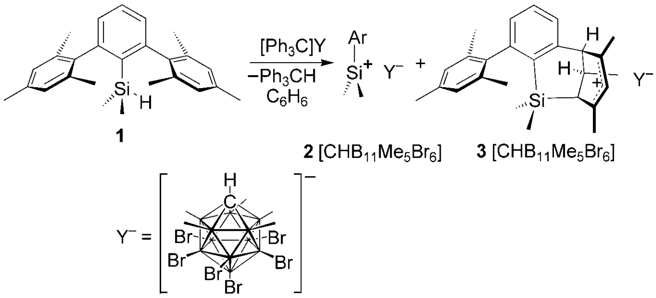
DOI: 10.1002/anie.200900098

Synthesis and Crystal Structure of a Silyl-Stabilized Allyl Cation Formed by Disruption of an Arene by a Protonation–Hydrosilylation Sequence**

Simon Duttwyler, Yun Zhang, Anthony Linden, Christopher A. Reed, Kim K. Baldridge,* and Jay S. Siegel**

Dedicated to Josef Michl on the occasion of his 70th birthday

Allyl cations, which are well-known primarily from solution NMR spectroscopy in traditional superacidic media,[1] have remained elusive in crystalline form. Indeed, these rare guests in the chemist's lab have normally arrived unannounced during attempts to prepare other reactive species.[2] Recent investigations focused on the conversion of silane **1** into the silylium ion $\mathbf{2}^+$, which is stabilized by Si–π interactions (Scheme 1).[3] A side path of these studies led to the isolation of a crystalline bicyclic allylic cation $\mathbf{3}^+$ that is formed with concomitant disruption of an aromatic ring. Invited or not, the solid-state structure of $\mathbf{3}^+$ teaches us much about this important class of organic intermediates and suggests an intricate stereochemistry, which reveals a likely mechanism for this unexpected transformation.



Scheme 1. Formation of $\mathbf{2}^+$ and $\mathbf{3}^+$ by hydride removal from silane **1**. Ar = 2,6-(2,4,6-trimethylphenyl)phenyl.

A generally successful method for producing silyl cation reactive intermediates involves the abstraction of hydride from a silane by the trityl cation. To that same end, treatment of terphenylsilane **1** with the trityl salt $[Ph_3C][CHB_{11}Me_5Br_6]$ afforded, in addition to the intended silylium carborane $\mathbf{2}[CHB_{11}Me_5Br_6]$, a small amount of a second compound, as indicated by NMR spectroscopy.[3] Attempts to crystallize pure $\mathbf{2}[CHB_{11}Me_5Br_6]$ from *ortho*-dichlorobenzene/hexane yielded instead yellow prisms of the minor product $\mathbf{3}[CHB_{11}Me_5Br_6]$ (Scheme 1), the identity of which was determined by X-ray crystallography (Figure 1).[4]

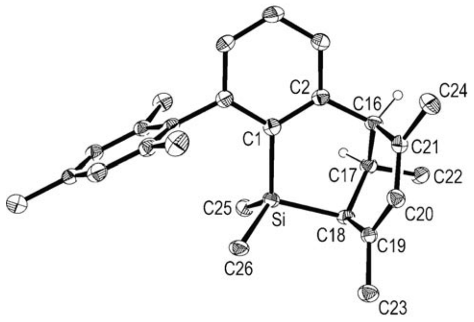


Figure 1. ORTEP of $\mathbf{3}^+$ with ellipsoids set at 30% probability. Hydrogen atoms are omitted for clarity (except for those at C16 and C17).

The crystal structure of $\mathbf{3}[CHB_{11}Me_5Br_6]$ consists of well-separated cations and anions, and $\mathbf{3}^+$ can be described as a silabicyclo[3.3.1]nonenyl cation with the formal positive charge distributed over a five-atom unit Si-C18-C19-C20-C21. Selected bond lengths and angles are given in Table 1. The unusually short sp^3–sp^2 C18–C19 bond, and unusually long Si–C18 bond relative to normal lengths, set up a long-short-long-short distortion pattern from C18 to C21. Carbon atoms C16, C18–C21, C23, and C24 all lie in the mean plane through them within 0.025(4) Å, and the sum of angles around C19 and C21 is 360.0(4)° for each atom, indicating trigonal planar coordination.

