UC Riverside

UC Riverside Previously Published Works

Title

The X-ray structure of a vinyl cation.

Permalink

<https://escholarship.org/uc/item/0zg1q6g6>

Journal

Angewandte Chemie (International ed. in English), 43(12)

ISSN

1433-7851

Authors

Müller, Thomas
Juhasz, Mark
Reed, Christopher A

Publication Date

2004-03-01

DOI

10.1002/anie.200352986

Peer reviewed

vinyl cations under superacidic reaction conditions at temperatures below -100°C was achieved in the early 1990s and provided important information about their electronic structure.^[5] We report herein the X-ray structure of the β -silyl substituted vinyl cation **1**, which provides the first direct experimental structural information about this important class of reaction intermediates.^[6] In addition, the molecular structure of cation **1** gives direct structural evidence for the occurrence of β -silyl hyperconjugation in carbocations.^[7]

Vinyl cation **1** was prepared by reaction of the alkynylsilane **2** with trityl ion as described previously for related cations (see Scheme 1).^[8] The counterions were either tetra-

Scheme 1. Synthesis of vinyl cation **1**.

kis(pentafluorophenyl)borate, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, or the hexabromocarborane, $[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$, chosen for their extreme inertness.^[9] The former has advantages in NMR experiments because its salts form high concentrations of liquid clathrates while the latter is better for growing crystals. Cation **1** was characterized in a benzene solution by multinuclear NMR spectroscopy (see Table 1). The appearance of a single ^{29}Si NMR signal at $\delta^{29}\text{Si} = 29.1$ ppm indicates ring closure to a species that is symmetric on the NMR timescale. The $\text{C}=\text{C}^+$ unit of the vinyl cation is readily identified by the low-field resonance of the positively charged C^α atom at $\delta^{13}\text{C} = 202.4$ ppm and that attributed to C^β at $\delta^{13}\text{C} = 75.3$ ppm. These NMR chemical shifts are very close to those found for similar β -silylsubstituted vinyl cations and are characteristic for the electronic situation found for a $\text{C}=\text{C}$ double bond formed from a positively charged dicoordinated carbon atom and a second sp^2 -hybridized trigonal carbon center.^[5,8]

No solvent effect on the NMR chemical shift can be detected in aromatic hydrocarbons, that is, in toluene virtually the same NMR chemical shifts are observed ($\delta^{29}\text{Si} = 28.9$; $\delta^{13}\text{C}$ (C^α) = 202.7; $\delta^{13}\text{C}$ (C^β) = 75.5 ppm, see Table 1). This indicates negligible cation solvent interactions at room temperature. In toluene solution the salts **1** $[\text{B}(\text{C}_6\text{F}_5)_4]$ and **1** $[\text{CB}_{11}\text{H}_6\text{Br}_6]$ are stable for weeks and this unusual stability is attributed to (1) the essentially nonnucleophilic reaction conditions and (2) the high thermodynamic stability due to the combined effect of two β -silyl substituents.

The influence of the β -silyl substituents on the electron distribution in cation **1** is indicated by the marked down-field shift of the ^{29}Si resonance at $\delta = 29.1$ ppm compared to the precursor alkynylsilane ($\delta = -16.9$ ppm). This is in agreement with significant delocalization of positive charge from the C^α atom to the β -positioned silyl groups. Furthermore, the $^1J(\text{Si}-\text{C})$ coupling constant between the C^β atom and the silicon atoms is extremely small ($^1J(\text{Si}-\text{C}) = 15.7$ Hz, compared to regular $^1J(\text{Si}-\text{C}) \approx 60$ Hz in trialkylvinylsilanes).^[10,11] This

Vinyl Cations

The X-ray Structure of a Vinyl Cation**

Thomas Müller,* Mark Juhasz, and
Christopher A. Reed*

Dedicated to Prof. Yitzhak Apeloig
on the occasion of his 60th birthday.

