Pergamon

Tetrahedron 57 (2001) 3645–3656

TETRAHEDRON

The first silatropylium ion stabilized by rigid σ-frameworks: preparation, properties, and some reactions

Tohru Nishinaga, Yoshiteru Izukawa and Koichi Komatsu*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Received 2 October 2000; accepted 21 November 2000

Abstract—The first cyclic π-conjugated silylium ion, the silatropylium ion **5** annelated with three bicyclo[2.2.2]octene units having a mesityl group on the silicon atom, was prepared with tetrakis(pentafluorophenyl)borate (TPFPB) as a counter anion in CD_2Cl_2 at $-50°C$ by hydride abstraction from the corresponding silacycloheptatriene (silepin). The observed chemical shifts of ^1H, ^{13}C, and ^{29}Si NMR for cation **5** were in agreement with the calculated values. These results and NICS calculations indicated that cation **5** has the aromaticity approaching that of the tropylium ion. When cation **4** having a methyl group instead of a mesityl group and cation **5** were generated in the presence of two equivalents of acetonitrile, the acetonitrile complexes **16** and **17** with considerable covalent-bond character were formed. For the complexes **16** and **17**, the exchange process of acetonitrile was observed for the first time as an acetonitrile complex of a silyl cation, and the intermediacy of a pentavalent silicon was demonstrated. When cations **4** and **5** were generated by the use of triphenylmethyl perchlorate instead of triphenylmethyl TPFPB, covalent perchlorate esters **18** and **19** having the O–Si covalent bond were formed instead of ionic salts. By treatment with water, the perchlorate ester **18** was found to undergo a novel rearrangement to give a cyclopentene derivative **20a** spiro-connected with bicyclo[2.2.2]octane at the 3-position. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

From the viewpoint of the comparison between the chemistry of carbon and that of silicon, a trivalent silyl cation (a silylium ion) has attracted great interest of the organic and organometallic chemists, and many efforts have been devoted to synthesize the silylium ion in condensed phases during the last decades.[1] However, most of the claims on the proof for the silylium ion[2–4] were challenged.[5–11] For example, much debate[8–11] has been made whether $[Et_3Si(toluene)]^+B(C_6F_5)_4^-$ prepared by Lambert[3] and i-$Pr_3Si^+CB_{11}H_6Br_6^-$ prepared by Reed[4] have silylium ion character or not. The first 'free' silylium ion was reported by Lambert and Zhao in 1997, that is, the trimesitylsilylium ion stabilized mainly by the steric protection of the silicon atom by bulky substituents.[12] Also a cation having a nonclassical delocalized structure was shown to be free from coordination with solvents or counter anion.[13] More recently a salt of a homocyclotrisilenylium ion was isolated by Sekiguchi and was found to have no interaction with counter anion from the X-ray structural analysis.[14] In this case, the aromatic homoconjugation as observed in the carbon analog is supposed to stabilize the silylium ion center.

Then a question arises if the silylium ion can be stabilized by the aromatic conjugation with 2p orbitals of carbons. The recent achievement of silaaromatic compounds[15] such as silabenzene,[16] silanaphthalene,[17] and silacyclopentadienyl dianion[18,19] has revealed that the aromatic conjugation between the 3p orbital of silicon and 2p orbitals of carbons is possible. However, there has been no study to convincingly answer the question as to the cationic conjugated systems involving the silylium ion. The early theoretical calculations at a very low level on silacyclopropenylium ion indicated the absence of any significant aromatic stabilization.[20] However, in the same paper, the silacyclopentadienyl anion was also shown to be non-aromatic,[20] which contradicts the recent results of calculations at a higher level.[21] More adequate calculation method would be required for a reliable conclusion on the aromaticity of silacyclopropenylium ion to be reached.

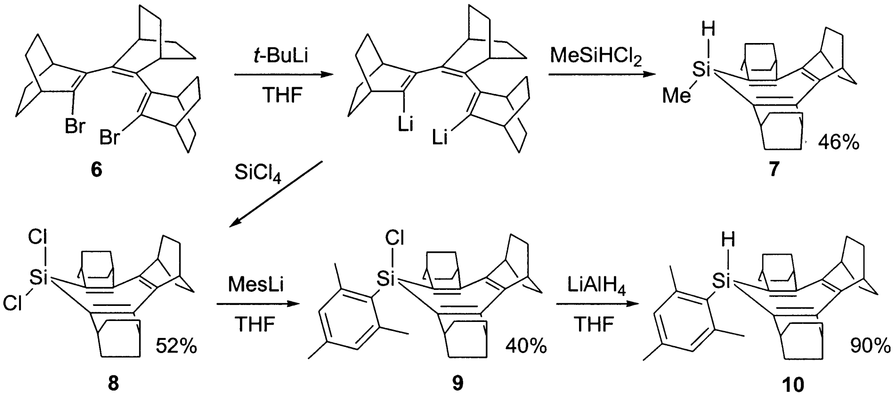
As another potentially aromatic system, a silicon analog of the tropylium ion (**1**), i.e. the silatropylium ion (**2**), is also a good candidate for the examination of the above question. However, the attempted preparation of the dibenzosilatropylium ion (**3**) by Olah's group was not successful and they concluded that silylium ions are not stabilized in solution by incorporation of the silicon atom into a potentially aromatic ring system.[5b] Even in the gas phase, a recent suggestion of the silatropylium ion (**2**) as one of the $C_6H_7Si^+$ isomers observed in an FT ICR mass spectrum[22] was disproved by a subsequent experimental study showing that it was a rearranged isomer, $C_6H_6{\cdot}SiH^+$.[23] Theoretical studies have

---

Keywords: aromaticity; cycloheptatrienes; NMR; silicon heterocycles; theoretical studies; tropylium ions; X-ray crystal structures.

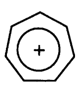
* Corresponding author. Tel.: +81-774-38-3172; fax: +81-774-38-3178; e-mail: komatsu@scl.kyoto-u.ac.jp

PII: S0040-4020(01)00253-8

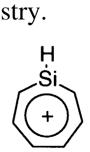


Scheme 1.

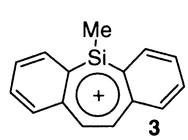
indicated that cation **2** is less stable than 'silabenzyl cation' by 9 kcal mol^{-1}.[24] Thus the synthesis and characterization of the silatropylium ion remains as a major challenge in organosilicon chemistry.



1



2



3

The attempted observation of cation **3** was performed in acetonitrile with perchlorate as a counter anion[5b] before a recent guideline was established for the possible generation of silylium ion in condensed phase. The guideline is that (1) the silylium ion center should be surrounded by bulky substituents and (2) the cation should be prepared in the presence of a low-coordinating counter anion and (3) in a low coordinating solvent.[1e,f,12] In addition, the annealation with benzene ring(s) is known to thermodynamically destabilize the tropylium ion (**1**),[25] and therefore would not be appropriate for the study of the silatropylium ion. For the realization of the silatropylium ion, we designed a modification of the seven-membered ring with rigid σ-frameworks, that is, annealation with bicyclo[2.2.2]-octene (abbreviated as BCO) units. In our previous study, such structural modification with BCO units was found to be the most effective in stabilizing the tropylium ion.[26] In the present paper are described the detailed accounts on the preparation and characterization of the first silatropylium ion derivative **5** stabilized by such a structural modification and the presence of a bulky mesityl group on silicon;[27] also an attempt made to prepare a derivative with a methyl group on silicon (**4**) and the reactions of **4** and **5** with acetonitrile or perchlorate ion are described together with the results of theoretical calculations.

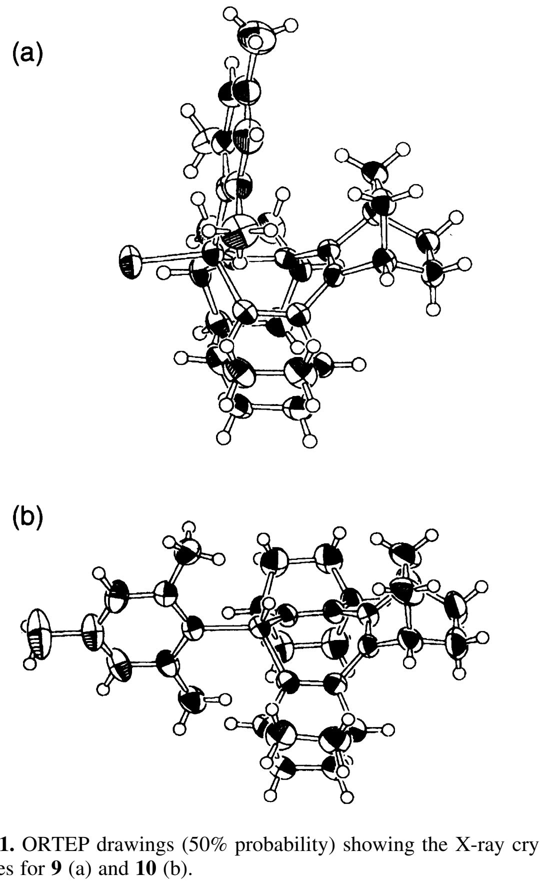
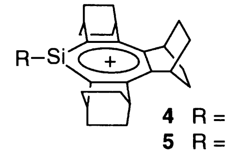


Figure 1. ORTEP drawings (50% probability) showing the X-ray crystal structures for **9** (a) and **10** (b).