Computations emulate well the experimental structure and provide insight into the orbitals over which the positive charge is distributed. The structure suggests an interaction of the Si–C σ bond with the allyl π system. β-Silyl stabilization of carbenium ions has much precedence and has been exploited synthetically.[6]

One hypothesis to account for the formation of $\mathbf{3}^+$ involves a protonation/hydrosilylation mechanism

---

[*] Y. Zhang, Prof. C. A. Reed
Center for S and P Block Chemistry, Department of Chemistry
University of California
Riverside, CA 92521 (USA)
E-mail: chris.reed@ucr.edu
S. Duttwyler, Priv.-Doz. Dr. D. A. Linden, Prof. K. K. Baldridge,
Prof. J. S. Siegel
Organic Chemistry Institute, University of Zurich
Winterthurerstrasse 190, 8057 Zurich (Switzerland)
E-mail: jss@oci.uzh.ch

[**] We thank the Swiss and US National Science Foundation for research support.

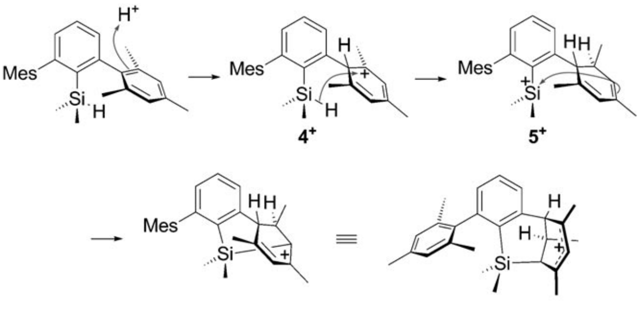
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200900098.

Table 1: Selected bond lengths [Å] and angles [°] for the calculated and the single-crystal X-ray structure of $\mathbf{3}^+$.

Parameter	Expt	Calcd[a]	Parameter	Expt	Calcd[a]
C18–C19	1.414(5)	1.4136	C19-C23	1.486(5)	1.4871
C19–C20	1.426(5)	1.4213	C21-C24	1.489(6)	1.4863
C20–C21	1.359(6)	1.3620	C21-C16	1.506(6)	1.5124
Si–C18	1.966(4)	2.0278	C19-C20-C21	120.4(4)	121.13
Si–C1	1.892(4)	1.8797	C18-C19-C20	120.9(4)	120.92
Si–C25	1.869(4)	1.8647	C23-C19-C20	117.3(4)	118.06
Si–C26	1.868(4)	1.8609	C20-C21-C16	121.8(4)	121.06
C16–C17	1.526(5)	1.5336	C20-C21-C24	120.6(4)	121.58
C17–C18	1.545(5)	1.5326	C1-Si-C18	104.4(2)	102.18
C17–C22	1.526(5)	1.5297	Si-C18-C19	107.8(3)	103.30

[a] Computed at the M06-2X/DZ(2df,pd) level of theory (see Ref. [5]).

(Scheme 2). If a mesityl ring of **1**, the most basic component in the mixture, reacts with a proton source at the *ipso* position, a Wheland intermediate $\mathbf{4}^+$ would form. The acid source could be a protonated silanol formed from $\mathbf{2}^+$ and trace water. H_3O^+ is known to protonate mesitylene in benzene solution.[7] A subsequent intramolecular hydride transfer from silicon to an *ortho* carbon atom of $\mathbf{4}^+$ affords silylium ion $\mathbf{5}^+$. This formal silylium ion–diene system collapses to give cation $\mathbf{3}^+$. The proposed reaction sequence offers an explanation for the observed connectivity and relative stereochemistry in the product; external protonation with concomitant intramolecular hydride transfer leads to the observed configuration with an *exo* H at C16 and *endo* H at C17.



Scheme 2. Proposed protonation/hydrosilylation mechanism for the formation of $\mathbf{3}^+$.

