The Elusive 7-Silanorbornadien-7-ylium: Synthesis and Characterization of Nitrilium and Oxonium Ions Deriving from 2,3-Benzo-7-silanorbornadien-7-ylium

Julia Schuppan,[†] Bernhard Herrschaft,[‡] and Thomas Müller*,[‡]

Institut für Anorganische Chemie der Goethe-Universität Frankfurt, Marie Curie Strasse 11, 60439 Frankfurt/Main, Federal Republic of Germany, and Fachinstitut für Anorganische und Allgemeine Chemie der Humboldt Universität Berlin, Hessische Strasse 1-2, 10115 Berlin, Federal Republic of Germany

　　Silylnitrilium (**6**) and Silyloxonium (**7**) ions have been synthesized by reaction of 2,3-benzo-1,4,5,6,7-pentaphenyl-7-silanorbornadiene, **4**, with trityl tetrakis(pentafluorophenyl)borate in benzene in the presence of acetonitrile and diethyl ether, respectively, and have been identified by NMR spectroscopy, supported by density functional calculations of the NMR chemical shift. Solvent-free 2,3-benzo-1,4,5,6,7-pentaphenyl-7-silanorbornadien-7-ylium, **3**, could not be detected under the applied conditions (room temperature, aromatic hydrocarbons or −60 °C, dichloromethane). The results of density functional calculations for the model compound 2,3-benzo-7-phenyl-7-silanorbornadien-7-ylium, **8**, and isomeric $C_{16}H_{13}Si^+$ species suggest that **3** undergoes in hydrocarbon solution a facile exothermic rearrangement to the highly reactive π-type complex PhSi$^+$//tetraphenylnaphthalene.

Introduction

　　Recent progress in silylium ion chemistry[1] has culminated in the synthesis and characterization of solvent-free silylium ions, which are protected sterically[2] and/or are part of aromatic[3] or homoaromatic[4] systems. Alternatively, silyl cations can be stabilized by intramolecular electron donation from remote donor substituents, leading to solvent-free ions with coordination numbers for silicon >3.[5−7] The donating substituent can have either lone pairs (i.e., amino,[5a,b] phosphino,[5c] alkoxy,[5c] or thioalkyl[5c] groups), π-bonds (i.e., C=C,[6a,b] C≡C[6c] bonds or aryl groups[6d,e]), or σ-bonds (i.e., SiH bonds).[6e,7] This interaction leads to a considerable electron transfer from the donor group to silicon; thus the silyl cation character of these positively charged species is disputable.[8,9] Similarly, in cationic species formed by the intermolecular reaction of transient silylium ions with solvent molecules in which silicon adopts coordination numbers 4 and higher, the positive charge is transferred to a large extent to the coordinated solvent molecule. Such stable cationic compounds are formed from silylium ions and solvents such as amines, nitriles, ethers, and even aromatic hydrocarbons, giving silylated ammonium ions,[2a,10] nitrilium ions,[11] oxonium ions,[12] and arenium ions,[13] respectively. These compounds are characterized by dissociation energies of 25−100 kcal mol^{-1}, which range from donor−acceptor

---

　　* Corresponding author. Fax: +49 69 79829188. E-mail: Dr.Thomas.Mueller@chemie.uni-frankfurt.de.
　　† Fachinstitut für Anorganische und Allgemeine Chemie der Humboldt Universität Berlin.
　　‡ Institut für Anorganische Chemie der Goethe-Universität Frankfurt.

　　(1) For recent reviews on silyl cations: (a) Maerker, C.; Schleyer, P. v. R. in *The chemistry of organosilicon compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, p 513. (b) Lickiss, P. D. In *The chemistry of organosilicon compounds*; Rappoport, Z., Apeloig, Y., Ed.; Wiley: New York, 1998; Vol. 2, p 557.
　　(2) (a) Lambert, J. B.; Zhao, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 400. (b) Müller, T.; Zhao, Y.; Lambert, J. B. *Organometallics* **1998**, *17*, 278. (c) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001. (d) Kraka, E.; Sosa, C. P. Gräfenstein, J.; Cremer, D. *Chem. Phys. Lett.* **1997**, *9*, 279.
　　(3) (a) Nishinaga, T.; Izukawa, Y.; Komatsu, K. *J. Am. Chem. Soc.* **2000**, *122*, 9312. (b) Nishinaga, T.; Izukawa, Y.; Komatsu, K. *Tetrahedron* **2001**, *57*, 3645. (c) For earlier unsuccessful attempts, see: Olah, G. A.; Rasul, G.; Heiliger, L.; Bausch, J.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1992**, *114*, 7737.
　　(4) Sekiguchi, A.; Matsuno, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2000**, *122*, 11250.
　　(5) (a) Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reyé, C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1311. (b) Belzner, J.; Schär, D.; Kneisel, B. O.; Herbst-Irmer, R. *Organometallics* **1995**, *14*, 1840. (c) Berlekamp, U.-H.; Jutzi, P.; Mix, A.; Neumann, B.; Stammler, H.-G.; Schoeller; W. W. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2048.

　　(6) (a) Jutzi, P.; Bunte, A. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1605. (b) Steinberger, H.-U.; Müller, T.; Auner, N.; Maerker, C.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 626. (c) Müller, T.; Meyer, R.; Lennartz, D.; Siehl, H.-U. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3074. (d) Werner, K.; Meyer, R.; Müller, T. *Book of Abstract 34th Organosilicon Symposium*; White Plains, NY, 2001; P2-9. (e) Lickiss, P. D.; Masangane, P. C.; Sohal, W. *Book of Abstract 34th Organosilicon Symposium*; White Plains, NY, 2001; p C-16.
　　(7) Müller, T. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 3033.
　　(8) Maerker, C.; Kapp, J.; Schleyer, P. v. R. *Organosilicon Chemistry: From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, 1995; p 329.
　　(9) Ottosson, C.-H.; Cremer D. *Organometallics* **1996**, *15*, 5309.
　　(10) (a) Hensen, K.; Zengerley, T.; Pickel, P.; Klebe, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 725. (b) Bassindale, A. R., Stout. *Tetrahedron Lett.* **1985**, *26*, 3403. (c) Hensen, K.; Zengerley, T.; Müller, T.; Pickel, P. *Z. Anorg. Allg. Chem.* **1988**, *558*, 21. (d) MacLachlan, M. J.; Bourke, S. C.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 2126.
　　(11) For examples of silylnitrilium ions, see: (a) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247.(b) Kira, M.; Hino, T.; Sakurai, H. *Chem. Lett.* **1993**, 555. (c) Bahr, S. R.; Boudjouk, P. *J. Am. Chem. Soc.* **1993**, *115*, 4514. (d) Xie, Z.; Liston, D. J.; Jelinek, T.; Mitro, V.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1993**, 384. (e) Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430. (f) Johannsen, M.; Jorgensen, K. A.; Helmchen, G. *J. Am. Chem. Soc.* **1998**, *120*, 7637.

interactions to covalent bonds, and indicate that the silylium ion character is lost.[8,9]

The 7-silanorbornadien-7-ylium **1** is a particularly interesting example of intramolecular stabilization of the electron-deficient silicon by a remote C=C double bond, leading to a high thermodynamic and kinetic stability,[8] reminiscent of its carbon congener, the 7-norbornadienyl cation.[14] As an example of a bishomosilacyclopropenyl cation, **1** is of great interest from the viewpoints of its aromaticity, structure, and reactivity. Several isomeric $C_6H_7Si^+$ ions including the silabenzyl cation, the silatropylium cation, and the π-complex C_6H_6/SiH^+, **2**, are, however, lower in energy than **1**.[15] In the gas phase only silabenzyl cation and **2** were identified in a FT-ICR experiment.[16] Although recently a silatropylium cation was synthesized,[3] the preparation of cations of the type **1** remains as an open challenge in organosilicon chemistry. Here we report on attempts to synthesize 2,3-benzo-7-silanorbornadienyl cation **3** and on the first example of the synthesis and NMR characterization of nitrilium and oxonium ions deriving from 2,3-benzo-7-silanorbornadienyl cation **3** (Scheme 1).