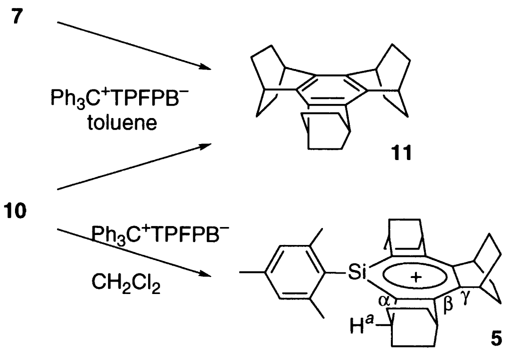


4 R = Me
5 R = Mes

2. Results and discussion

2.1. Preparation and characterization of the silatropylium ion 5

For the preparation of silatropylium ions **4** and **5**, the precursor silacycloheptatrienes (silepins) **7**[28] and **10** were prepared from the dibromide of BCO trimer **6**[29] in the following way, as shown in Scheme 1. Dibromide **6** was dilithiated with 4 equiv. of *t*-BuLi at −60°C and then allowed to react with dichloromethylsilane or with tetrachlorosilane to give silepin **7** in 66% or dichlorosilepin **8**[28] in 55% yield, respectively. Dichlorosilepin **8** was allowed to react with mesityllithium to give mesitylchlorosilepin **9** in 40% yield, which was then reduced to silepin **10** in 90% yield by treatment with $LiAlH_4$. The molecular structures of silepins **9** and **10** determined by X-ray crystallography are shown in Fig. 1. In



Scheme 2.

the crystal, the mesityl group takes the 'axial' position for **9** and the 'equatorial' position for **10**. The molecular structure of **10** with the 'equatorial' mesityl group might be unfavorable for the hydride abstraction by such a bulky reagent like triphenylmethyl cation for steric reasons. In solution, however, the rapid ring inversion should take place[28] to bring the mesityl group to the axial position for the hydride abstraction from the Si–H bond to proceed readily.

First the hydride abstraction was attempted in the presence of a non-coordinating anion in a non-coordinating solvent. When an attempt was made to generate the silatropylium ion **4** or **5** by hydride abstraction from the silepin **7** or **10** with an equivalent of triphenylmethyl tetrakis(pentafluorophenyl)-borate (TPFPB) in toluene-d_8 (C_7D_8) under vacuum at -50°C, only a ring contraction occurred to show the ^{1}H NMR signals for the BCO-annealated benzene **11** (Scheme 2), possibly via a non-classical ion, **11**·R–Si$^+$, which corresponds to $C_6H_6{\cdot}SiH^+$ observed in the gas phase.[23] On the other hand, when the hydride abstraction was conducted in dichloromethane-d_2 (CD_2Cl_2) at -50°C, the reaction of silepin **10** gave the ^{29}Si, ^{1}H and ^{13}C NMR signals corresponding to silatropylium ion **5**,[†] as shown in Fig. 2 and Table 1. Here, apparently a bulky substituent such as a mesityl group was necessary for stabilizing the silatropylium ion.[‡] At temperatures higher than -50°C, silatropylium ion **5** decomposed to give benzene **11** as was observed in C_7D_8 at low temperatures. Thus, CD_2Cl_2 with its medium polarity and small size is favorable for approaching the silylium ion center to weakly coordinate to it and preventing the rearrangement at the temperature below -50°C while C_7D_8 with its lower polarity and a larger molecular size cannot stabilize the cationic species by coordination[9,11] even at low temperatures.

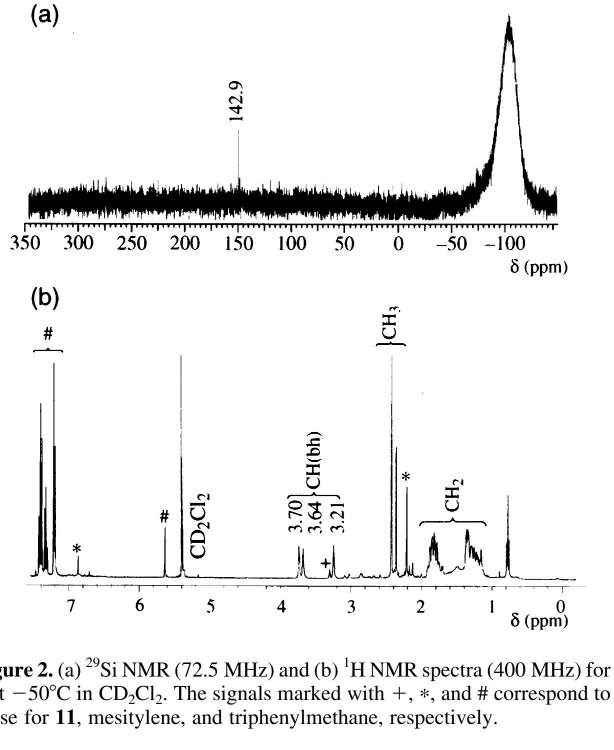


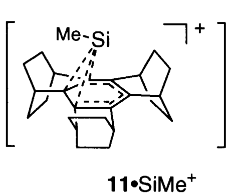
Figure 2. (a) ^{29}Si NMR (72.5 MHz) and (b) ^{1}H NMR spectra (400 MHz) for **5** at -50°C in CD_2Cl_2. The signals marked with +, *, and # correspond to those for **11**, mesitylene, and triphenylmethane, respectively.

The ^{29}Si NMR signal of silatropylium ion **5** was observed at δ 142.9 ppm in CD_2Cl_2, which is 192.2 ppm downfield shifted compared with the precursor silepin **10** (δ -49.3). This is taken as clear evidence for the silylium ion character of **5**. The observed ^{29}Si chemical shift is also in fair agreement with the value calculated for **5** (δ 159.9; GIAO/HF/6-311+G(2df,p)(Si), 6-31+G*//B3LYP/6-31G*).[30] This method of calculation is known to reproduce the experimental value observed for the trimesitylsilylium ion.[31] The ^{29}Si chemical shift of **5** is 28 ppm downfield shifted compared with the solid-state ^{29}Si NMR chemical shift (δ 115) of i-$Pr_3Si^+CB_{11}H_6Cl_6^-$, which was shown to have some interaction between the silylium ion center and the chlorine atom of the counter ion.[4d] Thus, the interaction between the silylium ion center of **5** and CD_2Cl_2 should be smaller than the case for i-$Pr_3Si^+CB_{11}H_6Cl_6^-$.

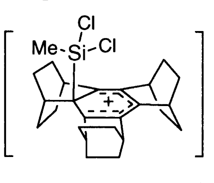
The chemical shift of the BCO bridgehead (bh) protons is useful for judging the presence of a diamagnetic ring current because they are rigidly fixed in the same plane as a silatropylium ion ring.[32] As shown in Fig. 2b, the signals for these protons of **5** were observed at δ 3.70, 3.64, and 3.21 ppm. These signals except for the signal at δ 3.21 were 0.8–0.9 ppm downfield shifted compared with those for the neutral precursor **10** (δ_{bh} 2.81 (4H), 2.61 (2H)), indicating the presence of a diamagnetic ring current and thus aromaticity in **5**. The signal at δ 3.21 is assigned to the proton (H^a) which sticks out in the shielding zone of a mesitylene ring. This upfield shift of ca. 0.4 ppm due to the mesityl group was also reproduced by the calculations (δ_{bh} 3.2, 3.2, 2.8; GIAO/HF/6-311+G(2df,p)(Si), 6-31+G*//B3LYP/6-31G*).

[†] At the hydride abstraction reaction, ca. 0.5 equiv. of trityl cation was not consumed and about 6% of **11** and mesitylene were also formed. The fate of the possible species such as Mes–Si$^+$ generated upon the ring contraction of **5** is not known, but such a species and its degradation products would also work to abstract hydride from **10**.

