stereochemistry of the isomer **5a**, where **5a**:**5b**=77.5:22.5. Phenylation of the products with phenyllithium or phenylmagnesium bromide in ether gave the compound **3**, as an isomeric mixture of **3a**:**3b**= 77.0:23.0. From the combination of the above reactions, the predominant stereochemistry in the phenylation with phenyllithium was 95.6% for **5a** and 92.9% for **5b**, and with phenylmagnesium bromide was 97.4% for **5a** and 96.5% for **5b**.

Reactions of 2-Silanorbornanes with Dichlorocarbene. Method A: The following general procedure was used. A mixture of 880 mg (2.0 ml) of phenyl(bromodichloromethyl)mercury, prepared by the reported procedure,[38] and 2.0 mmol of 2-silanorbornane in 3 ml of dry benzene was displaced into a 50 ml two necked flask equipped with a reflux condenser topped with a nitrogen inlet tube and magnetic stirring unit. The flask then was immersed into an oil bath kept at 90 °C. The solution was stirred and heated at reflux for 10 h. Filtration gave phenylmercury(II) bromide, yielding usually above 90% in good purity (mp 275 °C). The filtrate was free from the solvent, the remaining material subsequently was analyzed by NMR and GLC and the product was isolated by preparative TLC. The yields of the insertion product were 1) 22% for 6-*exo*-dichloromethyl-2,2-dimethyl-2-silabicyclo[2.2.1]heptane (**18**), 2) 11% for 6-*exo*-dichloromethyl-2-*exo*-methyl-2-*endo*-phenyl-2-silabicyclo-[2.2.1]heptane (**19a**), 3) 13% for 6-*exo*-dichloromethyl-2-*endo*-methyl-2-*exo*-phenyl-2-silabicyclo[2.2.1]heptane (**19b**). In each reaction, the starting material was almost recovered.

Method B: To a solution of 2,2-dimethyl-2-silabicyclo-[2.2.1]heptane (**1**) (10 g, 0.07 mol), 50% aqueous sodium hydroxide (145 ml), benzene (14.5 ml) and benzyltrimethylammonium chloride (0.29 g, 28 mmol), chloroform (43.5 ml, 0.25 mol) was added slowly with vigorous stirring for a period of 7.5 h at 60 °C. After additional stirring for 2 h, diethyl ether (50 ml) was added and the organic layer was centrifuged. After similar operation was carried out 10 times, the ethereal layer was dried over sodium sulfate and the solvent was removed by distillation. The residue was distilled under reduced pressure to give 6-*exo*-dichloromethyl-2,2-dimethyl-2-silabicyclo[2.2.1]heptane (**18**) (11.4 g, 0.05 mol) in 71.3% yield. Bp 117 °C (9 mmHg, 1 mmHg≈ 133.322 Pa); n_D^{20} 1.5116.

18: NMR (CCl_4) δ 0.12 (3H, s, Si-$CH_{3(exo)}$), 0.23 (3H, s, Si-$CH_{3(endo)}$), 0.32 (1H, d, J=14.5 Hz, $H_{3(endo)}$), 0.66 (1H, dd, $J_{(3exo),(3endo)}$=14.5 Hz, $J_{(3exo),(4)}$=6.0 Hz, $H_{(3exo)}$), 1.20—1.72 (5H, m, $H_{(1),(5),(7)}$), 2.43 (1H, ddd, $J_{(6endo),(6\text{-}exo\text{-}CH)}$=9.0 Hz, J=9.0 Hz, J=6.0 Hz, $H_{(6endo)}$), 2.57 (1H, m, $H_{(4)}$), 5.43 (1H, d, $J_{(6\text{-}exo\text{-}CH),(6endo)}$=9.0 Hz, $CHCl_2$); IR (TF) 2930 (s), 2830 (s), 1460 (w), 1440 (m), 1400 (m), 1300 (s), 1290 (m), 1280 (w), 1250 (s), 1210 (s), 1120 (s), 1050 (s), 1000 (w), 970 (m), 900 (m), 840 (s) cm^{-1}; MS *m/e* (rel intensity) 224 (M^++2, 0.1), 222 (M^+, 0.3) 140 (14), 139 (M^+-CHCl_2, 100), 95 (29), 93 (81), 79 (72), 59 (48); High resolution MS, $C_8H_{15}Si$ (M^+-CHCl_2), obsd *m/e* 139.0943 (calcd 139.0943). Calcd for $C_9H_{16}Cl_2Si$: C, 48.73; H, 7.23%. Found: C, 48.22; H, 7.08%.

19a: NMR (CCl_4) δ 0.32 (3H, s, Si-$CH_{3(exo)}$), 0.74—0.84 (2H, m, $H_{(3)}$), 1.25—1.82 (5H, m, $H_{(1),(5),(7)}$), 2.27 (1H, ddd, $J_{(6endo),(6\text{-}exo\text{-}CH)}$=8.5 Hz, J=8.5 Hz, J=6.0 Hz, $H_{(6endo)}$), 2.60—2.75 (1H, m, $H_{(4)}$), 5.39 (1H, d, $J_{(6endo),(6\text{-}exo\text{-}CH)}$=8.5 Hz, $CHCl_2$), 7.20—7.59 (5H, m, C_6H_5); MS *m/e* (rel intensity) 286 (M^++2, 0.1), 284 (M^+, 0.2), 201 (M^+-CHCl_2, 100), 157 (38), 155 (99), 123 (12), 121 (62), 105 (19), 93 (21), 91 (32), 79 (dd), 74 (10), 59 (19); High resolution MS, $C_{13}H_{17}Si$ (M^+-CHCl_2), obsd *m/e* 201.1095 (calcd 201.1098).