Results

The precursor silane, 2,3-benzo-1,4,5,6,7-pentaphenyl-7-silanorbornadiene, **4**, was synthesized by standard reactions shown in Scheme 2. The 1-H silole **5** was obtained in 85% yield in a two-step reaction by cyclization of 1,4-dilithiotetraphenylbutadiene[17a,18,19] with silicochloroform in diethyl ether and subsequent Grignard reaction with PhMgBr. The final 4+2 cycloaddition between pentaphenylsilole **5** and benzyne[17] gave *anti* **4**[20] as a single stereoisomer in 41% yield.

Scheme 1

Scheme 2[a]

[a] (a) Li/Et$_2$O rt. (b) HSiCl$_3$/Et$_2$O −196 °C → rt. (c) PhMgBr/THF rt. (d) Mg, *ortho* C$_6$H$_4$FBr, THF.

Table 1. NMR Chemical Shifts of Silane 4 and Cations 6 and 7[a]

compound[a]	δ^{29}Si	δ^{13}C$^{1/4}$	δ^{13}C$^{2/3}$	δ^{13}C$^{5/6}$	δ^{13}C$^{8/9}$	δ^{13}C$^{10/11}$
anti **4**	37.4	58.69	146.79	145.07	122.36	125.64
6	8.9	59.91	146.81	143.28	122.95	124.90
7	3.7	60.21	147.01	143.38	122.48	124.97

[a] For the atom numbering see Scheme 4.

4 was identified by one- and two-dimensional NMR spectroscopy. Characteristic for the 7-silanorbornadiene skeleton is the unusually deshielded silicon resonance at δ^{29}Si = 37.4.[21] A complete assignment of the carbon skeleton of **4** could be made on the basis of two-dimensional NMR spectroscopy and comparison with literature data for benzonorbornadiene[22] (see Table 1 and Experimental Part). The *anti* orientation of the phenyl substituent at silicon with respect to the annelated benzene ring was finally confirmed by a single-crystal X-ray structure analysis (see below).

Suitable crystals for X-ray analysis of pentaphenylsilole **5** were obtained by recrystallization of the crude product from toluene. The molecular structure of **5** is shown in Figure 1.[23,24] The central five-membered ring is planar (dihedral angle θCSiC(1)C(2)C(3)) = 0°), and the endocyclic C=C double (136.1, 136.7 pm) and C−C single bond length (150.9 pm) indicate localized bonds in the silacyclopentadiene ring. The C-phenyl groups are twisted out of the plane of the five-membered ring by 34° (Ph(C(1) and Ph(C4)) and 70° (Ph(C(2) and Ph(C3)).

(12) For examples of silyloxonium ions, see: (a) Kira, M.; Hino, T.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6697. (b) Olah, G. A.; Li, X.-Y.; Wang, Q.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 8962. (c) Xie, Z.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2519. (d) Driess, M.; Barmeyer, R.; Monsé, C.; Merz, K. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2308.

(13) (a) Lambert, J. B.; Zhang, S.; Stern, C.; Huffman, J. C. *Science* **1993**, *260*, 1917. (b) Lambert, J. B.; Zhang, S. *J. Chem. Soc., Chem. Commun.* **1993**, 383. (c) Lambert, J. B.; Zhang, S. *Science* **1994**, *263*, 984. (d) Schleyer, P. v. R.; Buzek, P.; Müller, T.; Apeloig, Y.; Siehl, H.-U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1471. (e) Olsson, L.; Cremer, D. *Chem. Phys. Lett.* **1993**, *6*, 360. (f) Arshadi, M.; Johnels, D.; Edlund, U.; Ottoson, C.-H. Cremer, D. *J. Am. Chem. Soc.* **1996**, *118*, 5120. (g) Olah, G. A.; Rasul, G.; Buchholz, H. A.; Li, X.-Y.; Prakash, G. K. S. *Bull. Soc. Chim. Fr.* **1995**, *132*, 569. (h) Olah, G. A.; Rasul, G.; Buchholz, H. A.; Li, X.-Y.; Sandford, G.; Prakash, G. K. S. *Science* **1994**, *263*, 983. (i) Reed, C. A.; Xie, Z. *Science* **1994**, *263*, 985. (g) Pauling, L. *Science* **1994**, *263*, 983.

(14) (a) Winstein, S.; Ordronneau, C. *J. Am. Chem. Soc.* **1960**, *82*, 2084. (b) Story, P. R.; Saunders: M. *J. Am. Chem. Soc.* **1962**, *84*, 4876. (c) Brookhart, M.; Lustgarten, R. K.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 6352. (d) Olah, G. A.; Liang, G.; Mateescu, G. D.; Riemenschneider, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 8698. (e) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 6803. (f) Bremer, M.; Schötz, K.; Schleyer, P. v. R.; Fleischer, U.; Schindler, M.; Kutzelnigg W.; Koch, W.; Pulay, P. *Angew. Chem., Int. Ed.* **1989**, *28*, 1042.

(15) (a) Nicolaides, A.; Radom, L. *J. Am. Chem. Soc.* **1996**, *118*, 10561. (b) Nicolaides, A.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 11933. (c) Nicolaides, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 9769.
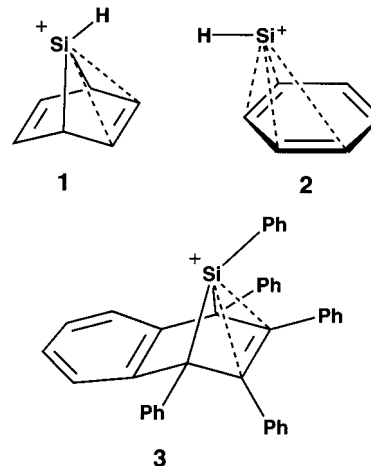
(16) (a) Jarek, R. L.;. Shin, S. K. *J. Am. Chem. Soc.* **1997**, *119*, 6376. (b) Nagano, Y.; Murthy, S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 10805. (c) Murthy, S.; Nagano, Y. Beauchamp, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 3573.

(17) (a) Gilman, H.; Cottis, S. G.; Atwell, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 1596. (b) Gilman, H.; Cottis, S. G.; Atwell, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 5584. (c) Schriewer, M.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105, 897*.
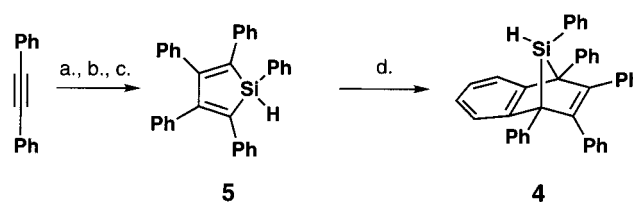
(18) Jutzi, P.; Karl, A. *J. Organomet. Chem.* **1981**, *214*, 289.

(19) Joo, W.-C.; Hong, J. H.; Choi, S.-B.; Son, H.-E. *J. Organomet. Chem.* **1990**, *391*, 27.

(20) The isomer with the substituent at silicon of highest priority on the opposite side of the silylene bridge relative to the annelated benzene ring is called the *anti* isomer throughout the text.

(21) (a) Sakurai, H.; Nakadaira, Y.; Koyama, T.; Sakaba, H. *Chem. Lett.* **1983**, 213. (b) Williams, E. A. In *The chemistry of organosilicon compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Vol. 1, p 511.