[‡] When the hydride abstraction of the methyl-substituted silepin **7** was conducted in CD_2Cl_2, the NMR measurements at room temperature (^{1}H NMR δ 3.54 (s, 6H), 2.03 (d, 12H), 1.62 (d, 6H), 1.28 (d, 6H): ^{13}C NMR δ 34.5, 26.9, 24.8; the signal for the sp^2 carbon could not be identified) revealed that the product was not the silatropylium ion **4** but presumably the rearranged isomer with a non-classical structure, i.e. **11**·Me–Si$^+$ or **11**·Me–SiCl$_2$$^+$. Further characterization will be reported elsewhere.



11•SiMe$^+$



11•SiMeCl$_2$$^+$

Table 1. The ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts (δ, ppm) for **5**, **7**, **10**, and **16–19** in CD_2Cl_2

Compd	^{1}H NMR					^{13}C NMR						^{29}Si NMR
	Mes-H	SiH	CH	CH$_2$	CH$_3$	Tropyl	Aryl	CH	CH$_2$	CH$_3$	CN	
5	–[a]		3.70 (2H) 3.64 (2H) 3.21 (2H)	1.85 (12H) 1.30 (12H)	2.41 (6H) 2.36 (3H)	175.9 153.2 149.7	144.8 143.8 128.0 118.7	36.8 35.1 34.9	25.1 24.2 23.9	25.9 21.4		142.9
7[b]		4.47 (1H)	2.80 (4H) 2.74 (2H)	1.7–1.0 (24H)	0.22 (3H)	151.2 141.4 134.5		34.2 33.9 33.0	26.8 26.7 26.5 26.3 25.8 25.7	−0.6		–[c]
10[d]	6.78 (2H)	4.81 (1H)	2.81 (4H) 2.61 (2H)	1.8–1.0 (24H)	2.40 (6H) 2.22 (3H)	152.0 145.5 141.8	138.7 128.2 127.9	34.4 33.5 33.1	27.1 26.7 26.0 25.9 25.2	24.6 20.8		−49.3
16[d,e]			2.95 (2H) 2.90 (2H) 2.74 (2H)	1.8–0.9 (24H)	2.61 (3H) 0.83 (3H)	159.1 141.1 130.0		32.6 31.3	25.9 25.3 25.1 25.0 24.6 24.0	25.9	120.4	−1.7
17[d,e]	6.70 (2H)		2.85 (2H) 2.76 (2H) 2.65 (2H)	1.8–1.0 (18H) 1.0–0.6 (4H) 0.17 (2H)	3.07 (3H) 2.25 (6H) 2.13 (3H)	153.6 145.8 141.4	142.4 130.1 128.8 118.7	32.4 32.3 31.7	28.2 25.7 25.2 24.6 23.1	22.5 20.8 5.4	125.6	−15.9
18			2.93 (2H) 2.91 (2H) 2.85 (2H)	1.8–0.9 (24H)	0.80 (3H)	157.2 141.1 135.4		33.5 33.4 32.4	26.6 26.1 25.5 25.3 25.2 24.5	−5.7		8.9
19	6.71 (2H)		3.10 (2H) 2.74 (2H) 2.67 (2H)	1.8–1.2 (18H) 1.1–0.7 (4H) 0.59 (2H)	2.36 (6H) 2.20 (3H)	151.6 146.5 141.5	141.3 135.4 128.9 123.0	33.0 32.9 31.6	28.5 26.6 26.0 25.2 25.1 24.9	24.3 20.9		−6.0

[a] A signal for the two mesityl ring protons is overlapped with signals for triphenylmethane.
[b] In C_6D_6.
[c] The signal could not be observed.
[d] There is some overlap in ^{13}C NMR signals.
[e] At −80°C.

The ^{13}C NMR signals for the sp^2 carbons of **5** in CD_2Cl_2 (δ 175.9, 153.2, 149.7 ppm; Table 1) showed downfield shifts compared with the signals of silepin **10** in CD_2Cl_2 (δ 152.0, 145.5, 141.8), indicating considerable positive-charge delocalization in the seven-membered ring. The most downfield shifted signal (δ 175.9) is assigned to the β-carbon based on the calculated chemical shifts for **5** (α-C, 147 ppm; β-C, 185; γ-C, 150). These results imply that a contribution of the sila-allylic resonance structure is important for the positive-charge delocalization.

In order to estimate the structure and aromaticity of the silatropylium ion and the degree of interaction between the silatropylium ion and CH_2Cl_2, theoretical calculations were performed for Me_3Si^+, tropylium ion (**1**), silatropylium ion (**2**), and BCO-annealated silatropylium ion **5**, together with the CH_2Cl_2 complexes, i.e. $Me_3Si^+\cdot CH_2Cl_2$, **2**·CH_2Cl_2, and **5**·CH_2Cl_2. As shown in Fig. 3a and b, while **2** took a completely planar conformation, the central seven-membered ring of the optimized structure for **5** at B3LYP/6-31G* level was not planar but in a boat form. This non-planarity of the seven-membered ring in **5** is apparently due to the steric repulsion between bridgehead protons at the stern part. The bending angles at the bow and the stern parts were 12° and 27°, respectively. Like the other structural features of **5**, the three carbon atoms around the silicon atom were located in almost the same plane with silicon (the sum of the bond angles, 359°) and the mesitylene ring was perpendicular to the mean plane of the silatropylium ion ring.

In spite of the non-planarity of the central ring in **5**, the nucleus independent chemical shifts[21b] at 1 Å above and below the ring (NICS(1); GIAO/HF/6-31+G*//B3LYP/6-31G*) for **5**

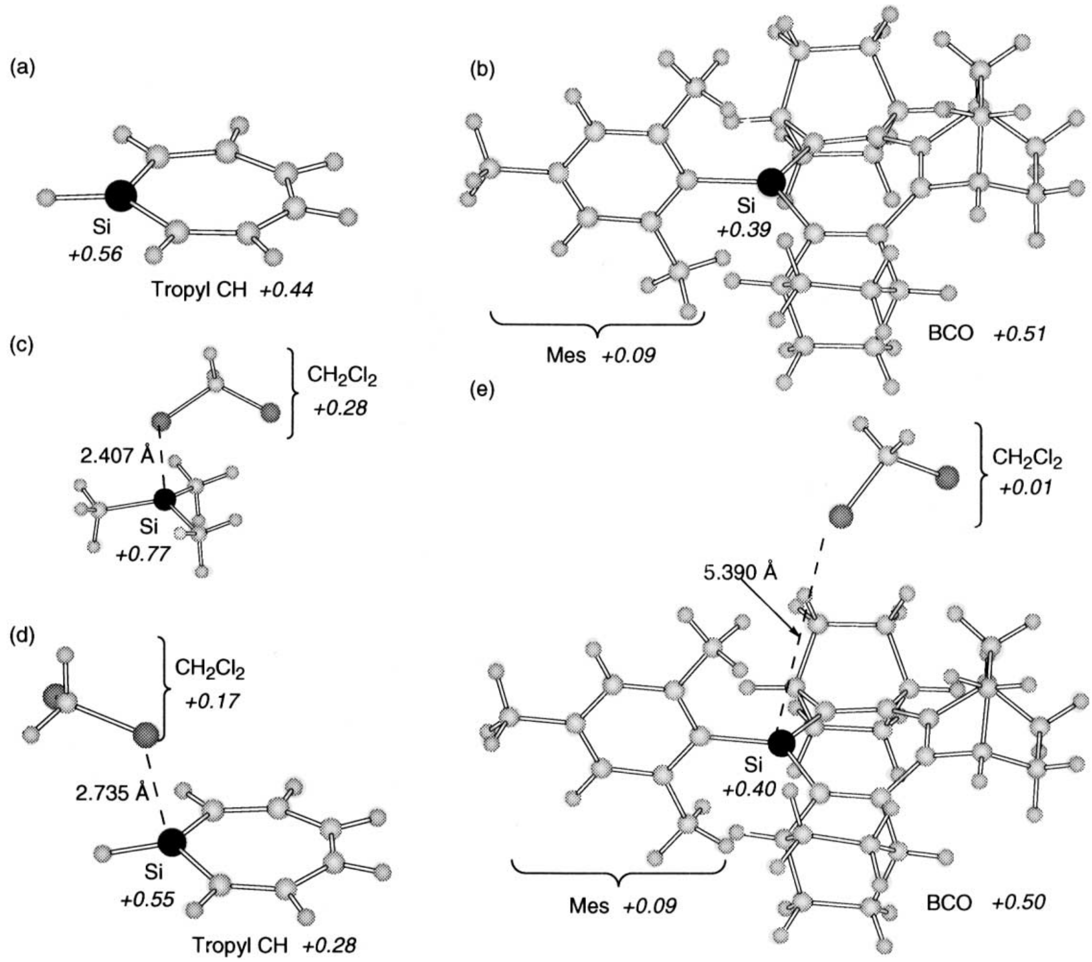
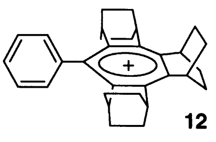


Figure 3. The optimized structures of **2** (a), **5** (b), $Me_3Si^+{\cdot}CH_2Cl_2$ (c), $\mathbf{2}{\cdot}CH_2Cl_2$ (d), and $\mathbf{5}{\cdot}CH_2Cl_2$ (e) at B3LYP/6-31G(d) level. The Si–Cl distances and *Mulliken charges* on silicon atoms and other units are given.