A test of this mechanistic hypothesis comes from intentional treatment of **1** with strong Brønsted acids. In contrast to the mechanistic hypothesis, addition of 1 equiv of triflic acid (TfOH) in benzene—one of the strongest oxyacids[8]—did not give **3**[OTf], but afforded the silyl triflate $ArSiMe_2OTf$ in quantitative yield. Apparently, the negatively polarized Si–H hydrogen atom acts as a Brønsted base towards triflic acid, and trapping of a silylium ion species by the coordinating triflate anion occurs at a much faster rate than ring protonation/hydrosilylation.

An acid that would function as proposed in Scheme 2 would be an arenium carborane [arene-H]$[CHB_{11}X_5Y_6]$ (X = H, Me, halogen, Y = halogen), a class of redox-inert protic acids that are even stronger than triflic acid and with less coordinating anions, and which are capable of protonating a mesityl ring to a high degree.[9] Would such an arenium species such as the toluenium ion ($CH_3C_6H_6^+$) convert **1** into $\mathbf{3}^+$? Indeed, treatment of **1** with 1 equiv of $[CH_3C_6H_6][CHB_{11}Me_5Br_6]$ afforded $\mathbf{3}[CHB_{11}Me_5Br_6]$ as the single product [Eq. (1)]. It was isolated as a yellow powder in high yield and characterized by a second X-ray crystallographic analysis, NMR spectroscopy (^1H, ^{13}C, ^{29}Si, ^{11}B), and IR spectroscopy. GC-MS analysis of the reaction quenched with different nucleophiles supports the formation of neutral compounds that are consistent with $\mathbf{3}^+$ as the precursor.

$$\mathbf{1} \xrightarrow[\text{C}_6\text{H}_6,\ \text{RT, 12 h}]{[\text{CH}_3\text{C}_6\text{H}_6][\text{CHB}_{11}\text{Me}_5\text{Br}_6]} \underset{93\,\%}{\mathbf{3}\,[\text{CHB}_{11}\text{Me}_5\text{Br}_6]} \qquad (1)$$

One- and two-dimensional NMR experiments in $[D_2]$dichloromethane allowed a detailed characterization of $\mathbf{3}[CHB_{11}Me_5Br_6]$ in solution (Table 2). Carbon atoms C19, C20, and C21 resonate at 225, 129, and 197 ppm, respectively. The deshielding is slightly less pronounced than in comparable allyl cations,[1c] a fact that might be a result of σ–π conjugation between the Si–C bond and the allyl π system. Carbon atom C18 resonates at 69 ppm, which is shifted downfield in comparison to the other saturated carbon atoms and is not in the range of usual sp^3 ^{13}C signals.[10] This observation might again be attributed to a certain diene character of the C18–C21 system. Yet, to depict the silyl fragment as cationic $ArMe_2Si^+$ is not justified: the ^{29}Si NMR shift of $\mathbf{3}^+$ is found at $\delta = -4.2$ ppm, a value typically found in tetracoordinate, neutral silicon species.[11]

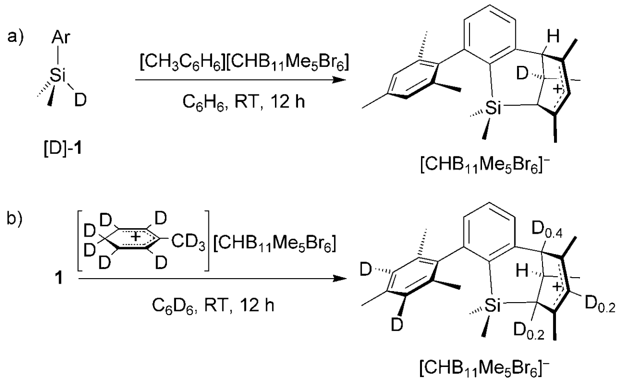
Table 2: Experimental and calculated ^{13}C and ^1H NMR shifts of $\mathbf{3}^+$.