(22) Reitz, T. J.; Grunewald, G. L. *Org. Magn. Reson.* **1983**, *21*, 596.
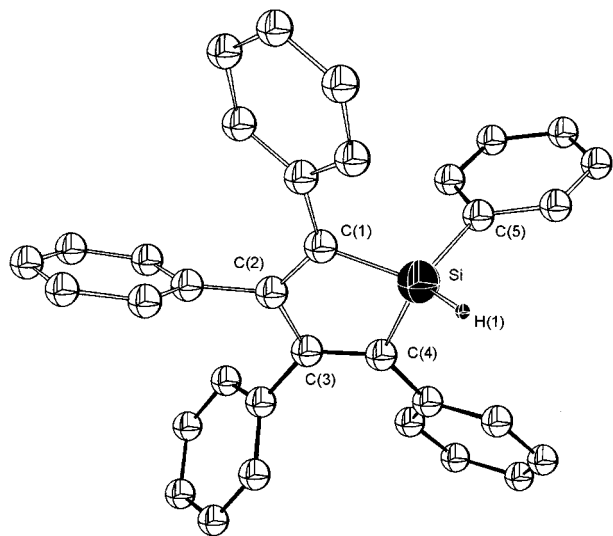
Figure 1. Molecular structure of 1-H silole **5** in the crystal. All hydrogen atoms but H(1) have been omitted for clarity. Selected bond lengths [pm] and bond angles [deg]: C(1)−Si(1) 186.87(19); C(4)−Si(1) 186.2(2); Si(1)−C(5) 186.51-(18); C(1)−C(2) 136.7(3); C(2)−C(3) 150.9(3); C(3)−C(4) 136.1(3); C(2)−C(1)−Si(1) 107.60(14); C(1)−C(2)−C(3) 115.75(16); C(4)−C(3)−C(2) 116.06(16); C(3)−C(4)−Si(1) 107.84(14); C(4)−Si(1)−C(1) 92.74(9).
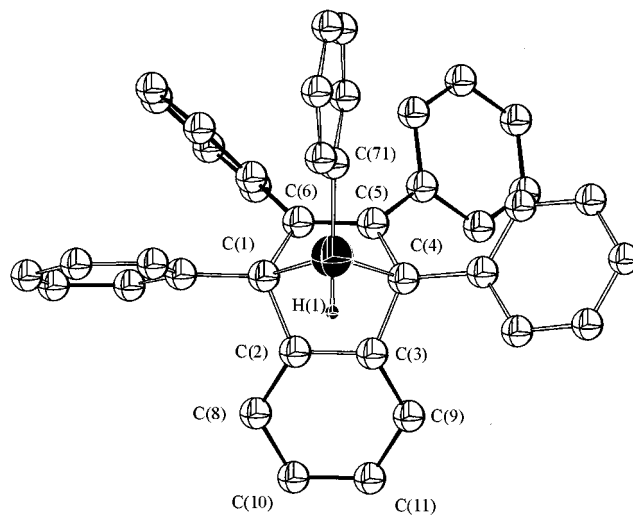

Figure 2. Molecular structure of *anti* **4** in the crystal. All hydrogen atoms but H(1) have been omitted for clarity. Selected bond lengths [pm] and bond angles [deg]: C(1)−C(2) 153.3(4); C(1)−C(6) 154.1(4); C(1)−Si(7) 190.8(3); C(2)−C(8) 137.7(4); C(2)−C(3) 140.2(4); C(8)−C(10) 139.1-(4); C(10)−C(11) 137.7(5); C(11)−C(9) 139.8(5); C(9)−C(3) 138.4(4); C(3)−C(4) 153.5(4); C(4)−C(5) 155.4(4); C(4)−Si-(7) 190.3(3); C(5)−C(6) 135.7(4); Si(7)−C(71) 186.0(3); C(4)−Si(7)−C(1) 82.97(15).

Suitable crystals for X-ray analysis of **4** were obtained by recrystallization of the crude product from dichloromethane. The molecular structure of **4** (Figure 2)[24,25] is typical for this class of compounds.[26] Remarkably, the SiC(1) and SiC(4) bond lengths are relatively long (190.8 and 190.3 pm) and the CSiC bond angle is very acute (83.0°). Steric overcrowding around Si(7) enforces a nearly perpendicular conformation of the 7-phenyl substituent with respect to a plane spanned by C(2)C(3)C-(6)C(5) (θ(C(74)C(71)C(6)C(5)) = 106.1°).

When the first attempt was made to generate 2,3-benzo-1,4,5,6,7-pentaphenyl-7-silanorbornadien-7-ylium, **3**, by hydride abstraction reaction[27] from **4** with 1 equivalent of trityl tetrakis(pentafluorophenyl)borate (TPFPB) in benzene-d_6 at room temperature (rt), a fragmentation process occurred (Scheme 3), shown by ^{1}H and ^{13}C NMR signals of 1,2,3,4-tetraphenylnaphthalene (TPN) (see Experimental Part). Similar results were obtained in toluene at rt and at −10 °C. On the other hand, when the reaction was conducted in a 1:2 mixture of acetonitrile-d_3 and benzene-d_6 at rt, ^{1}H, ^{13}C,

and ^{29}Si NMR signals corresponding to silylnitrilium ion, **6**, formed from acetonitrile-d_3 and **3**, were observed (Scheme 3, Table 1).[11] The ^{29}Si NMR spectrum of the solution consists of one singlet at δ^{29}Si = 8.9, and the ^{13}C NMR shows a complete set of 17 signals which can be assigned to the carbon skeleton of 2,3-benzo-1,4,5,6,7-pentaphenyl-7-silanorbornadiene (see Table 1 and Experimental Part). The ^{29}Si NMR signal of **6** is ca. 30 ppm high field shifted compared to other examples of trialkylsilyl- or triarylsilylnitrilium ions,[11] which results from the different bonding situation in **6**. The assignment is supported by the good agreement between the experimentally determined δ^{29}Si with the calculated value for the model compound **9** (δ^{29}Si = −11.4, see Table 2, Scheme 4),[28,29] since the substituent effect of +17.7 for the two β-phenyl groups[21] attached to C(1) and C(4) in **6** is not considered in the calculations for **9** (see Table 2). Similarly, the silyloxonium ion, **7**,[12] was obtained by the reaction of **4** with TPFPB in a 1:2 mixture of diethyl ether-d_{10} and benzene.

These results indicate that the silyl cation **3** is not stable in hydrocarbons; however cations that result from Lewis acid−base reactions of **3** with polar solvents such as acetonitrile and diethyl ether like **6** and **7** are stable. This parallels the situation found recently for a silatropylium ion,[3] which undergoes ring contraction reactions in toluene. In that case the fragmentation could be prevented using CD$_2$Cl$_2$ as solvent.[3] Reaction of **4** with TPFPB in CD$_2$Cl$_2$ at −70 to −60 °C gives a dark red solution with one single ^{29}Si NMR signal at 22.2

(23) Crystallographic data for **5**: C$_{34}$ H$_{26}$ Si; M_w 462.64, monoclinic, 2/*m*, 2nd setting, space group *P*21/*c* (no. 14) a = 1639.6(3) Å, b = 622.40-(10) Å, c = 2442.7(5), α = 90°, β = 91.96(3)°, γ = 90°, V = 2.4913(8) nm^3, Z = 4, D_{calc} = 1.233 Mg/m^3, abs coeff = 0.115 mm^{-1}, F(000) = 976, reflections collected = 29 272, independent reflections = 6664 [R(int) = 0.1359], GOF = 0.848, R1 = 0.0525 [$I > 2\sigma(I)$], wR2 = 0.1062 (all data).

(24) All structures were solved and refined using *SHELXL-97*, Sheldrik, G. M. University of Göttingen, Germany.

(25) Crystallographic data for *anti* **4**: C$_{80}$ H$_{60}$ Si$_2$; M_w 1077.46, monoclinic 2/*m*, space group *P*2$_1$/*n* (no. 14), a = 1770.3(2) Å, b = 1623.9-(2) Å, c = 2026.9(2) Å, α = 90°, β = 92.180(10)°, γ = 90°, V = 5.8227-(11) nm^3, Z = 4, D_{calc} = 1.229 Mg/m^3, abs coeff = 0.108 mm^{-1}, F(000) = 2272, reflections collected = 9384, independent reflections = 9384 [R(int) = 0.0000], GOF = 0.886, R1 = 0.0532 [$I > 2\sigma(I)$], wR2 = 0.1435 (all data).

(26) Preut, H.; Mayer, B.; Neumann, W. P. *Acta Crystallogr.* **1983**, *21*, C39, 1118.

(27) (a) Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *97*, 3237. (b) Mayr, H.; Basso, N. *J. Am. Chem. Soc.* **1992**, *114*, 3060. (c) Apeloig, Y.; Merin-Aharoni, O.; Danovich, D.; Ioffe, A.; Shaik, S. *Isr. J. Chem.* **1993**, *33*, 387.