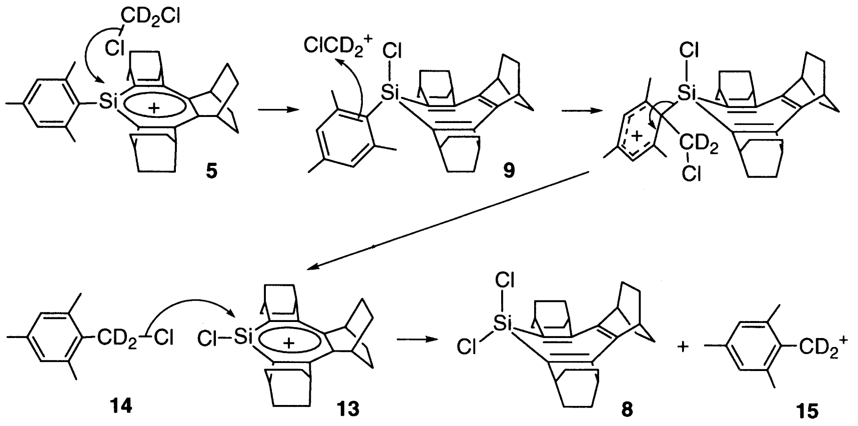
were −6.5 and −7.5, respectively, which are comparable to those of **2** (NICS(1)=−7.3). This result supported the conclusion that the observed downfield shifts of bridgehead protons for **5** were due to a diamagnetic ring current on a silatropylium ion ring. For the estimation of the aromaticity of **5**, the downfield shifts of the bridgehead protons were compared with those for the carbon analog, **12**. The downfield shifts for **12** upon going from the neutral precursor (δ_{bh} 2.88 (2H), 2.67 (4H)) to the ion (δ_{bh} 4.09, 4.06, 3.17)[26c] were 1.2–1.4 ppm except for H^a. Thus, the downfield shifts in **5** (0.8–0.9 ppm except for H^a) were somewhat smaller than the values in **12**, probably due to the less effective aromatic conjugation between the 3p orbital of silicon and 2p orbitals of carbons, but the aromaticity of **5** is comparable to that of **2** as mentioned above. Based on the theoretical indices for aromaticity, i.e. NICS(1) and magnetic susceptibility exaltation (Λ)[33] for unsubstituted tropylium ion (**1**) and silatropylium ion (**2**), the aromaticity of **2** (NICS(1)=−7.3, Λ=−15.6) could be roughly estimated to be about 70% of that of **1** (NICS(1)=−10.7, Λ=−20.1).



12

As concerns the subject of the interaction between the silylium ion center and the solvent, CH_2Cl_2, the Si–Cl distance for $\mathbf{2}{\cdot}CH_2Cl_2$ (Fig. 3d) was calculated to be considerably longer (2.735 Å) than that for Me_3Si–Cl (2.112 Å) as a model compound for the covalent molecule. This Si–Cl distance for $\mathbf{2}{\cdot}CH_2Cl_2$ is still 0.33 Å longer than that for $Me_3Si^+{\cdot}CH_2Cl_2$ (2.407 Å; Fig. 3c), and also the Mulliken charge on CH_2Cl_2 in $\mathbf{2}{\cdot}CH_2Cl_2$ (+0.17) is less than that in $Me_3Si^+{\cdot}CH_2Cl_2$ (+0.28). Furthermore, the stabilization energy for CH_2Cl_2 coordination in $\mathbf{2}{\cdot}CH_2Cl_2$ (7.7 kcal mol^{-1}) as estimated from the energy difference between $\mathbf{2}{\cdot}CH_2Cl_2$ and the sum of **2** and CH_2Cl_2 is smaller than the case for $Me_3Si^+{\cdot}CH_2Cl_2$ (18.2 kcal mol^{-1}). Thus, the cyclic conjugation of the silatropylium ion apparently reduces the interaction between the silylium ion center and CH_2Cl_2.

In addition, the optimized structure of $\mathbf{5}{\cdot}CH_2Cl_2$ showed that the Si–Cl distance (5.390 Å) was further elongated. The Si–Cl distance is much longer than the sum of the van der Waals radii of silicon and chlorine (3.8–4.0 Å), indicating no direct interaction between the silylium center and CH_2Cl_2. The absence of the interaction would be ascribed not only to the bulky substituent on the silicon atom but also to the thermodynamic stability of **5** caused by annelation with BCO units. From the comparison of the charge on silicon of **2** (+0.56) and **5** (+0.39), BCO units are shown



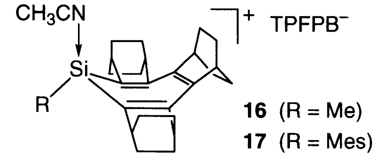
Scheme 3.

to be effective in further delocalizing the positive charge on silicon. On the other hand, the stabilization energy estimated from the energy difference between **5**·CH_2Cl_2 and the sum of **5** and CH_2Cl_2 was not negligible (2.5 kcal mol^{-1}). This stabilization energy would be caused mainly by the dipole interaction between **5** and the CH_2Cl_2 molecule and would be important for the stabilization of **5** in solution.

The silatropylium ion **5** is stable at temperatures below −50°C, but it slowly abstracts the chloride ion from CD_2Cl_2 to furnish dichlorosilepin **8** at −50°C ($t_{1/2}$~6 h). The possible mechanism is illustrated in Scheme 3. First, the chloride ion is abstracted slowly from the solvent by **5** to produce silepin **9** and the chloromethyl cation. Such an abstraction of the chloride ion from CH_2Cl_2 by the silylium ion has been reported previously.[4a,34] Then the produced chloromethyl cation exerts an electrophilic aromatic substitution on the mesitylene ring of **9** to cleave the Si–Mes bond to generate the highly reactive chlorosilatropylium ion **13** and (chloromethyl)mesitylene **14**. The second chloride abstraction by **13** from **14** furnishes dichlorosilepin **8** and the benzyl cation **15**. Finally, the benzyl cation **15** abstracts hydride from triphenylmethane which was generated upon the formation of **5**. In support of the above mechanism, the formation of tetramethylbenzene-d_2 ($C_{10}H_{12}D_2$) was confirmed by GC-MS analysis.

2.2. Reaction of the silatropylium ions with acetonitrile

When the hydride abstraction of silepin **7** or **10** using triphenylmethyl TPFPB was conducted in CD_2Cl_2 in the presence of 2 equiv. of CH_3CN, the ^{29}Si, ^{1}H and ^{13}C NMR signals corresponding to the CH_3CN complex, **16** or **17**, were observed (Table 1). Upon comparison of the NMR data of **17** with the silatropylium ion **5** and with the precursor silepin **10**, the chemical shifts of **17** were closer to those of **10** rather than **5**. The ^{29}Si NMR signal of **17** showed only 33.4 ppm downfield shift from that of **10**. The bridgehead protons and the sp^2 carbons also showed only a slight downfield shift from those of **10**. These results indicate that the diamagnetic ring current in **5** was quenched by coordination with CH_3CN and the positive charge is delocalized not into the seven-membered ring but into CH_3CN. The complexes **16** and **17** were found to be stable at room temperature under inert atmosphere: even the methyl substituted derivative **16** did not undergo the rearrangement as was observed in CD_2Cl_2 in the absence of CH_3CN.



16 (R = Me)
17 (R = Mes)

As shown in Fig. 4, the optimized structure of **17** at the B3LYP/6-31G(d) level demonstrates that a CH_3CN molecule is strongly coordinated to the silicon atom of **5**, in contrast to the case of **5**·CH_2Cl_2, due to the much greater nucleophilicity of CH_3CN. Also the calculated Mulliken charge on total BCO units (+0.10) supports the conclusion derived from the NMR results described above that the positive charge is not substantially delocalized into the seven-membered ring carbons. On the other hand, the Mulliken charge of CH_3CN in **17** (+0.29) and the stabilization energy for CH_3CN coordination on **5** (14.2 kcal mol^{-1}), estimated from the energy difference between **17** and the sum of **5** and CH_3CN, were smaller than the cases for Me_3Si^+·CH_3CN (+0.36, 51.3 kcal mol^{-1}) and **2**·CH_3CN (+0.36, 34.6 kcal mol^{-1}). Also the distance of Si–N (1.926 Å) for **17** was 0.03 Å and 0.01 Å longer than the calculated Si–N distance for Me_3Si·CH_3CN (1.894 Å) and for **2**·CH_3CN (1.916 Å), respectively. These results indicate that the interaction of the BCO-annelated silatropylium ion

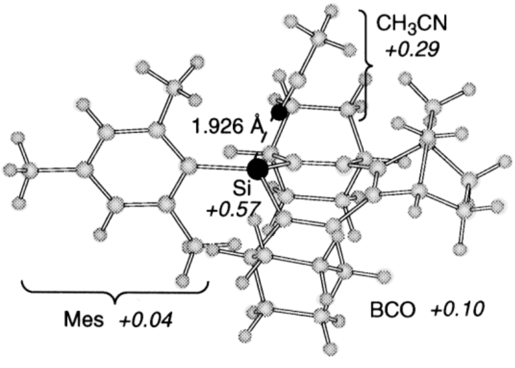


Figure 4. The optimized structure of **17** at B3LYP/6-31G(d) level. The Si–N distance and *Mulliken charges* on silicon atoms and other units are given.