Vinyl cations,^[1] the dicoordinated unsaturated analogues of trivalent carbenium ions, were first detected by Grob and co-workers in the early 1960s in solvolysis reactions of α -aryl vinyl halides.^[2] In the 1970s numerous investigations established vinyl cations as reaction intermediates in solvolysis reactions of activated alkenyl halides^[3] and in reactions of electrophiles with alkynes.^[4] The direct NMR detection of

[*] Dr. T. Müller
Institut für Anorganische und Analytische Chemie
der Johann Wolfgang Goethe-Universität Frankfurt/Main
Marie Curie Strasse 11, 60439 Frankfurt/Main (Germany)
Fax: (+49) 697-982-9188
E-mail: dr.thomas.mueller@chemie.uni-frankfurt.de
M. Juhasz, Prof. Dr. C. A. Reed
Department of Chemistry
University of California, Riverside 92521-0403 (USA)
Fax: (+1) 909-787-2027
E-mail: chris.reed@ucr.edu

[**] We thank Dr. Fook Tham for solution of the X-ray crystal structure. This work was supported by NSF grant CHE-0095206 and by the German Israeli Foundation (GIF).

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

Table 1: Experimental and theoretical ^{13}C and ^{29}Si NMR spectroscopic data of **1**. Coupling constants $^nJ(\text{XY})$ in Hz.

	$\delta^{13}\text{C}^\alpha$	$\delta^{13}\text{C}^\beta$	$\delta^{13}\text{C}^{1/3}$	$\delta^{13}\text{C}^2$	$\delta^{13}\text{C}^q$	$\delta^{13}\text{C}^{\text{CH}_3}$	$\delta^{13}\text{C}^{\text{SiMe}_2}$	$\delta^{29}\text{Si}$
1 ^[a]	202.4 $^3J(\text{CH}) = 5.2$	75.3 $^1J(\text{SiC}) = 15.7$	15.0 $^1J(\text{CH}) = 121.1$ $^1J(\text{SiC}) = 56.2$	15.8 $^1J(\text{CH}) = 131.8$	33.5 $^2J(\text{CH}) = 4.2$	26.6 $^1J(\text{CH}) = 131.8$	0.9 $^1J(\text{CH}) = 123.0$ $^1J(\text{SiC}) = 55.7$	29.1 $^1J(\text{SiC}) = 55.3$ $^1J(\text{SiC}) = 15.7$
1 ^[b]	202.7	75.5	15.2	16.2	33.8	26.8	1.0	28.9
1 ^[c,d]	215.7 $^3J(\text{CH}) = 5.1$	82.6 $^1J(\text{SiC}) = 10.2$	20.3 $^1J(\text{CH}) = 120.3$ $^1J(\text{SiC}) = 50.3$	20.7 $^1J(\text{CH}) = 127.7$	39.4 $^2J(\text{CH}) = 3.0$	29.6 $^1J(\text{CH}) = 128.4$	3.7 $^1J(\text{CH}) = 121.7$ $^1J(\text{SiC}) = 49.1$	31.8 $^1J(\text{SiC}) = 50.3, 49.1, 10.2^{\text{[e]}}$

[a] In $[\text{D}_6]\text{benzene}$ at 300 K. [b] In $[\text{D}_8]\text{toluene}$ at 300 K. [c] NMR chemical shifts δ calculated at the GIAO/B3LYP/6-311G(2d,p)//MP2/6-31G(d) level, $\sigma(^{13}\text{C}, \text{TMS } T_d) = 183.6$, $\sigma(^{29}\text{Si}, \text{TMS } T_d) = 329.1$. Nuclear chemical shift constants $^nJ(\text{XY})$ calculated at the GIAO/B3LYP/6-311G(d,p)//MP2/6-31G(d) level. [d] For the different silicon atoms (Si^1 , Si^2) and the carbon atoms which are interrelated by the molecular motions ($\text{C}^{1/3}$, C^{SiMe_2} , C^{CH_3}), the mean values are given. [e] Coupling between Si and $\text{C}^{1/3}$, CH_3 and C^β , respectively.

suggests a rather unusual bonding situation between the C^β atom and the adjacent silicon atoms.