(28) (a) Ditchfield R. *Mol. Phys.* **1974**, *27*, 789. (b) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

(29) For the NMR calculations and the NBO analysis the conformer of **9** with the phenyl group in the mirror plane of the molecule was used. Although this conformer is slightly higher in energy than the unsymmetrical minimum (by 1.3 kcal mol^{-1}), it is a more realistic model for the experimentally investigated *anti* **6**, since in the starting silane *anti* **4** the phenyl substituent at silicon adopts a similar conformation due to steric overcrowding.
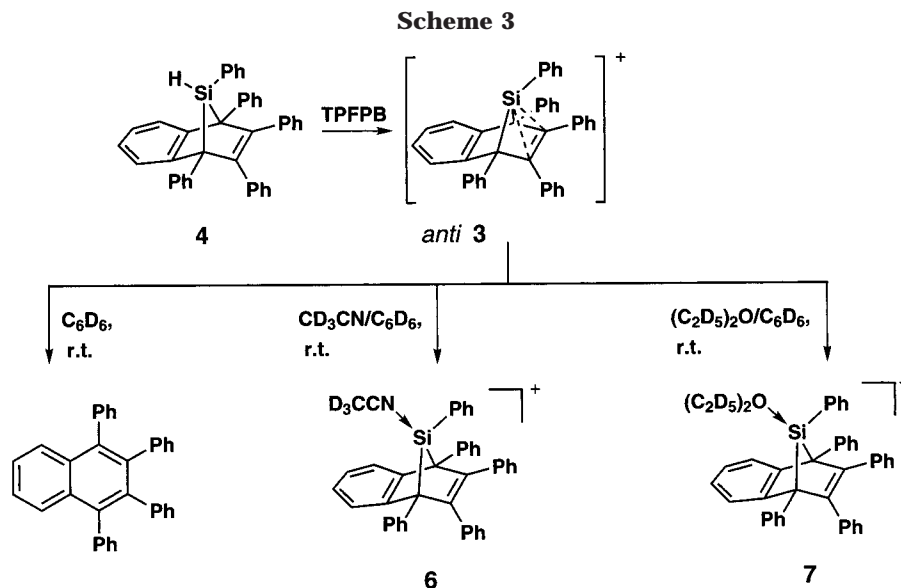
Scheme 3

Table 2. Calculated δ^{29}Si and Calculated Orbital Occupations (NBO, in au) for 7-Silanorbornadienyl Cations and Related Compounds

| compd	δ^{29}Si^a	occ (3p)Si^b	occ $\pi(C^5C^6)^b$
1	−149.7		
syn **8**	−5.4	0.324	1.942
anti **8**	−70.7	0.367	1.691
anti **8a**	−111.0	0.298	1.683
15	249.4		
9	−11.4	0.308	1.895
10	−21.5		
11	−8.9		

^{a} At GIAO/B3LYP/6-311+G (2df,p) (Si) 6-31G(d) (C, H, N, O).
^{b} Calculated using the B3LYP/6-31G(d) electron density.

ppm. This is not consistent with the formation of *anti* **3**, since density functional calculations predict for the model cation *anti* **8a** δ^{29}Si = −111.0 (Table 2, Scheme 4). Instead, the observed δ^{29}Si suggests the formation of a chlorosilane (NMR chemical shift range for R$_2$-ArSiCl: δ^{29}Si = 16.1−26.6);[30] however ^{1}H NMR and ^{13}C NMR spectra obtained from this solution could not be adequately interpreted. At higher temperatures rapid decomposition occurs and a complex product mixture was obtained. Therefore, the nature of the observed species formed in the reaction of **3** with TPFPB in CD$_2$-Cl$_2$ remains in doubt.

The results of calculations[31] for 2,3-benzo-7-silanor-bornadienylium, **8**, and related isomers at the hybrid density functional B3LYP/6-311+G(d,p)//B3LYP/6-31G-(d) + ZPVE level of theory[32] reveal that according to the isodesmic equation 1a both cations, *syn* and *anti* **8**, are stabilized compared to trimethylsilylium by 13.3 and 20.6 kcal mol^{-1}. Comparison with dimethylphenylsilyl-ium (eq 1b) indicates that approximately 3.8 (*syn* **8**) and
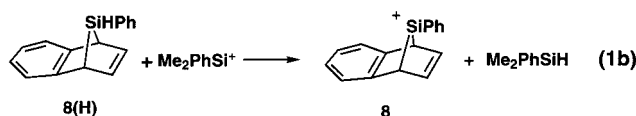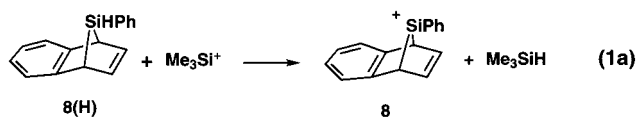
10.4 kcal mol^{-1} (*anti* **8**) result from intramolecular interaction of the positively charged silicon and the homoallylic π-system (either C=C bond or fused benzene ring) in **8**. The isodesmic equations indicate that *anti* **8** is more stabilized by the interaction between the positively charged silicon with the remote C=C bond than the *syn* isomer by the similar interaction with the fused benzene ring. Qualitatively, this can be attributed to the loss of delocalization in the benzene ring, which accompanies the stabilization in *syn* **8**.[33] This interaction between the empty 3p(Si) and high lying π-type MOs of either the C=C bond (*anti* **8**) or the benzene ring (*syn* **8**) is apparent in the calculated structures of both ions (Figure 3, Table 3). In *syn* **8**, the Si^7 bridge is bent toward the annelated benzene ring (bent angle α = 96.7°), leading to relatively small Si−C^2 separation (223.4 pm). In addition the C^2−C^3 bond (143.0 pm) is considerably elongated compared to the C^2−C^3 in *anti* **8** (140.7 pm). Similarly, the calculated structure of *anti* **8** shows that the PhSi^7 group is bent toward the C^5=C^6 bond (α = 92.1°). The Si−C^5 separation is only 215.1 pm and the C^5=C^6 bond length is markedly increased (138.5 pm for *anti* **8** compared to 134.3 pm calculated for the silane *anti* **8(H)** or 134.1 pm for *syn* **8**). These structural features are even more apparent in *anti* **8a**, a C_s symmetric minimum structure in which the phenyl group at silicon is in the same plane as the formally empty 3p(Si) orbital, thus minimizing the resonance stabilization of the silyl cation by the attached phenyl group.[34] For this conformer, which is 0.72 kcal mol^{-1} higher in energy than *anti* **8**, a bending angle α = 88.2° is predicted, which leads to a Si^7−C^5 distance of 211.8 pm and a markedly elongated C^5=C^6 bond (139.6 pm).

(30) Uhlig, F.; Hermann, U.; Marsmann H. *^{29}Si NMR database system* Vers. 2.0; Hamburg, 2000.
(31) (a) All calculations were performed with *Gaussian 94*, Revisions C2-E2, and *Gaussian 98*, Revisions A3-A7, Gaussian, Inc.: Pittsburgh, PA, 1995 and 1999.
(32) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, 2000.
(33) The same arguments have been used already by Bartlett and Giddings to rationalize the vastly different solvolysis rates of *anti* 7-norbornenylbrosylates and *anti* 7-benzonorbornenylbrosylates. Bartlett, P. D.; Giddings, W. P. *J. Am. Chem. Soc.* **1960**, *82*, 1240.
(34) Optimization of *syn* **8** in the point group C_s with the 7-phenyl substituent in the same plane as the formally empty 3p(Si) leads either to *anti* **8** or to **15** (B3LYP/6-31G(d)).