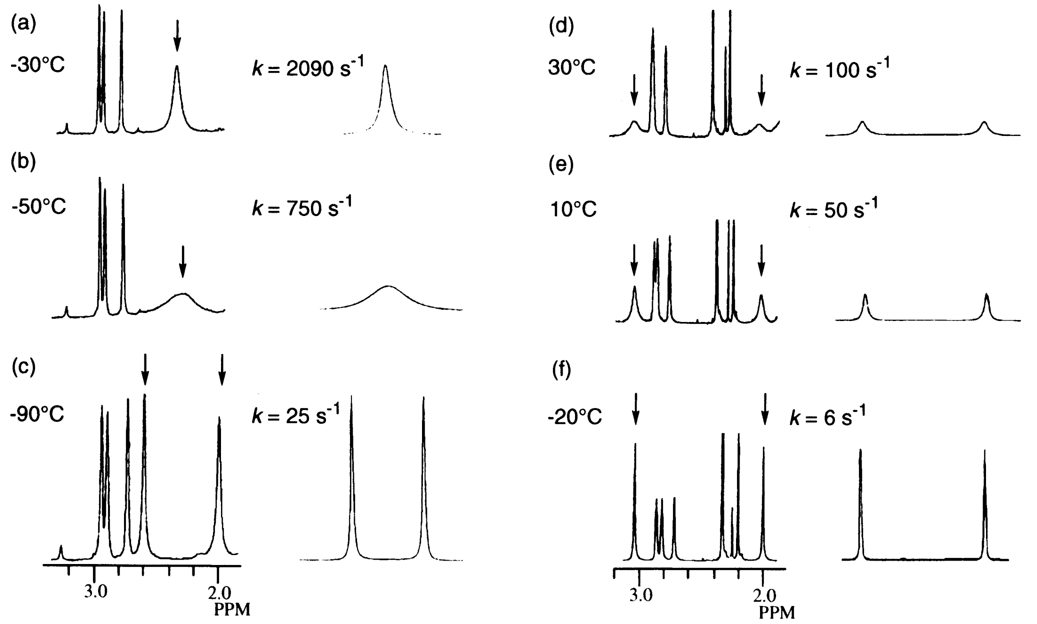
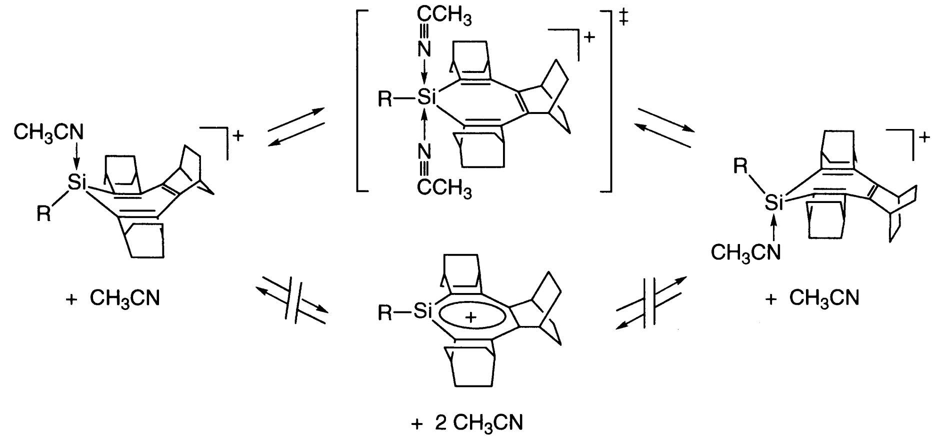


Figure 5. The expanded ^{1}H NMR spectra and their simulations (a)–(c) for **16** and (d)–(f) for **17** at various temperatures. The signals with arrows are for the methyl groups of complexed and free acetonitrile.

5 with CH_3CN is somewhat reduced due to the presence of BCO units and the mesityl group. However, the combination of these effects was not sufficient for making the silylium ion **5** free from the interaction with CH_3CN.

For the CH_3CN complexes **16** and **17**, the exchange between the free and complexed CH_3CN was found to be observable with the variable temperature ^{1}H NMR technique as shown in Fig. 5. Such dynamic behavior of the CH_3CN exchange on silylium ion in solution is of interest in connection with the mechanism of the reaction involving a recently reported chiral and Lewis-acidic silyl cationic catalyst having a 1,1′-binaphtyl backbone.[35] A claim for the silyl cation as the catalyst was contradicted by Olah et al., who concluded that the catalyst is not the silylium ion but the silylnitrilium ion.[36] Once the transition state for the exchange of CH_3CN in a trialkylsilylated acetonitrilium ion was suggested to involve the dissociation process forming free CH_3CN and the silylium ion.[37] If this is the case, the catalyst would also involve the silylium ion state. However, as described below, our dynamic NMR experiment on **16** and **17** showed the opposite result; the transition state involves the association process, probably via a pentacoordinated silicon.

In the ^{1}H NMR for **17** at −20°C (Fig. 5f), two sharp signals for the free and complexed CH_3CN were observed with the integrated ratio of 1:1. This shows that 1 equiv. of CH_3CN was coordinated to **5** forming a silylium ion–CH_3CN 1:1 complex as shown in the above calculations and not a 1:2 complex having a pentavalent silicon. As the temperature was raised (Fig. 5d and e), broadening of the signals was observed, indicating that the free and complexed CH_3CN molecules were exchanging rapidly on an NMR time scale. In this system, however, the coalescence point could not be reached due to the low boiling point of the solvent (CD_2Cl_2). On the other hand, in the case of **16**, the independent signals for free and complexed CH_3CN, which were observed at low temperatures (e.g. −90°C; Fig. 5c), were coalesced and became a single signal at room temperature. From the line shape analyses and Arrhenius



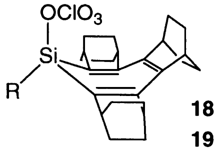
Scheme 4.

plots, activation parameters for the exchange process were determined to be $\Delta H^{\ddagger}=5.7\pm0.5$ kcal mol^{-1} and $\Delta S^{\ddagger}=-19.5\pm2$ eu for **16** and $\Delta H^{\ddagger}=7.3\pm0.5$ kcal mol^{-1} and $\Delta S^{\ddagger}=-25.0\pm2$ eu for **17**. The large negative values of $\Delta S^{\ddagger}$ clearly indicate that the transition-state structure is highly ordered with much steric constraint for both cases and should involve the pentacoordinated silicon as shown in Scheme 4.

The formation of a pentacoordinated silicon at the transition state would be caused by the high Lewis acidity of the silicon atom in silylnitrilium ions **16** and **17**. Such a pentavalent silyl cation coordinated with two CH_3CN molecules was previously suggested to form in an equilibrium with tetracoordinated species when an excess amount of CH_3CN was present.[7] In addition, the dissociation of the complex into CH_3CN and silylium ion requires more energy for the non-π-conjugated silylium ion than for the π-conjugated one (see above). Thus, the mechanism of the CH_3CN exchange for the silylium ion with non-π-conjugation would also not involve the trivalent silylium ion state but the pentavalent state, and hence the catalyst having a binaphthyl backbone would be best described as the silylnitrilium ion and not the silylium ion, as pointed out by Olah.[36]

2.3. Reaction of the silatropylium ions with perchlorate ion

In contrast to the ionic salt of triphenylmethyl perchlorate, triphenylsilylium ion reacts with the perchlorate ion to give the covalent perchlorate ester.[5a] In order to examine again if the combination of aromatic stabilization and steric protection in silylium ion **5** prevents the formation of such a covalent bond, the hydride abstraction from silepins **7** and **10** was conducted using triphenylmethyl perchlorate at low temperatures to room temperature. For both reactions, the ^{29}Si, ^{1}H and ^{13}C NMR signals of the products **18** and **19** (Table 1) showed only small downfield shifts from the neutral precursors **7** and **10** as in the cases of CH_3CN complexes **16** and **17**, indicating that the silatropylium ion character was lost and covalent perchlorate esters were formed. These esters **18** and **19** were also stable at room temperature under inert atmosphere.