Carbon atom	$^{13}C_{expt}$[a]	$^{13}C_{calcd}$[c]		$^1H_{expt}$[a,b]	$^1H_{calcd}$	
C16	54.5	55.6	(53.8)	3.78	3.36	(3.47)
C17	40.6	42.1	(41.5)	3.11	2.76	(2.74)
C18	69.3	71.4	(69.2)	4.03	3.76	(3.84)
C19	225.2	210.2	(208.6)	–	–	–
C20	129.4	121.2	(120.4)	6.98	6.28	(6.45)
C21	196.8	193.0	(189.7)	–	–	–
C22	21.3	20.8	(20.7)	1.39	1.31	(1.16)
C23	34.6	31.6	(31.2)	2.78	2.41	(2.33)
C24	29.0	27.8	(27.2)	2.65	2.49	(2.35)

[a] Determined by HSQC and HMBC experiments and given in ppm with respect to solvent peaks of CD_2Cl_2 (54.0 ppm for ^{13}C, 5.32 ppm for ^1H). [b] H attached to the corresponding carbon atom. [c] M06-L/DZ+(2df,pd)//M06-2X/DZ(2df,pd); number in parentheses is in dichloromethane. C22, C23, C24 hydrogen values averaged: C22: 1.24, 1.30, 1.39 (1.06, 1.13, 1.28); C23: 2.01, 2.48, 2.74 (1.94, 2.38, 2.67); C24: 2.05, 2.93, 2.49 (1.94, 2.71, 2.39); see also the Supporting Information.

Experiments with deuterated reactants or reagents were carried out to gain further insight into the mechanism that leads to $\mathbf{3}^+$. According to Scheme 2, acidic $[D_9]$toluenium ion ($CD_3C_6D_6^+$) would afford a product with deuterium at the C16 *exo* position but not at C17. Conversely, deuterated silane [D]-**1** in combination with toluenium ion ($CH_3C_6H_6^+$) should give rise to the cation labeled only at C17.

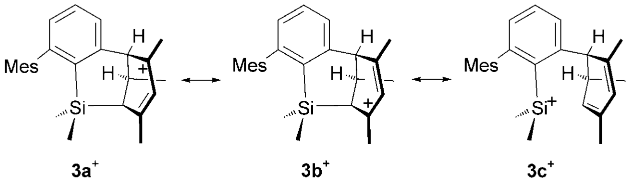
The reaction of [D]-**1** under protic conditions yielded only the product *endo*-deuterated at C17 (Scheme 3a). The negatively polarized deuterium atom in [D]-**1** does not seem to be involved in Brønsted acid–base chemistry and acts exclusively as a reducing agent towards the Wheland intermediate **4**$^+$ when arenium acids are used.



Scheme 3. Deuteration experiments using a) [D]-**1** with $CH_3C_6H_6^+$, and b) **1** with $CD_3C_6D_6^+$.

In the experiment with acidic [D$_9$]toluenium, positions C16, C18, and C20 were partially deuterated, and the *meta* positions of the mesityl ring were fully deuterated (Scheme 3b). The degree of deuteration was inferred from integration of ^{1}H NMR spectra and from ^{2}H and ^{13}C NMR measurements.[12] Reversible protonation of the mesityl rings of **1** leads to H/D scrambling and some "washing in" of H to the toluenium species. This scrambling accounts for the presence of some H in the *ipso* position of the cationic ring of **3**$^+$. After the hydride transfer has taken place, H/D exchange continues on the unchanged mesityl ring,[13] which is most likely due to a slight excess of toluenium ions. The central ring is not deuterated under the reaction conditions. Orbital analysis supports this observation; the basic HOMO of **3** is expressed predominantly on the unchanged mesityl ring.

The question arises as to whether **3**$^+$ is best described as a silyl-stabilized allyl cation or a diene-coordinated silylium ion (Scheme 4). From a valence bond perspective the principal resonance structures of **3**$^+$ to consider are **3a**$^+$, **3b**$^+$, and **3c**$^+$. As pointed out above, the long-short-long-short pattern along Si-C18-C19-C20-C21 and the ^{13}C NMR signals of C18–C21 are in agreement with a certain silylium ion–diene character, **3c**$^+$. However, the observed structure deviates little from the hypothetical ideal allylic cation depicted by only **3a**$^+$ and **3b**$^+$. Silylium ions stabilized by π systems exhibit Si–C distances of more than 2.1 Å and chemical shifts $\delta(^{29}Si) > 55$ ppm;[3,14] neither is the case for **3**$^+$.