Scheme 4

anti **8**   *syn* **8**   *anti* **8a**

D = H_3CCN : **9**
D = C_6H_6 : **10**
D = Me_2O : **11**

12
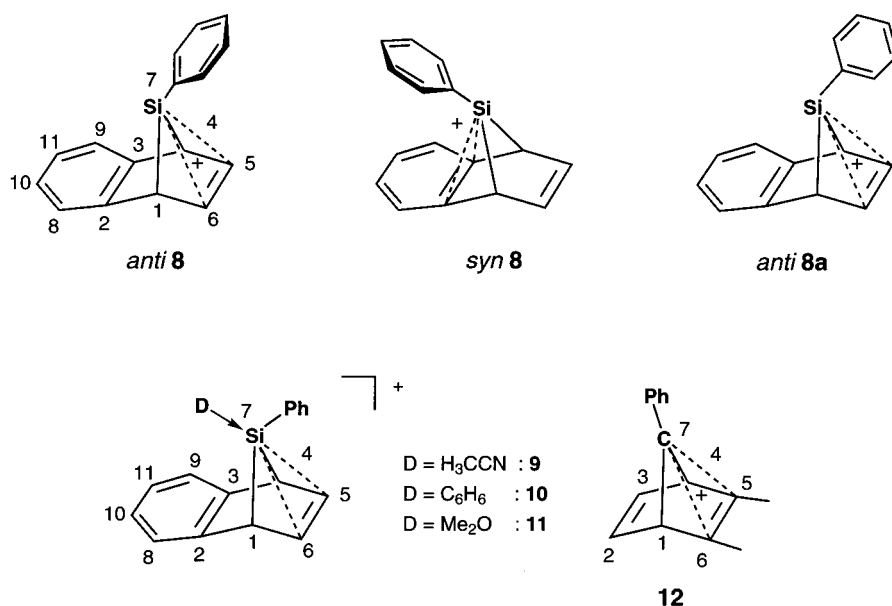
A very similar conformation of the phenyl group at Si[7] is realized also in the precursor silane *anti* **4** as a result of the steric requirements caused by the close proximity of the five phenyl substituents in *anti* **4**. Thus, *anti* **8a** is certainly the model compound in our theoretical study, which is closest to the experimentally investigated species. A NBO analysis[35] for *anti* **8a** reveals that the main contribution to the charge delocalization results from interaction between the 3p(Si) and the remote $C^5=C^6$ bond, leading to a significantly depleted π orbital (occupation 1.683 e) and a significant population of the formally empty 3p(Si) orbital (0.298 e). In the relaxed structure *anti* **8**, in which conjugation between the phenyl substituent and the formally empty 3p(Si) is operating, the population of the formally empty 3p(Si) orbital is higher (0.367 e); however the homoallylic interaction is smaller, leading to a less depleted $\pi(C^5=C^6)$ (see Table 2). In the cation−solvent complexes **9**−**11** the solvent molecule approaches the silicon at distances between 192 pm (**9**, **11**) and 244 pm (**10**, see Table 3, Scheme 4). As the positive charge in cations **9**−**11** is partially transferred further away from silicon to the solvent molecule, the demand for homoconjugative stabilization is consequently smaller. This is apparent from the calculated structural parameters (see Table 3), as well as from an analysis of the charge distribution: that is, in **9**, the Si^7C^5 separation (241.7 pm, $\alpha = 109.7°$) is clearly larger than in the free cation, *anti* **8**, and the $C^5=C^6$ bond length approaches the value calculated for the 7-H-silane *anti* **8** (H) in agreement with a higher occupation number for the $\pi(C^5=C^6)$ orbital (occupation 1.895 e, $r(C^5=C^6) = 135.2$ pm).

Quantum chemical calculations of NMR chemical shifts have been shown to be a reliable tool for the identification and characterization of silyl cations.[1a,2b,d,6b,7,13d−h] Quite remarkably, the calculated δ^{29}Si NMR chemical shifts for all 7-silanorbornadienyl cations are extremely high field shifted (see Table 2).

These unusually shielded ^{29}Si resonances for silylium ions reflect the unique bonding situation in these ions, with the positively charged silicon in a formal 3+2 coordination. Furthermore, the calculated δ^{29}Si is extremely sensitive to the substitution at silicon and even to the actual conformation of the substituent. Thus, for the parent cation **1** a very shielded δ^{29}Si $= -147^{36}$ is calculated and for the cation **8** δ^{29}Si varies from δ^{29}Si $= -111$ (*anti* **8a**) to δ^{29}Si $= -5.7$ (*syn* **8**, see Table 2) depending (i) on the conformation of the phenyl substituent and (ii) on the stereochemistry at Si[7]. Clearly, this shift in δ^{29}Si parallels the decreasing homoconjugative interaction comparing the parent cation **1** with *anti* **8a**, *anti* **8**, and *syn* **8**. Even for the tetracoordinate **9** δ^{29}Si is high field shifted by ca. 30 ppm compared to trialkylsilyl- or triarylsilylnitrilium ions,[11] indicating residual homoconjugative interaction between Si[7] and the π orbital of the ($C^5=C^6$) bond.

Remarkable in all three cations **8** is the nonplanar coordination of the Si[7] and in particular the direction of the bending of the phenyl group. The silicon center in cations **8** is markedly pyramidalized, and the $Si^7−C^{71}$ bond in all cations **8** is clearly bent toward the interacting CC bond; i.e., in *syn* **8** bent toward C^2C^3 (pyramidalization angle $\beta = 17.8°$)[37] and in *anti* **8** and *anti* **8a** toward C^5C^6 ($\beta = 18.1°$ and $22.9°$, see Figure 3). Simple steric interactions should result in a bending of $Si^7−C^{71}$ away from the interacting CC bond into the *anti* half space of the Si[7] bridge. Similar geometric situations are found in the crystal structure of 2,3-dimethyl-7-phenyl-2-norbornen-7-ylium, **12**, although the 7-phenyl group does tip by only 4.4° toward the C=C bond.[38] Tilting of the phenyl group toward the interacting CC bond ($\beta > 0°$) maximizes the overlap between the empty 3p(Si) and the filled π orbital of the C=C bond (see Scheme 5). The longer Si^7C^1(bridgehead) distance in **8** compared to the C^7C^1 distance in carbocation **12** implies that this bending is more emphasized

(35) (a) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO 4.0*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 1996. (b) Reed, A. E.; Curtiss, L. A., Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(36) δ^{29}Si (**1**) $= -148.5$ at IGLO/II′/MP2/6-31G(d).[8]
(37) The pyramidalization angle β is defined as the angle between the $Si^7−C^{71}$ bond and the plane spanned by $Si^7C^1C^4$.
(38) Laube, T. *J. Am. Chem. Soc.* **1989**, *111*, 9224.