18 (R = Me)
19 (R = Mes)

As shown in Fig. 6, the optimized structure of ester **19** at the B3LYP/6-31G(d) level indicates that the distance of Si–O is 1.787 Å, which is 0.105 Å longer than that for Me_3SiOH (1.682 Å) as a model compound for the covalent compound. Also, this distance is 0.021 and 0.027 Å longer than the calculated Si–O distance for Me_3SiClO_4 (1.766 Å) and for **2**·ClO_4 (1.760 Å), respectively. The stabilization energy for the formation of a covalent bond between silatropylium ion **5** and the perchlorate ion (104.7 kcal mol^{-1}), estimated from the energy difference between **19** and the sum of **5** and the perchlorate ion, was smaller than the cases for $Me_3Si\cdot ClO_4$ (152.1 kcal mol^{-1}) and **2**·ClO_4 (133.7 kcal mol^{-1}). Thus, the cyclic conjugation and steric congestion in **5** again reduced the interaction between the silylium ion and perchlorate ion, but the combination of these effects was not sufficient for making the silylium ion free from the interaction with the perchlorate ion.

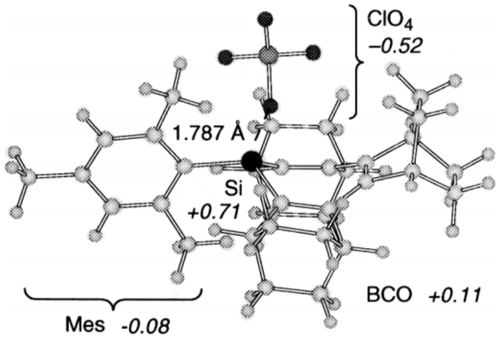
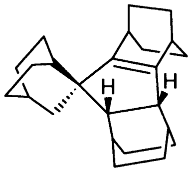
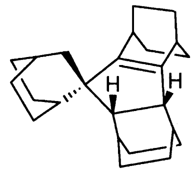


Figure 6. The optimized structure of **19** at B3LYP/6-31G(d) level. The Si–O distance and *Mulliken charges* on silicon atoms and other units are given.

The perchlorate ester **18** was found to react with water causing a novel rearrangement with ring contraction to give a new polycyclic hydrocarbon. Based on ^{1}H and ^{13}C NMR spectra with DEPT measurements, mass spectrum, and elemental analysis, the product (60% yield) was assumed to have a cyclopentene structure with a spiro-connected bicyclic framework. The possible structure of this product appeared to be either the isomer **20a** or **20b**, and the NMR analysis revealed that the product was composed of a single isomer. Its structure was finally determined by X-ray crystallography to be **20a**, as shown in Fig. 7.



20a



20b

The possible mechanism for the formation of **20a** is depicted in Scheme 5. First, water attacks the highly Lewis acidic silicon atom of **18** to give hydroxysilepin and perchloric acid, which protonates the triene part to form the Int-1. The PM3 calculations indicated that the Int-1 would rearrange to the Int-2, in which a double bond is strongly coordinated to the silyl cation with the carbon atoms charged negatively. Then the second attack of water

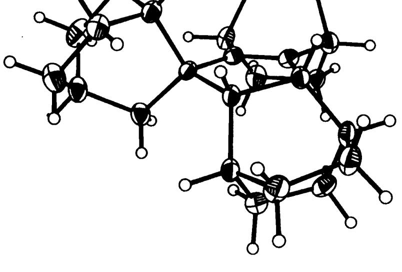
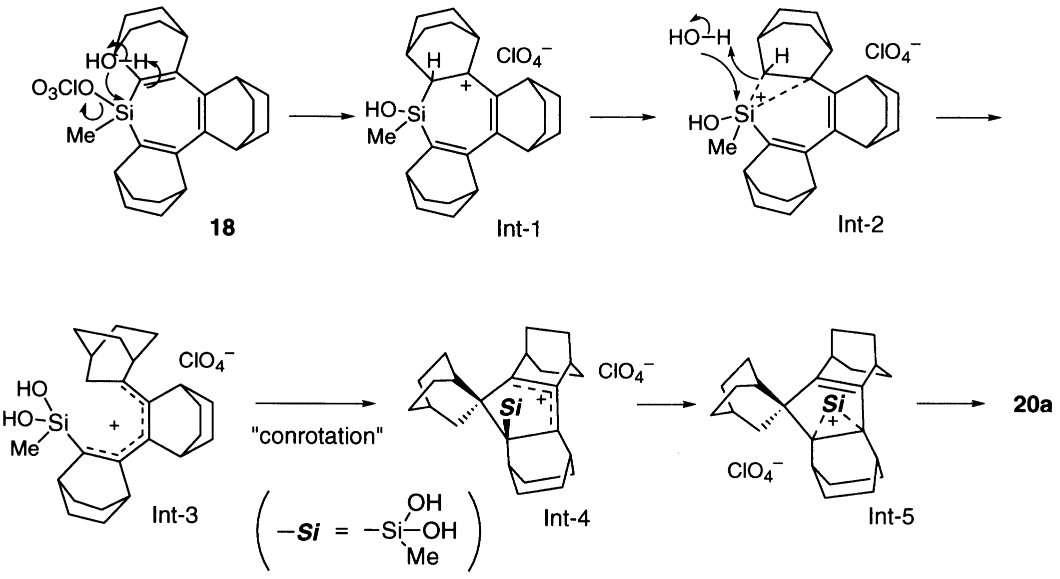


Figure 7. ORTEP drawing (50% probability) showing the X-ray crystal structure of **20a**.



Scheme 5.

molecule occurs to give the Int-3, which has the pentadienyl cation π-system. The thermal electrocyclization of the Int-3 proceeds in a conrotatory fashion, thus establishing the stereoselectivity at the spiro-junction carbon in the Int-4. For the moment we do not have good reasoning for the following process, but apparently two hydrogen atoms are required to replace the siliconium ion in the Int-5 to furnish hydrocarbon **20a**.

3. Conclusion

We have succeeded in the first NMR observation of the silatropylium ion derivative **5** with the aid of annealation with rigid BCO frameworks and of placement of a bulky substituent on silicon. This study revealed not only that the silatropylium ion is aromatic but that the aromatic stabilization is effective for reducing the interaction between the silylium ion center and a solvent having weak nucleophilicity like CH_2Cl_2. On the other hand, when a solvent with stronger nucleophilicity such as CH_3CN was added or the perchlorate ion was present instead of TPFPB as a counter anion, the combination of the aromatic stabilization and steric protection could not prevent the formation of a covalent bond between the silylium ion center and CH_3CN or the perchlorate ion.

For the CH_3CN complexes **16** and **17**, the exchange process of CH_3CN could be observed with the dynamic NMR technique. Such a measurement on the exchange of CH_3CN on a silylium ion was performed for the first time. The exchange process was found to proceed through a highly ordered transition state, which would involve the pentacoordinated silicon atom. On the other hand, the reaction of perchlorate ester **18** with water caused a novel rearrangement with a ring contraction to give hydrocarbon **20a**. This novel reaction is considered to be triggered by the attack of water on silicon atom of **18**. In conclusion, both the CH_3CN exchange reaction in **16** and **17** and the rearrangement observed for **18** are due to the high Lewis acidity of silicon atom in **16**–**18**. Thus, although these compounds did not show any silylium ion character, they still have unique properties which were not observed in the neutral precursors, silepins **7**–**10**.

4. Experimental

4.1. General

Melting points were measured on a Yanaco MP-500D apparatus and are uncorrected. Elemental analyses were performed at the Microanalysis Division of Institute for Chemical Research, Kyoto University. ^1H, ^{13}C and ^{29}Si NMR spectra were recorded on a Varian Mercury-300 (^1H, ^{13}C) or a JEOL JNM-GX 400 (^1H, ^{13}C, ^{29}Si) spectrometer. GC-MS spectrum was measured on a Shimadzu QP 5050A system. Preparative GPC separation was performed with a JAI LC-908 chromatograph equipped with JAIGEL 1H and 2H columns using toluene as eluent. THF was distilled over sodium benzophenone ketyl. Dibromide of BCO trimer (**6**) was prepared following the literature procedure.[29] All the reagents used were commercial materials unless otherwise noted.