Scheme 4. Principal resonance forms of **3**$^+$.

A natural bond orbital (NBO) analysis of **3**$^+$ allows a segmentation of the Si-C18-C19-C20-C21 fragment into Lewis forms with a p orbital cation acceptor on C19 interacting strongly with the Si-C18 σ bond and the C20-C21 π bond as donors. The analysis indicates significant delocalization of 4 electrons among three orbitals (σ, p, and π), with occupancies of 1.67, 0.67, and 1.71 electrons, respectively. The effective polarization of the Si–C bond results in a percentage contribution of 23 % from Si and 77 % from C compared to a normal Si–C bond with around 30 % from Si and 70 % from C. The overall NBO picture of the cation is one in which resonance form **3b**$^+$ dominates but **3a**$^+$ and **3c**$^+$ are significant contributors of roughly equal importance.

The reactivity of **3**$^+$ further supports silyl-stabilized allyl cationic character. Treatment of **3**$^+$ with nucleophiles of different hardness (CN$^-$, H_2O, or F$^-$) affords elimination products formed by proton abstraction at C23 and C24, as evidenced by ^{1}H NMR spectroscopy and GC-MS; addition to the silicon nucleus is not observed. Cations with a higher silylium ion character, such as **2**$^+$, give addition products R_3SiNu exclusively upon treatment with nucleophiles.[3,15] In conclusion, although **3c**$^+$ has to be considered as a resonance structure to account for the observed bond lengths and the ^{13}C NMR spectrum, other data suggest its relevance is limited. The picture of a silyl-stabilized allyl cation is more apposite.

Received: January 7, 2009

Keywords: allyl cations · arenes · carboranes · hyperconjugation · silyl cations

---

[1] a) G. A. Olah, P. R. Clifford, Y. Halpern, R. G. Johanson, *J. Am. Chem. Soc.* **1971**, *93*, 4219–4222; b) G. A. Olah, H. Mayr, *J. Am. Chem. Soc.* **1976**, *98*, 7333–7340; c) *Carbonium Ions* (Eds.: G. A. Olah, P. von R. Schleyer), Wiley, New York, **1968**, chap. 18; d) *Stable Carbocation Chemistry* (Eds.: G. K. Surya Prakash, P. von R. Schleyer), Wiley, New York **1997**, chap. 14; e) G. A. Olah, G. K. Prakash, *Carbocation Chemistry*, Wiley, New York, **2004**, chap. 8.
[2] To our knowledge, there have been only three reports on crystal structures of allyl cations that are not stabilized by heteroatoms or additional π systems. a) A cyclobutenyl cation: G. Maier, R. Emrich, K. D. Malsch, K. A. Schneider, M. Nixdorf, H. Irngartinger, *Chem. Ber.* **1985**, *118*, 2798–2810; b) the cyclopentenyl cation: J. B. Lambert, L. Lin, V. Rassolov, *Angew. Chem.* **2002**, *114*, 1487–1489; *Angew. Chem. Int. Ed.* **2002**, *41*, 1429–1431; M. Otto, D. Scheschkewitz, T. Kato, M. M. Midland, J. B. Lambert, G. Bertrand, *Angew. Chem.* **2002**, *114*, 2379–2380; *Angew. Chem. Int. Ed.* **2002**, *41*, 2275–2276; T. Müller, *Angew. Chem.* **2002**, *114*, 2380–2382; *Angew. Chem. Int. Ed.* **2002**, *41*, 2276–2278; J. B. Lambert, *Angew. Chem.* **2002**, *114*, 2382; *Angew. Chem. Int. Ed.* **2002**, *41*, 2278; J. N. Jones, A. H. Cowley, C. L. B. Macdonald, *Chem. Commun.* **2002**, 1520–1521; c) A bicyclic cyclopentenyl cation: K. Ogawa, S. Minigeshi, K. Komatsu, T. Kitigawa, *J. Org. Chem.* **2008**, *73*, 5248–5254.