syn **8**   *anti* **8**   *anti* **8a**

15   **9**
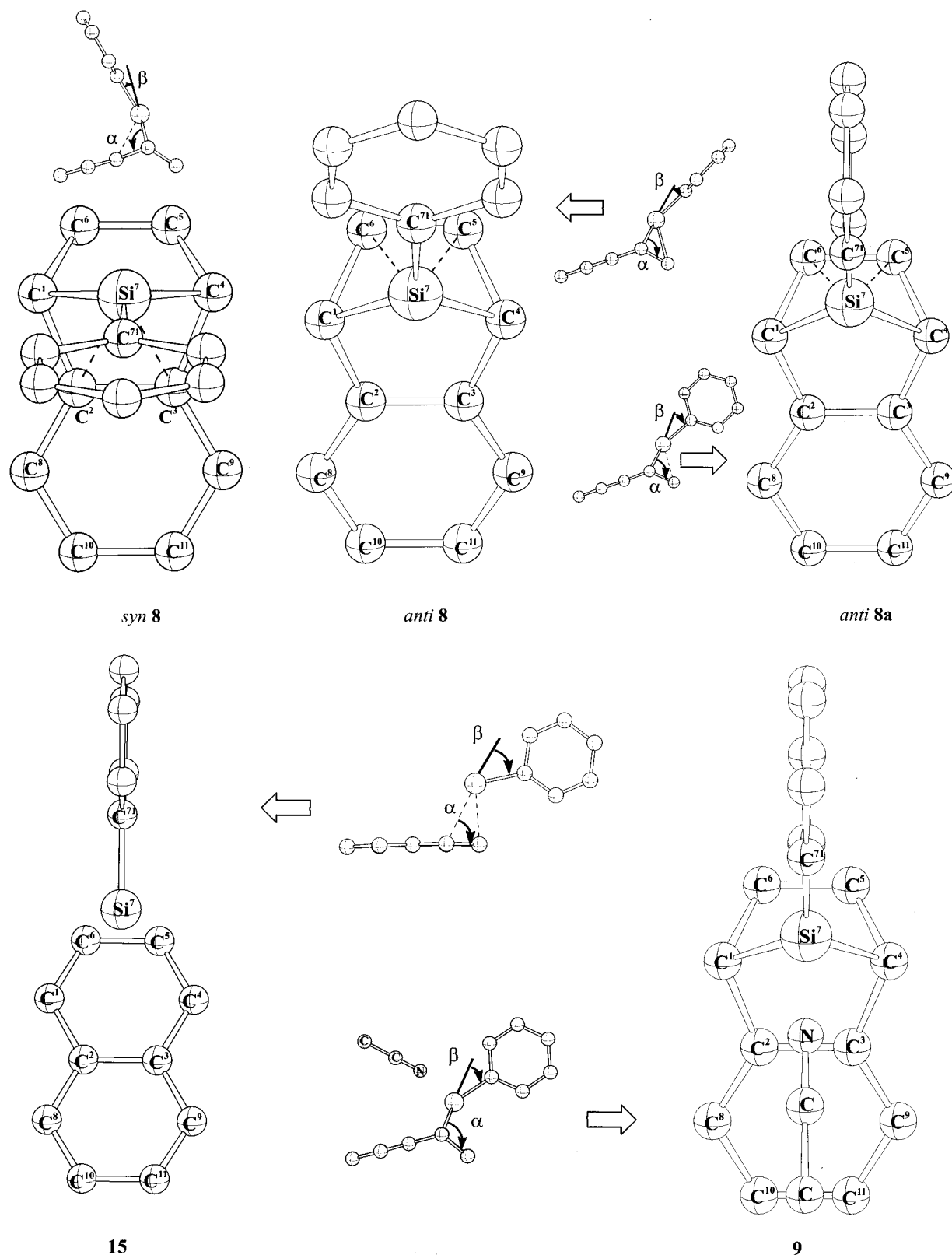
Figure 3. Calculated structures of compounds *syn* **8**, *anti* **8**, *anti* **8a**, **9**, and **15** (at B3LYP/6-31G(d), see also Table 3). All hydrogen atoms have been omitted for clarity.

for the 7-silanorbornadienyl cations than for **12** or related boranes.[38,39]

Model calculations for the 7-silanorbornadienyl cation **1** and its carbon congener support these qualitative arguments. A potential energy scan (see Figure 4) along the pyramidalization angle β for both cations reveals that in the lowest energy conformation of the silyl cation

1 the silicon is strongly pyramidalized ($\beta = 36.7°$) and that this conformation is 5 kcal mol^{-1} more stable than the classical planar arrangement ($\beta = 0°$). In contrast, pyramidalization of the silicon center away from the interacting C=C bond in **1** ($\beta < 0°$) results in destabilization. Further pyramidalization of the silicon center in **1** toward the interacting C=C bond leads to inter-
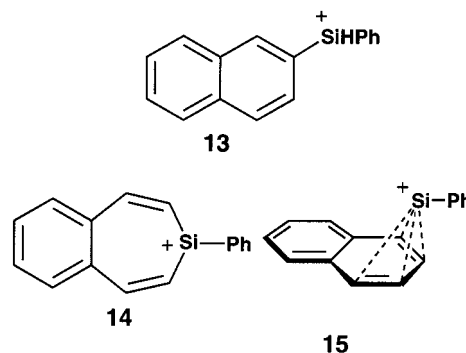
Table 3. Calculated Bond Lengths in 7-Silanorbornadienyl Cations and Related Compounds (B3LYP/6-31G(d))

compd	PG	SiC¹	SiC⁵	SiC²	C¹C²	C²C³	C⁵C⁶	C²C⁸	C⁸C¹⁰	C¹⁰C¹¹	Si⁷D	α	β
syn **8**	C₁	192.0	268.5	223.4	152.1	143.0	134.1	140.9	138.5	141.2		96.7	17.8
anti **8**	C₁	195.2	215.1	273.4	150.5	140.6	138.5	139.3	139.8	139.7		92.1	18.1
anti **8a**	Cₛ	200.7	211.8	277.6	149.3	140.7	139.6	139.4	139.7	139.4		88.2	22.9
15	C₁	286.2	239.1	332.5	142.1	144.0	143.3	141.6	137.9	141.6		65.8	52.9
9	C₁	191.6	241.7	264.6	152.0	141.1	135.2	139.3	140.0	139.7	192.0	109.7	34.8
10	C₁	193.6	234.4	267.7	151.4	141.1	136.0	139.3	139.9	139.7	243.6	104.1	37.6
11	C₁	191.7	238.6	264.9	152.4	141.0	135.3	139.3	140.0	139.7	191.7	107.6	37.6
anti **8(H)**	C₁	193.8	259.2	259.5	152.4	141.3	134.3	139.2	140.0	139.6		120.0	52.0
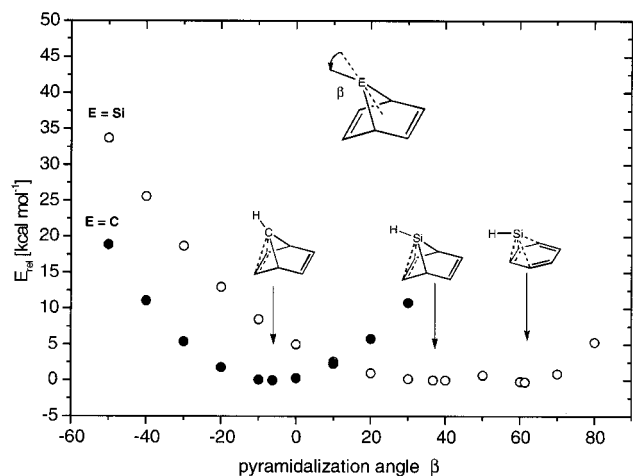
Figure 4. Relative energies (kcal mol^{-1}) of norbornadien-7-ylium (E = C) and 7-silanorbornadien-7-ylium, **1** (E = Si), with different degrees of pyramidalization β of the cationic center (at MP4(SDTQ)/6-311+G(d,p)//MP2/6-31G-(d)). The positions of minimum structures are indicated.

Scheme 5.   Qualitative Orbital Interactions for 1 at Different Pyramidalization Angles β: (a) $\beta < 0°$; (b) $\beta > 0°$
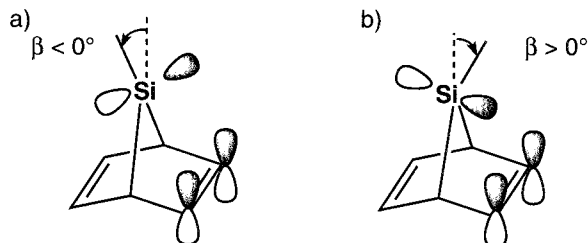
conversion of **1** to the slightly more stable complex SiH$^+$/C$_6$H$_6$, **2** (by 1.5 kcal mol^{-1}, at MP4/6-311+G(d,p)//MP2/6-31G(d)) . This is in striking contrast to the results for the carbon congener, the 7-norbornadienyl cation. The minimum structure is only slightly pyramidalized ($\beta = -6.3°$), and bending of the C^7–H bond in either direction leads to destabilization of the cation.

Calculations for several C$_{16}$H$_{13}$Si$^+$ isomers predict that *syn* and *anti* **8** are high lying local minima, the *anti* isomer being more stable by 4.7 kcal mol^{-1}. The interconversion *anti* **8** → *syn* **8** is connected with a barrier of 6.3 kcal mol^{-1}. Naphthylphenylsilylium, **13**, and 1-phenyl-4,5-benzosilatropylium, **14** (Scheme 6), are both markedly more stable than *anti* **8** (by 22.4 and 14.0 kcal mol^{-1}, respectively). In particular, the complex naph-

(39) (a) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880. (b) Fagan, P. J.; Burns, E. G.; Calabrese, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2979. (c) Schulman, J. M.; Disch, R. L.; Schleyer, P. v. R.; Bühl, M.; Bremer, M.; Koch, W. *J. Am. Chem. Soc.* **1992**, *114*, 7897.