The vinyl cation **1** is further characterized by a very intense band in the IR spectra at $\tilde{\nu} = 1987 \text{ cm}^{-1}$, which is assigned to the $\text{C}=\text{C}^+$ stretching vibration. This IR band is more intense than regular $\text{C}=\text{C}$ stretch vibrations of $\text{C}=\text{C}$ bonds and its position is strongly shifted to higher energy, which suggests a bond order of the $\text{C}=\text{C}^+$ bond in **1** significantly larger than 2.

Suitable crystals for X-ray analysis were obtained by recrystallization of **1** $[\text{CB}_{11}\text{H}_6\text{Br}_6]$ from 1,2-dichlorobenzene.^[12] The solid-state structure of the salt reveals that the vinyl cation is clearly separated from the carborane anion (see Figure 1). No bromine atom of the anion approaches the positively charged C^α atom to a distance smaller than 720 pm. The disilacyclohexane ring of the vinyl cation **1** adopts a regular chair conformation with the two silicon atoms and the C^β and C^α atoms nearly coplanar ($\theta(\text{SiC}^\beta\text{C}^\alpha\text{Si}) = 173.9^\circ$). As previously predicted by calculations^[13] and deduced from ^{13}C NMR chemical shift parameter,^[5,8] the molecule is linear around the dicoordinated carbon atom C^α (bond angle $\alpha(\text{C}^\beta\text{C}^\alpha\text{C}) = 178.8^\circ$), which indicates an sp hybridization for C^α and, as a consequence, the $\text{C}^\beta\text{--C}^\alpha$ double bond is unusually short (122.1 pm) and approaches the length of a regular $\text{C}\text{--C}$ triple bond. In addition, also the $\text{C}^\alpha\text{--C}$ single bond is short (144.9 pm). A quite remarkable feature of the molecular structure of **1** is the unusual length of the $\text{C}^\beta\text{--Si}$ single bonds (198.4 and 194.6 pm), around 10 pm longer than regular single bonds between sp^2 hybridized carbon atoms and tetracoordinated silicon.^[14] This bond elongation can be attributed to the interaction of the $\sigma(\text{C}^\beta\text{Si})$ bond with the empty 2p orbital at C^α (i.e. β -silyl hyperconjugation). Although the NMR results indicate that **1** is symmetric in solution, in the solid state the two silicon atoms in **1** are clearly different. Not only are the $\text{C}^\beta\text{--Si}$ single bonds markedly different from each other (by 3.8 pm) but also the $\alpha(\text{SiC}^\beta\text{C}^\alpha)$ bond angles can be clearly distinguished (115.5° and 133.0°). The more acute bond angle is associated with the longer $\text{Si}\text{--C}^\beta$ bond, which suggests more pronounced β silicon hyperconjugation for this group.

Density functional (B3LYP/6-31G(d)) as well as correlated ab initio calculations (MP2/6-31G(d))^[15,16] predict very similar molecular structures for **1**, and these calculated gas-phase structures closely match the experimental solid-state geometry of **1** (see Figure 2). In particular, the unsymmetrical

Figure 1. a) Perspective view of the asymmetric unit of the crystal structure of **1** $[\text{CB}_{11}\text{H}_6\text{Br}_5]$ (black Br; dark gray B; white C; gray Si). b) Molecular structure of vinyl cation **1** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn at 30% probability level). Selected bond length [pm] and bond angles $^\circ$: $\text{C}^\beta\text{--C}^\alpha = 122.1$, $\text{C}^\alpha\text{--C}^\alpha = 145.2$, $\text{Si}^2\text{--C}^\beta = 198.4$, $\text{Si}^1\text{--C}^\beta = 194.6$, $\text{C}^\beta\text{--C}^\alpha\text{--C}^\alpha = 178.8$, $\text{Si}^2\text{--C}^\beta\text{--C}^\alpha = 115.5$, $\text{Si}^1\text{--C}^\beta\text{--C}^\alpha = 133.0$.