4.1.1. 1-Hydro-1-methyl-2,3:4,5:6,7-tris(bicyclo[2.2.2]-octeno)silacycloheptatriene (7). To a stirred solution of dibromide **6** (210 mg, 0.44 mmol) in THF (10 mL) at −60°C was added dropwise a solution of 1.47N *t*-BuLi in pentane (1.2 mL, 1.76 mmol). Addition of each drop of *t*-BuLi solution caused yellow coloration. After stirring for 15 min at −60°C, dichloromethylsilane (0.08 mL, 88 mg, 0.77 mmol) was added dropwise to the reaction mixture, which gradually turned colorless. After being stirred for 30 min at −60°C, the mixture was allowed to warm to room temperature. The solvent was then removed by evaporation and the crude product was extracted with hexane. The extract was purified by preparative GPC eluted with toluene to give **7** (105 mg, 66%) as a white solid. **7**: mp >300°C (dec). For NMR data, see Table 1. Anal. Calcd for $C_{25}H_{34}Si$: C, 82.80; H, 9.45. Found: C, 83.00; H, 9.43.

4.1.2. 1,1-Dichloro-2,3:4,5:6,7-tris(bicyclo[2.2.2]octeno)-silacycloheptatriene (8). To a stirred solution of dibromide **6** (204 mg, 0.43 mmol) in THF (10 mL) at −50°C was added dropwise a solution of 1.5N *t*-BuLi in pentane (1.14 mL, 1.7 mmol). After stirring for 15 min at −60°C, tetrachlorosilane (0.06 mL, 89 mg, 0.52 mmol) was added dropwise to the reaction mixture, which gradually turned colorless. After being stirred for 30 min at −50°C, the mixture was allowed to warm to room temperature. The solvent was then removed by evaporation and the crude product was extracted with hexane. The extract was purified by preparative GPC eluted with toluene to give **8** (98 mg, 55%) as a white solid. **8**: mp 194–195°C; ^{1}H NMR (300 MHz, C_6D_6) δ 3.30 (s, 2H), 2.78 (s, 2H), 2.70 (s, 2H), 1.1–1.5 (m, 24H); ^{13}C NMR (67.8 MHz, C_6D_6, 25°C) δ 155.1, 141.8, 139.3, 33.7, 32.4, 32.3, 26.3, 25.9, 25.2. Anal. Calcd for $C_{24}H_{30}Cl_2Si$: C, 69.05; H, 7.24. Found: C, 68.53; H, 7.37.

4.1.3. 1-Chloro-1-mesityl-2,3:4,5:6,7-tris(bicyclo[2.2.2]-octeno)silacycloheptatriene (9). A solution of mesityllithium (0.18 mmol), prepared from bromomesitylene in THF and two equivalents of *t*-butyllithium in pentane, was added to a stirred solution of dichlorosilepin **8** (50 mg, 0.12 mmol) in THF (3 mL). The solution was stirred for 0.5 h at room temperature. The volatile compounds were removed in vacuo and the resulting pale yellow mixture was extracted with hexane and the insoluble materials were removed by filtration. The filtrate was subjected to preparative GPC eluted with toluene. Separation was effected by recycling the crude products eight times to give **9** (24 mg, 40%) as a white solid. A single crystal was obtained by slow recrystallization from pentane. **9**: mp 167–168°C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.64 (s, 2H), 3.17 (t, 2H), 2.72 (t, 2H), 2.63 (s, 2H), 2.31 (s, 6H), 2.17 (s, 3H), 1.8–1.4 (m, 16H), 1.18 (d, 2H), 0.94 (m, 2H), 0.76 (m, 2H), 0.31 (d, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 149.5, 144.7, 141.2, 139.7, 137.7, 129.6, 128.7, 33.5, 33.4, 32.0, 29.1, 27.1, 26.6, 25.8, 25.6, 24.7, 21.1; ^{29}Si NMR (78.5 MHz, CD_2Cl_2) δ −11.2. Anal. Calcd for $C_{33}H_{41}ClSi$: C, 79.08; H, 8.25. Found: C, 79.11; H, 8.26.

4.1.4. 1-Hydro-1-mesityl-2,3:4,5:6,7-tris(bicyclo[2.2.2]-octeno)silacycloheptatriene (10). A THF solution of $LiAlH_4$ (1 M, 0.250 mL, 0.25 mmol) was added to **9** (50 mg, 0.10 mmol) in THF (1.5 mL). The reaction mixture was stirred at 40°C for 18 h. The volatile compounds were removed in vacuo and the resulting mixture was extracted with hexane and the insoluble materials were removed by filtration. The filtrate was subjected to preparative GPC eluted with toluene to give **10** (42 mg, 90%) as a white solid. A single crystal was obtained by slow recrystallization from pentane. **10**: mp 185°C (dec). For NMR data, see Table 1. Anal. Calcd for $C_{33}H_{42}Si$: C, 84.91; H, 9.07. Found: C, 84.52; H, 9.29.

4.1.5. Preparation of silatropylium ion 5 in CD_2Cl_2. A 10 mm diameter Pyrex glass tube, which was connectable to a vacuum line and equipped with a 5 mm diameter NMR tube as a side arm, was prepared. Into the Pyrex glass tube were placed **10** (15.4 mg, 0.0330 mmol) and triphenylmethyl tetrakis(pentafluorophenyl)borate[38] (30.8 mg, 0.0330 mmol), and the tube was connected to a vacuum line. CD_2Cl_2 (0.75 mL), dried with CaH_2 overnight and with P_2O_5 for 1 h, was transferred into the Pyrex glass tube cooled with liquid nitrogen under vacuum, and the glass tube was sealed off. The reaction mixture was stirred at −50°C for 0.5 h. Then the solution was transferred into the side arm at −78°C. The cooled NMR tube was sealed off and was subjected to the NMR measurements.

4.1.6. Preparation of acetonitrile complexes 16 and 17 in CD_2Cl_2. Into a 5 mm diameter NMR tube which was connectable to a vacuum line, **7** or **10** (0.050 mmol) and triphenylmethyl tetrakis(pentafluorophenyl)borate (46 mg, 0.050 mmol) were placed, and the tube was connected to a vacuum line. CD_2Cl_2 (0.75 mL) and two equivalents of CH_3CN (5.2 μL, 0.10 mmol), dried with CaH_2 overnight and with P_2O_5 for 1 h, was transferred into the NMR tube cooled with liquid nitrogen under vacuum. The cooled NMR tube was sealed off, shaken well, and subjected to the NMR measurements.

4.1.7. Preparation of perchlorates 18 and 19 in CD_2Cl_2. Into a 5 mm diameter NMR tube which was connectable to a vacuum line, **7** or **10** (0.050 mmol) and triphenylmethyl perchlorate (17 mg, 0.050 mmol) were placed, and the tube was connected to a vacuum line. CD_2Cl_2 (0.75 mL), dried with CaH_2 overnight and with P_2O_5 for 1 h, was transferred into the NMR tube cooled with liquid nitrogen under vacuum. The cooled NMR tube was sealed off, shaken well, and subjected to the NMR measurements.

4.1.8. Reaction of perchlorate 18 with water. Into a stirred CD_2Cl_2 solution (0.75 mL) of **18** generated from **7** (9.6 mg, 0.026 mmol) and triphenylmethyl perchlorate (9.1 mg, 0.026 mmol), 10 μL (0.56 mmol) of water was added via a microsyringe. After a few minutes, the reaction mixture was evaporated in vacuo and separated with preparative HPLC (SiO_2) eluted with hexane to give **20a** (5.0 mg, 60% yield) as a white solid. A single crystal was obtained by slow recrystallization from pentane. **20a**: ^{1}H NMR (300 MHz, C_6D_6) δ 2.79 (dd, 1H), 2.73 (q, 1H), 2.48 (q, 1H), 2.28 (d, 1H), 1.9–1.1 (m, 30H); ^{13}C NMR (100 MHz, C_6D_6) δ 150.7 (C), 143.4 (C), 53.0 (C), 49.6 (CH), 48.2 (CH), 37.3 (CH), 34.3 (CH_2), 31.5 (CH), 30.1 (CH), 29.6 (CH_2), 28.7 (CH_2), 27.6 (CH), 27.3 (CH_2), 27.1 (CH), 26.8 (CH_2), 26.5 (CH_2), 26.1 (CH_2), 25.9 (CH), 25.9 (CH_2), 25.8 (CH_2), 25.0 (CH_2), 24.3 (CH_2), 22.9 (CH_2), 21.5 (CH_2). Anal. Calcd for $C_{24}H_{34}$: C, 89.37; H, 10.63. Found: C, 89.29; H, 10.66.

4.1.9. X-Ray crystallography of 9, 10, and 20. Data for compounds **9** and **10** were collected on a Rigaku AFC7R with graphite monochromated CuKα radiation and data for **20** were collected on a Bruker SMART APEX with graphite monochromated MoKα radiation.