Scheme 6

13

14   **15**
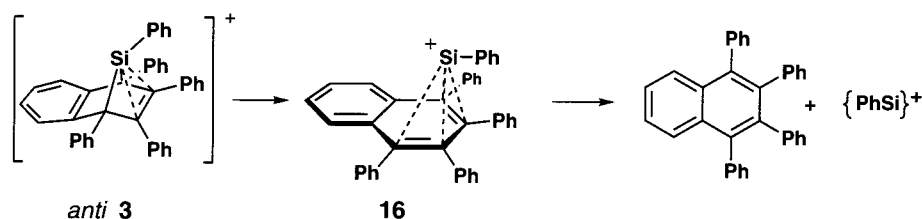
thalene/SiPh$^+$, **15**, is more stable than *anti* **8** by 5.4 kcal mol^{-1}. The monomolecular rearrangement, which transforms *anti* **8** into **15**, involves only a very small barrier of 1.8 kcal mol^{-1}; therefore it is plausible to assume that in the gas phase at rt a free cation *anti* **8** (and similarly the experimentally investigated cation *anti* **3**) has only a very short lifetime. In agreement with this theoretical finding, the complex [C$_6$H$_6$/SiH]$^+$ **2** and not 7-silanorbornadien-7-ylium **1** was identified as a stable C$_6$H$_7$Si$^+$ species in the gas phase in a recent FT-ICR experiment.[15,16a] While species such as **2** and **15** are long-lived species in the gas phase, their fate in the condensed phase is not clear. The occurrence of low-lying unoccupied molecular orbitals at silicon suggests that these compounds are, in solution, highly reactive toward nucleophiles. In addition, the arene groups in **2** and **15** are extremely good leaving groups. Therefore, these compounds are expected to be only short-living intermediates in the condensed phase. On the basis of these considerations it is plausible to assume that **3** rearranges at rt into the complex [PhSi/TPN]$^+$, **16**, which is the source for the observed formation of TPN in the experiments (see Scheme 7).[40]

On the other hand the highly electrophilic silyl cation **3**, which is formed as the first intermediate, can readily undergo reactions with solvent molecules, yielding tetracoordinated positively charged silicon species, e.g., silylnitrilium ion **6** and silyloxonium ion **7**. The barrier for the rearrangement to **16** is markedly increased by this complexation, and it is strongly dependent on the interaction energy (I_E) between **3** and the solvent. I_E between benzene and *anti* **8** calculated for the model complex **10** ($I_E = 10.1$ kcal mol^{-1}) is decisively smaller than I_E calculated for the silylnitrilium ion, **9**, and the silyloxonium ion, **11** ($I_E = 31.1$ (**9**) and $I_E = 28.7$ kcal mol^{-1} (**11**)). These calculational results suggest that the rearrangement of *anti* **3** to PhSi$^+$/TPN, **16**, which

(40) Further investigations on the fate of PhSi$^+$ and its degradation products are in progress and will be reported elsewhere.

Scheme 7

accounts for the experimentally observed formation of TPN, is 17−20 kcal mol^{-1} less favored in the presence of ethers or nitriles than in aromatic hydrocarbons, and it provides a rationalization for the observed stability of the silylnitrilium, **6**, and silyloxonium, **7**, compounds at rt.

Conclusion

Nitrilium and oxonium ions deriving from 2,3-benzo-7-silanorbornadienylium **3** have been prepared by hydride abstraction from the precursor 7-H-2,3-benzo-7-silanorbornadiene **4** in acetonitrile-d_3 and diethyl ether-d_{10}. All attempts to obtain the free silyl cation **3** in solvents of lower nucleophilicity lead to the formation of TPN and/or decomposition. Density functional calculations suggest that **3** (and similarly other 7-silanorbornadienyl cations) is not a stable species and undergoes at rt a facile monomolecular rearrangement leading to the complex **16**, which undergoes a subsequent fragmentation reaction and, therefore, accounts for the observed formation of TPN. For that reason, the prospects to obtain a free 7-silanorbornadienyl cation in solution are rather poor, in sharp contrast to its carbon congener the 7-norbornadienyl cation, which is one of the most stable carbocations.[14]

Theoretical Methods

The geometries of the cations **8**−**11** and **13**−**15** and transitions states **TS**(*syn*/*anti* **8**) and **TS**(*anti* **8**/**15**) have been uniformly optimized[29] at the DFT level[30] employing Becke's three-parameter hybrid method using the LYP correlational functional (B3LYP)[41] and the 6-31G(d) basis set. Transition states were located calculating a potential energy scan along the appropriate reaction coordinate, and the highest energy structure was then subject to transition state optimization using the "ts" routine of G98. The connection of transition states with minimum structures was established using the IRC method.[42] Frequency calculations at the B3LYP/6-31G-(d) level have been performed to verify minimum structures and transition states.[43] Relative energies, interaction energies (I_E), and activation barriers at 0 K have been calculated utilizing B3LYP single-point energies with the larger 6-311+G(d,p) basis set and have been refined by adding unscaled zero-point energies calculated at B3LYP/6-31G(d). Potential energy scans along the pyramidalization mode of norbornadien-7-

ylium and **1** have been performed at the MP4(SDTQ)/6-311+G(d,p)//MP2/6-31G(d) level of theory.[43,44]

NMR chemical shift calculations have been uniformly performed at the DFT GIAO/B3LYP level using the 6-311+G(2df,p) basis set for Si and the 6-31G(d) basis set for C, H, N, O (σ(^{29}Si)(TMS) 332.1).[26] The electronic structure of the investigated compounds was analyzed using NBO theory.[35]

Experimental Part

General Remarks. All reactions and operations were carried out under argon or nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled before use. Spectra were recorded with the following instruments. NMR: Bruker AM 300 (^{29}Si) and DPX 300 (^{1}H, ^{13}C, ^{19}F). ^{1}H NMR: The protio-solvent signal was used as internal standard δ(CHCl$_3$) = 7.24, δ(C$_6$H$_6$) = 7.15. ^{13}C NMR: The solvent signal was used as internal standard δ(CDCl$_3$) = 77.0, δ(C$_6$D$_6$) = 128.0. ^{29}Si NMR: TMS (δ(TMS) = 0) was used as external standard. ^{19}F NMR: CFCl$_3$ (δ(CFCl$_3$) = 0) was used as external standard. IR: Perkin-Elmer 1600 Fourier transform spectrometer.

1,2,3,4,5-Pentaphenylsilole 5.[17a,18,19] A 28.5 g sample (160 mmol) of diphenylacetylene was added in portions to 1.33 g (192 mmol) of freshly grated lithium in 200 mL of diethyl ether. After 3.5 h stirring at room temperature the brown reaction mixture with a yellow precipitate was cooled to liquid nitrogen temperature. After 15 min 28.3 mL of silicochloroform was added, and the reaction mixture was maintained in the liquid nitrogen bath for an additional 5 min. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature. One hour stirring at room temperature completed the reaction. The solvent and excess silane were then removed in vacuo, and the crude 1-chlorosilole was dissolved in 50 mL of THF. A 96 mmol portion of freshly prepared phenyl Grignard reagent (from 2.43 g (100 mmol) of magnesium and 10.1 g (96 mmol) of phenyl bromid) in 60 mL of THF was then added, and the greenish reaction mixture was stirred for 16 h at room temperature. After hydrolysis (ammonium chloride, ice, diethyl ether) the organic layer was separated and dried over sodium sulfate. Removal of the solvent and recrystallization of the crude product gave 31 g of **5** (85% yield).