Figure 2. Comparison of experimental (left) and calculated (right; underlined, MP2/6-31G(d); italic, B3LYP/6-31G(d)). Bond lengths [pm], bond angles $^\circ$, additional bond angles: $\text{Si}^2\text{--C}^\beta\text{--C}^\alpha = 115.5$, 112.3 , 118.0 , $\text{Si}^1\text{--C}^\beta\text{--C}^\alpha = 133.0$, 133.5 , 127.6 .

arrangement of the silicon atoms at the central $C=C^+$ unit is found in the theoretical structures, which indicates that this arrangement is a result of an intrinsic bonding situation in cation **1** and not a consequence of crystal lattice or similar intermolecular interactions in the condensed phase. The C_s symmetrical structure of **1**, which has two identical Si–C $^\beta$ bonds, **1** (C_s), is the transition structure for the degenerate interconversion of two cations **1** (at B3LYP/6-31G(d)). Compound **1** (C_s), however, is merely 0.7 kcal mol $^{-1}$ higher in energy than **1** (MP2/6-311G(d,p)//B3LYP/6-31G(d) + Δ ZPVE), which suggests a time-averaged symmetry for cation **1** in solution and in the gas phase.

The unusual position of the $C=C^+$ stretch vibration in the IR spectra of **1** is in agreement with the results of density functional calculations. Thus, a frequency calculation at the B3LYP/6-31G(d) level of theory predicts for the $C=C^+$ bond stretch vibration a very strong IR absorption at 1956 cm $^{-1}$, close to the experimental observed IR band (1987 cm $^{-1}$).^[18] Finally, calculations for NMR chemical shift^[19] and nuclear spin–spin coupling constants^[20] (see Table 1) agree well with the experiment, that is, $\delta^{29}\text{Si} = 31.8$ ppm^[21] compared to the measured value of 28.9 ppm. At the applied level of theory, $\delta^{13}\text{C}$ values for **1** are systematically predicted too far down field. The largest deviation is found for the ^{13}C NMR chemical shift of the positively charged C^α atom ($\Delta\delta^{13}\text{C} = 13.3$).^[22] Theoretical and experimental ^{13}C NMR chemical shifts for **1** are however linearly correlated thereby confirming the validity of the computed structure.^[23] An analysis^[20] of the computed spin–spin coupling constants reveal that the unusually small $^1J(\text{Si}C^\beta)$ constant (calculated 10.2 Hz,^[24] 15.7 Hz experimentally) is a consequence of the strongly reduced Fermi contact term.^[25] This result suggests a very small s-orbital contribution for the Si–C $^\beta$ bonds, in agreement with a natural-bond-order (NBO) analysis^[26] at the MP2/6-31G(d) level of theory, which indicate a contribution of the 3 s(Si) to the Si–C $^\beta$ σ bond of less than 15%. This analysis gives additional support for the occurrence of hyperconjugation in **1**. Strongly depleted Si–C $^\beta$ σ bonds (1.48 e and 1.77 e) and a formally empty C(2p) orbital at C^α with an occupation of 0.66 e are the result of electron delocalization from the bonding σ -Si–C $^\beta$ orbitals into the vacant C(2p). Thus, experimental (NMR, IR spectroscopic and structural) as well as theoretical data clearly indicate the occurrence of hyperconjugation between the occupied σ C $^\beta$ –Si orbitals and the empty 2p(C^α) orbital in vinyl cation **1**. This interaction can be straightforwardly described as resonance between the Lewis structures **A** and **B** (Scheme 2).^[27]

Scheme 2. Resonance structures for vinyl cation **1**.