Crystal data for **9** are as follows: $C_{33}H_{41}ClSi$; space group *P*-1; a=15.584(2) Å, b=17.833(3) Å, c=9.974(1) Å, β=91.77(1)°; V=2770.6(6) Å^3; Z=4; D_{calc}=1.202 g cm^{-3}; μ(CuKα)=17.62 cm^{-1}; total of 8238 reflections within 2θ=120.1° and $I>3\sigma(I)$. The final R factor was 4.7% (R_w=5.4%).

Crystal data for **10** are as follows: $C_{33}H_{42}Si$; space group

$P2_1/n$; a=11.9511(8) Å, b=16.2109(9) Å, c=14.168(1) Å, β=91.262(1)°; V=2744.2(3) Å^3; Z=4; D_{calc}=1.130 g cm^{-3}; μ(CuKα)=8.70 cm^{-1}; total of 5276 reflections within $I>2\sigma(I)$. The final R factor was 5.1% (R_w=5.0%).

Crystal data for **20** are as follows: $C_{24}H_{34}$; space group $P2_1/n$; a=6.2598(9) Å, b=18.285(3) Å, c=15.499(2) Å, β=93.963(3)°; V=1769.8(4) Å^3; Z=4; D_{calc}=1.210 g cm^{-3}; μ(MoKα)=0.067 mm^{-1}; total of 2507 reflections within $I>2\sigma(I)$. The final R factor was 8.0% (wR^2=21.0%).

All of these structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically calculated and fixed.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) (No. 10146102) from the Ministry of Education, Science, Sports and Culture, Japan.

References

1. (a) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191–1201. (b) Schleyer, P. v. R. *Science* **1997**, *275*, 39–40. (c) Belzner, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1277–1280. (d) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325–332. (e) Maerker, C.; Schleyer, P. v. R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Vol. 2, pp. 513–555. (f) Lickiss, P. D. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Vol. 2, pp. 557–594.
2. (a) Lambert, J. B.; Schulz, W. J.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201–2210. (b) Lambert, J. B.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 6364–6367. (c) Lambert, J. B.; Kania, L.; Schilf, W.; McConnell, J. A. *Organometallics* **1991**, *10*, 2578–2584.
3. (a) Lambert, J. B.; Zang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917–1918. (b) Lambert, J. B.; Zhang, S. *J. Chem. Soc., Chem. Commun.* **1993**, 383–384. (c) Lambert, J. B.; Zang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430–2443.
4. (a) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science* **1993**, *262*, 402–404. (b) Xie, Z.; Liston, D. J.; Jelink, T.; Mitro, V.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1993**, 384–386. (c) Xie, Z.; Bau, R.; Benesi, A.; Reed, C. A. *Organometallics* **1995**, *14*, 3933–3941. (d) Xie, Z.; Manning, J.; Reed, R. W.; Mathur, R.; Boyd, P. D. W.; Benesi, A.; Reed, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 2922–2928.
5. (a) Prakash, G. K. S.; Kenyaniyan, S.; Aniszfeld, L.; Heiliger, L.; Olah, G. A.; Stevens, R. C.; Choi, H. K.; Bau, R. *J. Am. Chem. Soc.* **1987**, *109*, 5123–5126. (b) Olah, G. A.; Rasul, G.; Heiliger, L.; Bausch, J.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1992**, *114*, 7737–7742.
6. Lickiss, P. D. *J. Chem. Soc., Dalton Trans.* **1992**, 1333–1338.
7. Kira, M.; Hino, T.; Sakurai, H. *Chem. Lett.* **1993**, 153–156.
8. (a) Pauling, L. *Science* **1994**, *263*, 983–983. (b) Olah, G. A.; Rasul, G.; Li, X.; Buchholz, H. A.; Sandford, G.; Prakash, G. K. S. *Science* **1994**, *263*, 983–984. (c) Lambert, J. B.; Zang, S. *Science* **1994**, *263*, 984–985. (d) Reed, C. A.; Xie, Z. *Science* **1994**, *263*, 985–986.
9. Schleyer, P. v. R.; Buzek, P.; Müller, T.; Apeloig, Y.; Siehl, H.-U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1471–1473.
10. Olah, G. A.; Rasul, G.; Buchholz, H. A.; Li, X.-y.; Prakash, G. K. S. *Bull. Soc. Chim. Fr.* **1995**, *132*, 569–574.
11. (a) Olsson, L.; Cremer, D. *Chem. Phys. Lett.* **1993**, *215*, 433–443. (b) Olsson, L.; Ottosson, C.-H.; Cremer, D. *J. Am. Chem. Soc.* **1995**, *114*, 7460–7479. (c) Arshadi, M.; Johnels, D.; Edlund, U.; Ottosson, C.-H.; Cremer, D. *J. Am. Chem. Soc.* **1996**, *118*, 5120–5131.
12. (a) Lambert, J. B.; Zhao, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 400–401. (b) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001–5008.
13. Steinberger, H.-U.; Müller, T.; Auner, N.; Maerker, C.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 626–628.
14. Sekiguchi, A.; Matsuno, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2000**, *122*, 11250–11251.
15. Apeloig, Y.; Karni, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Vol. 2, pp. 1–101.
16. Wakita, K.; Tokitoh, N.; Okazaki, R.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 5648–5649.
17. (a) Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1997**, *119*, 6951–6952. (b) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1999**, *121*, 11,336–11,344.
18. West, R.; Sohn, H.; Bankwitz, U.; Calabrese, J.; Apeloig, Y.; Mueller, T. *J. Am. Chem. Soc.* **1995**, *117*, 11608–11609.
19. Freeman, W. P.; Tilley, D.; Yap, G. P. A.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 882–884.
20. Gordon, M. S.; Boudjouk, P.; Anwari, F. *J. Am. Chem. Soc.* **1983**, *105*, 4972–4976.
21. (a) Goldfuss, B.; Schleyer, P. v. R. *Organometallics* **1995**, *14*, 1553–1555. (b) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318. (c) Goldfuss, B.; Schleyer, P. v. R. *Organometallics* **1997**, *16*, 1543–1552.
22. (a) Murthy, S.; Nagano, Y.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 3573–3574. (b) Nagano, Y.; Murthy, S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 10805–10811.
23. Jarek, R. L.; Shin, S. K. *J. Am. Chem. Soc.* **1997**, *119*, 6376–6383.
24. (a) Nicolaides, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 9769–9770. (b) Nicolaides, A.; Radom, L. *J. Am. Chem. Soc.* **1996**, *118*, 10561–10570. (c) Nicolaides, A.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 11933–11937.
25. Berti, G. *J. Org. Chem.* **1957**, *22*, 230–230.
26. (a) Komatsu, K.; Akamatsu, H.; Jinbu, Y.; Okamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 633–634. (b) Komatsu, K.; Akamatsu, H.; Aonuma, S.; Jinbu, Y.; Maekawa, N.; Takeuchi, K. *Tetrahedron* **1991**, *47*, 6951–6996. (c) Komatsu, K.; Nishinaga, T.; Maekawa, N.; Kagayama, A.; Takeuchi, K. *J. Org. Chem.* **1994**, *59*, 7316–7321.
27. A preliminary communication has appeared: Nishinaga, T.; Izukawa, Y.; Komatsu, K. *J. Am. Chem. Soc.* **2000**, *122*, 9312–9313.
28. Nishinaga, T.; Izukawa, Y.; Komatsu, K. *Chem. Lett.* **1998**, 269–270.

29. Komatsu, K.; Aonuma, S.; Jinbu, Y.; Tsuji, R.; Hirosawa, C.; Takeuchi, K. *J. Org. Chem.* **1991**, *56*, 195–203.
30. GAUSSIAN 98, Revision A.5, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone,V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1998.
31. Müller, T.; Zhao, Y.; Lambert, J. B. *Organometallics* **1998**, *17*, 278–280.
32. (a) Nishinaga, T.; Komatsu, K.; Sugita, N. *J. Chem. Soc., Chem. Commun.* **1994**, 2319–2320. (b) Nishinaga, T.; Kawamura, T.; Komatsu, K. *J. Org. Chem.* **1997**, *62*, 5354–5362. (c) Nishinaga, T.; Wakamiya, A.; Komatsu, K. *Chem. Commun.* **1999**, 777–778.
33. For the method of calculations see: Subramanian, G.; Schleyer, P. v. R.; Jiao, H. *Organometallics* **1997**, *16*, 2362–2369.
34. Kira, M.; Hino, T.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6697–6700.
35. Johannsen, M.; Jørgensen, K. A.; Helmchen, G. *J. Am. Chem. Soc.* **1998**, *120*, 7637–7638.
36. Olah, G. A.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1999**, *121*, 9615–9617.
37. Bahr, S. R.; Boudjouk, P. *J. Am. Chem. Soc.* **1993**, *115*, 4514–4519.
38. Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570–8571.