[3] S. Duttwyler, Q.-Q. Do, A. Linden, K. K. Baldridge, J. S. Siegel, *Angew. Chem.* **2008**, *120*, 1743 – 1746; *Angew. Chem. Int. Ed.* **2008**, *47*, 1719 – 1722.

[4] CCDC 715200 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[5] Structural, orbital, and property calculations were carried out using the Gaussian03[5a] and GAMESS[5b] software packages. Details of the computational methods are given in the Supporting Information. a) Gaussian03, Truhlar/Zhao module, Minnesota Supercomputer Center; b) M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, S. T. Elbert, *J. Comput. Chem.* **1993**, *14*, 1347.

[6] a) J. B. Lambert, Y. Zhao, R. W. Emblide, L. A. Salvador, X. Liu, J.-H. So, E. C. Chelius, *Acc. Chem. Res.* **1999**, *32*, 183 – 190; b) J. B. Lambert, *Tetrahedron* **1990**, *46*, 2677 – 2689; c) J. B. Lambert, L. Lin and S. Keinan, *Org. Biomol. Chem.* **2003**, *1*, 2559 – 2565; d) J. B. Lambert, C. Liu, T. Kouliev, *J. Phys. Org. Chem.* **2002**, *15*, 667 – 671; e) A. Klaer, W. Saak, D. Haase, T. Müller, *J. Am. Chem. Soc.* **2008**, *130*, 14956 – 14957; f) T. Müller, M. Juhasz, C. A. Reed, *Angew. Chem.* **2004**, *116*, 1569 – 1572; *Angew. Chem. Int. Ed.* **2004**, *43*, 1543 – 1546; g) M. Sugawara, J. Yoshida, *J. Org. Chem.* **2000**, *65*, 3135 – 3142; h) K. S. Hassall, J. M. White, *Org. Lett.* **2004**, *6*, 1737 – 1739; i) J. B. Lambert, Y. Zhao, *J. Am. Chem. Soc.* **1996**, *118*, 7867 – 7868; j) M. Schormann, S. Garratt, D. L. Hughes, J. C. Green, M. Bochmann, *J. Am. Chem. Soc.* **2002**, *124*, 11266 – 11267.

[7] C. A. Reed, *Chem. Commun.* **2005**, 1669 – 1677.

[8] R. D. Howells, J. D. Mc Cown, *Chem. Rev.* **1977**, *77*, 69 – 92.

[9] a) C. A. Reed, K.-C. Kim, E. S. Stoyanov, D. Stasko, F. S. Tham, L. J. Mueller, P. D. W. Boyd, *J. Am. Chem. Soc.* **2003**, *125*, 1796 – 1804; b) C. A. Reed, N. L. P. Fackler, K.-C. Kim, D. Stasko, D. R. Evans, *J. Am. Chem. Soc.* **1999**, *121*, 6314 – 6315.

[10] H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, Wiley-VCH, Berlin, **2005**.

[11] *NMR, Basic Principles and Progress*, *Vol. 17* (Eds.: P. Diehl, E. Fluck, R. Kosfeld), Springer, Berlin, **1981**, chap. 2.

[12] A reliable integration with errors of less than 5 % was achieved with the interval between two pulses $d_1 = 15$ s. The ^{2}H NMR spectra, being "negatives" of the ^{1}H spectra, were used to confirm the position of deuteration. The ^{13}C served the same purpose; the carbon nuclei adjacent to ^{2}H showed $^1J_{C,D}$ coupling and an isotope shift.[10]

[13] The deuterated solvent C_6D_6 was used as the reaction medium because $CD_3C_6D_6^+$ would have undergone a fast H/D exchange in C_6H_6.

[14] a) J. B. Lambert, S. Zhang, S. M. Ciro, *Organometallics* **1993**, *13*, 2430 – 2443; b) T. Müller, C. Bauch, M. Ostermeier, M. Bolte, N. Auner, *J. Am. Chem. Soc.* **2003**, *125*, 2158 – 2168.

[15] C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 325 – 332.