Received: October 1, 2003 [Z52986]

Published Online: February 16, 2004

Keywords: carbocations · computer chemistry · hyperconjugation · silicon · X-ray diffraction

- [1] For a recent monograph on vinyl cations: *Dicoordinated Carbocations* (Eds.: Z. Rappoport, P. J. Stang), Wiley, New York, **1997**.
- [2] a) C. A. Grob, J. Csapilla, G. Cseh, *Helv. Chim. Acta* **1964**, *47*, 1590; b) C. A. Grob in *Dicoordinated Carbocations* (Eds.: Z. Rappoport, P. J. Stang), Wiley, **1997**, chap. 1, p. 1.
- [3] a) M. Hanack, *Acc. Chem. Res.* **1976**, *9*, 364; b) T. Kitamura, H. Taniguchi, Y. Tsuno in *Dicoordinated Carbocations* (Eds.: Z. Rappoport, P. J. Stang), Wiley, New York, **1997**, chap. 7, p. 321; c) L. R. Subramanian, M. Hanack, *Chem. Rev.* **1972**, *72*, 1465.
- [4] For reviews see: a) V. Lucchini, G. Modena, L. Pasquato in *Dicoordinated Carbocations* (Eds.: Z. Rappoport, P. J. Stang), Wiley, New York, **1997**, chap. 6, p. 237.
- [5] H.-U. Siehl in *Dicoordinated Carbocations* (Eds.: Z. Rappoport, P. J. Stang), Wiley, **1997**, chap. 5, p. 189.
- [6] For a previous report on the isolation of the neutral solid metallacarborane $[\text{CpFe}^{\text{II}}\text{HCB}_9\text{H}_9\text{C}=\text{C}=\text{CH}_2]$ containing a $-\text{C}=\text{CH}_2$ group, see: L. I. Zakharkin, V. V. Kobak, *J. Organomet. Chem.* **1984**, *270*, 229.
- [7] The isoelectronic neutral methylene boranes $(\text{R}_3\text{Si})_2\text{C}=\text{B}-\text{R}$ were previously synthesized and structurally characterized. a) R. Boese, P. Paetzold, A. Tapper, R. Ziembinski, *Chem. Ber.* **1989**, *122*, 1057; b) M. Pilz, M. Stadler, R. Hunold, J. Allwohn, W. Massa, A. Berndt, *Angew. Chem.* **1989**, *101*, 761; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 784.
- [8] T. Müller, R. Meyer, D. Lennartz, H.-U. Siehl, *Angew. Chem.* **2000**, *112*, 3203; *Angew. Chem. Int. Ed.* **2000**, *39*, 3074.
- [9] C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 133.
- [10] Y. Takeuchi, T. Takayama in *The chemistry of organosilicon compounds*, Vol. 2 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998** chap. 6, p. 267.
- [11] A small $^1J(\text{SnC})$ coupling constant was detected in a related distannylmethylene borane. M. Pilz, H. Michel, A. Berndt, *Angew. Chem.* **1990**, *102*, 438; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 409.
- [12] Crystal data for **1** $[\text{CB}_{11}\text{H}_6\text{Br}_6]$, $\text{C}_{14}\text{H}_{33}\text{B}_{11}\text{Br}_6\text{Si}_2$, $M_r = 860.69$, crystal dimensions $0.19 \times 0.18 \times 0.04$ mm 3 , monoclinic, space group $P2(1)/c$, $a = 12.250(3)$, $b = 13.034(3)$, $c = 20.639(5)$ Å, $\beta = 104.293(6)^\circ$, $V = 3193.3(13)$ Å 3 , $Z = 4$, $\rho_{\text{calc}} = 1.790$ Mg m $^{-3}$, $\mu(\text{MoK}\alpha) = 7.701$ mm $^{-1}$, $T = 223(2)$ K, $F(000) = 1648$, $2\theta_{\text{max}} = 49.42^\circ$. 17628 reflections measured, of which 5441 were unique ($R_{\text{int}} = 0.0551$). Final $R_1 = 0.0481$ with $wR_2 = 0.1165$ for 5441 observed reflections with $I > 2\sigma(I)$. * Note: The bromo-carborane was over brominated by about 6%. The density was calculated by using the site occupancy factor ratio of 6%/94% for Br $^7/\text{H}^6$ attached to B 6 atom. The slight over bromination of the carborane is figured into the X-ray model and solution, thus improving the accuracy and R value. CCDC-220463 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
- [13] a) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, P. von R. Schleyer, *J. Am. Chem. Soc.* **1969**, *91*, 5350. b) For a review: Y. Apeloig, T. Müller in *Dicoordinated Carbocations* (Eds.: Z. Rappoport, P. J. Stang), Wiley, New York, **1997**, chap. 2, p. 9.
- [14] M. Kaftory, M. Kapon, M. Botoshansky in *The chemistry of organosilicon compounds*, Vol. 2 (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, chap. 5, p. 181.
- [15] All calculations were performed with Gaussian98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas,

