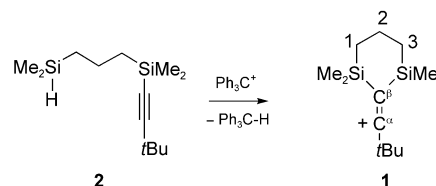


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vinyl cations under superacidic reaction conditions at temperatures below -100°C was achieved in the early 1990s and provided important information about their electronic structure.^[5] We report herein the X-ray structure of the β -silyl substituted 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 hexabromocborane, $[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$, 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 ($\delta^{29}\text{Si} = 28.9$; $\delta^{13}\text{C}(\text{C}^\alpha) = 202.7$; $\delta^{13}\text{C}(\text{C}^\beta) = 75.5$ 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

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

[a] In $[\text{D}_6]$ benzene at 300 K. [b] In $[\text{D}_8]$ 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** $[\text{CB}_{11}\text{H}_6\text{Br}_5]$ 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 ($\theta(\text{Si}^\beta\text{C}^\alpha\text{Si}) = 173.9^\circ$). 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 $\alpha(\text{Si}\text{--C}^\beta\text{--C}^\alpha)$ 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

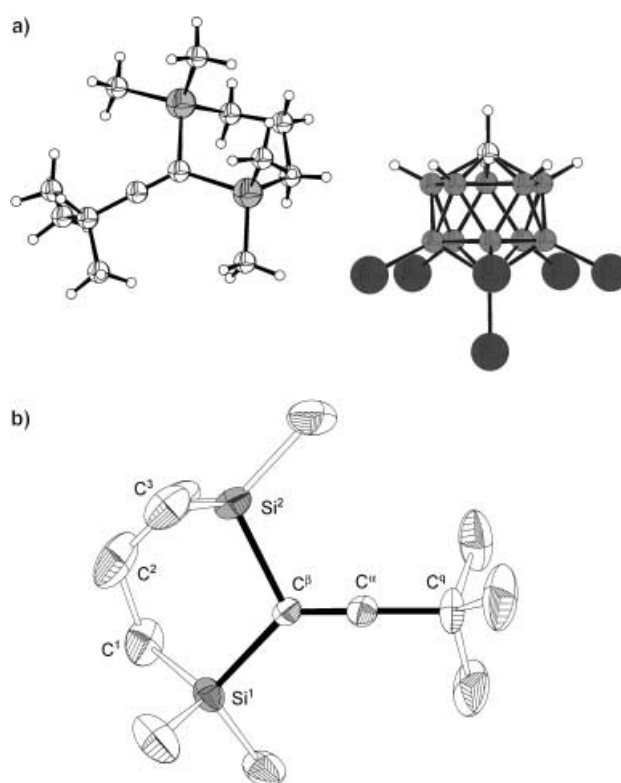


Figure 1. a) Perspective view of the asymmetric unit of the crystal structure of **1** $[\text{CB}_{11}\text{H}_6\text{Br}_5]$ (black Br; dark gray B; white C; gray Si). b) Molecular structure of vinyl cation **1** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn at 30% probability level).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

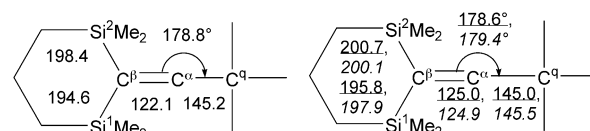
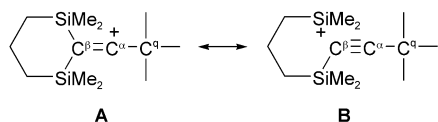


Figure 2. Comparison of experimental (left) and calculated (right; underlined, MP2/6-31G(d); italic, B3LYP/6-31G(d)). Bond lengths [pm], bond angles [°], additional bond angles: $\text{Si}^2\text{C}^\beta\text{--C}^\alpha = 115.5, 112.3, 118.0$, $\text{Si}^1\text{C}^\beta\text{--C}^\alpha = 133.0, 133.5,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

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 $0.7 \text{ kcal mol}^{-1}$ higher in energy than **1** (MP2/6-311G(d,p)//B3LYP/6-31G(d) + $\Delta ZPVE$), 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, $\delta^{29}\text{Si} = 31.8 \text{ ppm}$ ^[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 ($1.48e$ and $1.77e$) and a formally empty $C(2p)$ orbital at C^α with an occupation of $0.66e$ 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^β -Si orbitals and the empty $2p(C^\alpha)$ 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**.

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