Anal Calcd for C$_{29}$H$_{24}$Si: C 88.26, H 5.66. Found: C 88.07, H 5.66. ^{1}H NMR (CDCl$_3$ 300 MHz): δ 5.49 (s, 1 H, Si−H, $^{1}J_{SiH}$ = 202.7 Hz), 6.84−7.06, 7.31−7.41, 7.67−7.71 (3m, 25 H, C−H$_{arom}$). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 125.90, 126.53, 127.61, 127.87, 128.38, 129.31, 129.76, 130.26, 135.65 (CH), 130.58, 137.41, 138.72, 138.73 (C$_q$), 156.92 (C$_q$, C$_{2,3}$). ^{29}Si NMR (59.6 MHz, CDCl$_3$): δ −13.7 (dt, $^{1}J_{SiH}$ = 202 Hz, $^{3}J_{SiH}$ = 5 Hz). IR (KBr): ν 2118 cm^{-1} (s).

***anti*-2,3-Benzo-1,4,5,6,7-pentaphenyl-7-silanorbornadiene 4.**[17] A 4 g (8.6 mmol) sample of **5** was suspended in 100 mL of THF, and 0.63 g (26 mmol) of magnesium was added. A solution of 2.94 mL (26 mmol) of *ortho*-fluorobromobenzene in 20 mL of THF was then added slowly at room temperature.

(41) (a) Becke, A. D. *Phys. Rev.* **1988**, *A 38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(42) (a) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1989**, *90*, 2154.

(43) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio molecular orbital theory*; Wiley-Interscience: NY, 1986.

(44) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Phys. Chem.* **1980**, *72*, 4244.

After 30 min the reaction mixture turned brownish red. After 4 h stirring at room temperature all magnesium was consumed. The solvent was removed in vacuo, and the residue was treated with small portions of dichloromethane. The remaining salts were filtered off, and the solution was concentrated to a total volume of 15 mL. **4** crystallizes from this solution at −20 °C during 2−4 days in 41% yield (1.8 g).

^{1}H NMR (300 MHz, CDCl$_3$): δ 5.12 (s, 1 H, Si−H, $^1J_{SiH}$ = 201.2 Hz), 6.68−6.73 (m, 4 H), 6.93−7.20 (m, 18 H), 7.34−7.42 (m, 4 H), 7.45−7.52 (m, 1 H), 7.87−7.92 (m, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$):[45] δ 58.69 (C^a), 122.36 (C^b), 124.66 (C^c), 125.64 (C^d), 126.06 (C^e), 127.26 (C^f), 127.78 (C^g), 128.32 (C^h), 129.79 (C^i), 131.00 (C^l), 131.48 (C^m), 135.74 (C^n), 130.83 (C^k), 137.19, 137.46 (C^o, C^p), 145.07 (C^q), 146.79 (C^r). ^{29}Si NMR (59.6 MHz, CDCl$_3$): δ 37.4 (dt, $^1J_{SiH}$ = 201 Hz, $^3J_{SiH}$ = 5 Hz). IR (KBr): ν 2119 cm^{-1} (SiH).

Attempted Synthesis of Silyl Cation 3. A 200 mg (0.37 mmol) sample of **4** was mixed with 342 mg (0.37 mmol) of TPFPB and dried for 16 h in vacuo. A 2 mL portion of C$_6$D$_6$ was added to start the reaction. The mixture was stirred for 3 min at room temperature. The reaction mixture separates into two layers, a black-brown highly viscous lower phase and an orange-brown upper phase. Both layers were investigated by NMR spectroscopy. The upper phase contains triphenylmethane and tetraphenylnaphthalene, while from the lower phase no signals could be detected. Similar results were obtained in toluene at room temperature and at −10 °C.

^{13}C NMR (75.5 MHz, C$_6$D$_6$): triphenylmethane δ 57.08, 126.53, 128.53, 129.59 (CH), 144.24 (C$_q$); tetraphenylnaphthalene δ 125.21, 125.77, 126.31, 126.45, 126.85, 127.41, 131.17, 131.19 (CH), 131.92, 138.30, 138.75, 139.48, 140.43 (C$_q$).

6·[B(C$_6$F$_5$)$_4$]. A 200 mg (0.37 mmol) sample of **4** was mixed with 342 mg (0.37 mmol) of TPFPB and dried for 16 h in vacuo. A 1 mL portion of CD$_3$CN was added at room temperature to start the reaction. After 3 min 1.5 mL of C$_6$D$_6$ was added to completely dissolve the educts. After an additional 2 min of stirring at room temperature a clear orange-brown solution was obtained, from which a white microcrystalline powder separates after 2 h. The powder was separated, dried, and dissolved in dichloromethane. The solution in C$_6$D$_6$/CD$_3$CN and the solution of the white powder had identical ^{1}H, ^{13}C, and

^{29}Si NMR spectra, which showed besides the signals for triphenylmethane a complete set of the silylnitrilium salt **6**[B(C$_6$F$_5$)$_4$].

^{1}H NMR (300 MHz, C$_6$D$_6$): δ 6.71−7.46 (m), 8.09−8.13 (m). ^{13}C NMR (75.5 MHz, C$_6$D$_6$):[45] **6** δ 59.91 (C$_{a'}$), 122.95 (C$_{b'}$), 124.90(C$_{c'}$), 125.93 (C$_{d'}$), 126.32 (C$_{e'}$), 127.43 (C$_{f'}$), 127.97 (C$_{g'}$), 128.28 (C$_{h'}$), 129.86 (C$_{k'}$), 130.34 (C$_{i'}$), 131.38 (C$_{m'}$), 131.79 (C$_{l'}$), 136.72 (C$_{n'}$), 137.36, 137.93 (C$_{o'}$, C$_{p'}$), 143.28 (C$_{q'}$), 146.81 (C$_{r'}$); [B(C$_6$F$_5$)$_4$]$^-$, δ 149.0 (d, $^1J_{CF}$ = 245.6 Hz), 138.81 (d, $^1J_{CF}$ = 251.5 Hz), 137.0 (d, $^1J_{CF}$ = 241.5 Hz), 124.0 (br). ^{19}F NMR (282.4 MHz, C$_6$D$_6$): δ −167.73 (t, 8 F), 163.82 (t, 4 F), 133.50 (m, 8 F). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$): δ 8.9.

7·[B(C$_6$F$_5$)$_4$]. A method analogous to that already described for the synthesis of **6** was applied. A 1 mL sample of (C$_2$D$_5$)$_2$O was added at room temperature to an equimolar solid mixture of **4** and TPFPB (0.37 mmol each) to start the reaction. After 3 min 1.5 mL of C$_6$D$_6$ was added to completely dissolve the educts. After an additional 3 min of stirring at room temperature two layers were obtained. The upper orange-brown layer was separated. After 15 min a white solid precipitated and was investigated by NMR spectroscopy. The silyloxonium salt **7**·[B(C$_6$F$_5$)$_4$] was identified by its ^{1}H, ^{13}C, and ^{29}Si NMR spectra.

^{1}H NMR (300 MHz, C$_6$D$_6$): δ 6.73−7.44 (m), 8.14−8.19 (m). ^{13}C NMR (75.5 MHz, C$_6$D$_6$):[45] **7** δ 60.21 (C$_{a''}$), 122.48 (C$_{b''}$), 124.97 (C$_{c''}$), 126.11 (C$_{d''}$), 126.31 (C$_{e''}$), 127.38 (C$_{f''}$), 128.11 (C$_{g''}$), 128.20 (C$_{h''}$), 130.54 (C$_{i''}$), 130.72 (C$_{k''}$), 131.13 (C$_{m''}$), 132.09 (C$_{l''}$), 136.95 (C$_{n''}$), 137.78, 137.96 (C$_{o''}$, C$_{p''}$), 143.38 (C$_{q''}$), 147.01 (C$_{r''}$); [B(C$_6$F$_5$)$_4$]$^-$, δ 149.0 (d, $^1J_{CF}$ = 245.6 Hz), 138.81 (d, $^1J_{CF}$ = 251.5 Hz), 137.0 (d, $^1J_{CF}$ = 241.5 Hz), 124.0 (br). ^{19}F NMR (282.4 MHz, C$_6$D$_6$): δ −167.73 (t, 8 F), 163.82 (t, 4 F), 133.50 (m, 8 F). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$): δ 3.7.

Supporting Information Available: NMR spectra of **6** and **7** and X-ray structural data for **4** and **5**. Total energies (hartrees) and geometries for all calculated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010420C

---

(45) See Figures S1−S3 in the Supporting Information for the assignment.