- J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998** and Gaussian 03 (Revision B.03), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc. Pittsburgh, PA, **2003**.
- [16] a) A. D. Becke, *Phys. Rev. A* **1988**, 38, 3098; b) A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648; c) B. G. Johnson, P. M. W. Gill, J. A. Pople, *J. Chem. Phys.* **1993**, 98, 5612.
- [17] According to density functional calculations at the B3LYP/6-31G(d) level of theory β -disilyl substituted vinyl cations having π -donating substituents at C^α do not show this unsymmetrical arrangement of the β -silyl groups. Thus, for the analogous phenyl substituted vinyl cation, equal Si–C $^\beta$ bond lengths of 197.3 pm have been calculated.^[8]
- [18] The calculated frequency of $\tilde{\nu}=2031\text{ cm}^{-1}$ is scaled with the global scaling factor of 0.963 suggested by Rauhut and Pulay. G. Rauhut, P. Pulay, *J. Phys. Chem.* **1995**, 99, 3093.
- [19] a) R. Ditchfield, *Mol. Phys.* **1974**, 27, 789; b) K. Wolinski, J. F. Hilton, P. Pulay, *J. Am. Chem. Soc.* **1982**, 104, 5667; c) J. Cheeseman, G. W. Trucks, T. A. Keith, M. Frisch, *J. Chem. Phys.* **1996**, 104, 5497.
- [20] a) T. Helgaker, M. Watson, N. C. Handy, *J. Chem. Phys.* **2000**, 113, 9402; b) V. Sychrovsky, J. Gräfenstein, D. Cremer, *J. Chem. Phys.* **2000**, 113, 3530.
- [21] Mean value from $\delta^{29}(\text{Si}^1)=23.7\text{ ppm}$ and $\delta^{29}(\text{Si}^2)=39.9\text{ ppm}$.
- [22] DFT-based Gauge Independent Atomic Orbitals (GIAO) calculations fail to predict reliably $\delta^{13}\text{C}$ NMR chemical shift for the C=C $^+$ unit in vinyl cations. For reliable predictions of the $\delta^{13}\text{C}(C^\alpha)$, the coupled-cluster method must be applied, which is, however, for **1** technically not feasible. a) J. F. Stanton, J. Gauss, H.-U. Siehl, *Chem. Phys. Lett.* **1996**, 262, 183; b) H.-U. Siehl, T. Müller, H.-U. Siehl, *J. Phys. Org. Chem.* **2003**, 16, 577.
- [23] $\delta^{13}\text{C}^{\text{theo}}=(1.049\pm0.06)\delta^{13}\text{C}^{\text{exp}}+(3.50\pm0.53)$; $R=0.99991$, 7 data points, for details see Supporting Information.
- [24] Mean value from $^1J(\text{Si}^1\text{C}^\beta)=17.2\text{ Hz}$ and $^1J(\text{Si}^2\text{C}^\beta)=3.2\text{ Hz}$.
- [25] The Fermi contact contribution to $^1J(\text{Si}^1\text{C}^\beta)$ is +18.0 Hz, compared to +52.6 Hz for $^1J(\text{Si}^1\text{C}^1)$.
- [26] a) NBO 4.0. E. D. Glendening; J. K. Badenhoop, A. E. Reed, J. E. Carpenter, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **1996**; b) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, 88, 899.
- [27] Supporting Information (experimental details, analytical data, NMR spectra, absolute energies and structures of **1** at several theoretical levels, correlation between $\delta^{13}\text{C}^{\text{theo}}$ versus $\delta^{13}\text{C}^{\text{exp}}$) is available.