19b: NMR (CCl_4) δ 0.44 (3H, s, Si-$CH_{3(endo)}$), 0.49 (1H, dd, $J_{(3exo),(3endo)}$=14.2 Hz, $J_{(3endo),(4)}$=3.2 Hz, $H_{(3endo)}$), 1.10 (1H, dd, $J_{(3exo),(3endo)}$=14.2 Hz, $J_{(3exo),(4)}$=6.0 Hz, $H_{(3exo)}$), 1.23—1.92 (5H, m, $H_{(1),(5),(7)}$), 2.55 (1H, ddd, $J_{(6endo),(6\text{-}exo\text{-}CH)}$=9.0 Hz, J=9.0 Hz, J=6.0 Hz, $H_{(6endo)}$), 2.55—2.76 (1H, m, $H_{(4)}$), 5.47 (1H, d, $J_{(6\text{-}exo\text{-}CH),(6endo)}$= 9.0 Hz, $CHCl_2$), 7.20—7.59 (5H, m, C_6H_5); MS *m/e* (rel intensity) 286 (M^++2, 0.1), 284 (M^+, 0.1), 201 (M^+-CHCl_2, 47), 157 (37), 155 (100), 121 (64), 105 (18), 93 (25), 91 (24), 79 (58); High resolution MS, $C_{13}H_{17}Si$ (M^+-CHCl_2), obsd *m/e* 201.1086 (calcd 201.1098).

*Reduction of the Insertion Product (***18***) with Tributyltin Hydride.* **18** (80 mg) was heated tributylin hydride (500 mg) in the presence of di-*t*-butyl peroxide (20 mg) at 140 °C for 15 h in a sealed tube. By a GLC collection (Apiezon L 30%, 3m, 190 °C) of the reaction mixture, 6-*exo*-methyl-2,2-dimethyl-2-silabicyclo[2.2.1]heptane (**20**) was obtained. NMR (CCl_4) δ 0.01 (3H, s, Si-$CH_{3(exo)}$), 0.09 (3H, s, Si-$CH_{3(endo)}$), 0.15 (1H, d, $J_{(3endo),(3exo)}$=14.5 Hz, $H_{(3endo)}$), 0.52 (1H, ddd, $J_{(3exo),(3endo)}$=14.5 Hz, $J_{(3exo),(4)}$=6.5 Hz, $J_{(3exo),(5exo)}$=2.8 Hz, $H_{(3exo)}$), 0.91 (3H, d, $J_{(6\text{-}exo\text{-}CH),(6endo)}$ =6.8 Hz, 6-$CH_{3(exo)}$), 0.82—2.03 (6H, m, $H_{(1)(5),(6endo),(7)}$). Calcd for $C_9H_{18}Si$: C, 70.05; H, 11.76%. Found: C, 70.28; H, 11.84%.

*Reaction of 2,2-Dimethyl-6-*endo*-deuterio-2-silabicyclo[2.2.1]-heptane (***21***) with Phenyl(bromodichloromethyl)mercury.* The reaction of $PhHgCCl_2Br$ with the deuterio compound (**21**) (72.5% enriched by derterium) was carried out in a similar manner as described above. The product **22** was obtained in 17.4% yield. The retention time on GLC was identical with that of **18**. Deuterium analysis by NMR and mass spectrum showed 71% excess deuterium at 6-endo position in the product. IR spectrum showed 2160 cm^{-1} characteristic of C-D streching.

22: NMR (CCl_4) δ 0.12 (3H, s, Si-$CH_{3(exo)}$), 0.23 (3H, s, Si-$CH_{3(endo)}$), 0.32 (1H, d, $J_{(3endo),(3exo)}$=14.5 Hz, $H_{(3endo)}$), 0.66 (1H, dd, $J_{(3exo),(3endo)}$=14.5 Hz, $J_{(3exo),(4)}$=6.0 Hz, $H_{(3exo)}$), 1.20—1.72 (5H, m, $H_{(1),(5),(7)}$), 2.57 (1H, m, $H_{(4)}$), 5.44 (1H, s, $CHCl_2$); IR (TF) 2920 (s), 2850 (s), 2160 (w),

1470 (w), 1450 (m), 1410 (m), 1300 (m), 1290 (m), 1280 (w), 1250 (s), 1210 (s), 1120 (w), 1050 (s), 985 (s), 900 (m), 840 (s) cm^{-1}; MS *m/e* (rel intensity) 225 (M^++2, 0.2), 223 (M^+, 0.2), 141 (15), 140 (M^+-CHCl_2, 100), 139 (45), 95 (36), 93 (97), 80 (46), 79 (44), 59 (51); High resolution MS, $C_8H_{14}DSi$ (M^+-CHCl_2), obsd *m/e* 140.1002 (calcd 140.1004).

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