Vinyl Cations

The X-ray Structure of a Vinyl Cation**

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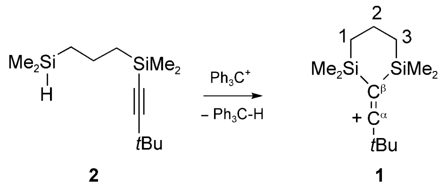
Dedicated to Prof. Yitzhak Apeloig
on the occasion of his 60th birthday.

Vinyl cations,[1] the dicoordinated unsaturated analogues of trivalent carbenium ions, were first detected by Grob and coworkers 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 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 tetrakis(pentafluorophenyl)borate, $[B(C_6F_5)_4]^-$, or the hexabromocarborane, $[CB_{11}H_6Br_6]^-$, 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 $\delta^{29}Si = 29.1$ ppm indicates ring closure to a species that is symmetric on the NMR timescale. The $C{=}C^+$ unit of the vinyl cation is readily identified by the low-field resonance of the positively charged C^α atom at $\delta^{13}C = 202.4$ ppm and that attributed to C^β at $\delta^{13}C = 75.3$ 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 C=C double bond formed from a positively charged dicoordinated carbon atom and a second sp^2-hybridized trigonal carbon center.[5,8]



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

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 ($\delta^{29}Si = 28.9$; $\delta^{13}C$ $(C^\alpha) = 202.7$; $\delta^{13}C$ $(C^\beta) = 75.5$ ppm, see Table 1). This indicates negligible cation solvent interactions at room temperature. In toluene solution the salts **1** $[B(C_6F_5)_4]$ and **1** $[CB_{11}H_6Br_6]$ 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 alkinylsilane ($\delta = -16.9$ 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(Si–C) coupling constant between the C^β atom and the silicon atoms is extremely small ($^1J(Si–C) = 15.7$ Hz, compared to regular $^1J(Si–C) \approx 60$ Hz in trialkylvinylsilanes).[10,11] This

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

	$\delta^{13}C^{\alpha}$	$\delta^{13}C^{\beta}$	$\delta^{13}C^{1/3}$	$\delta^{13}C^{2}$	$\delta^{13}C^{q}$	$\delta^{13}C^{CH_3}$	$\delta^{13}C^{SiMe_2}$	$\delta^{29}Si$
1[a]	202.4	75.3	15.0	15.8	33.5	26.6	0.9	29.1
	$^{3}J(CH)=5.2$		$^{1}J(CH)=121.1$	$^{1}J(CH)=131.8$	$^{2}J(CH)=4.2$	$^{1}J(CH)=131.8$	$^{1}J(CH)=123.0$	$^{1}J(SiC)=55.3$
		$^{1}J(SiC)=15.7$	$^{1}J(SiC)=56.2$				$^{1}J(SiC)=55.7$	$^{1}J(SiC)=15.7$
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
	$^{3}J(CH)=5.1$		$^{1}J(CH)=120.3$	$^{1}J(CH)=127.7$	$^{2}J(CH)=3.0$	$^{1}J(CH)=128.4$	$^{1}J(CH)=121.7$	$^{1}J(SiC)=50.3, 49.1, 10.2$[e]
		$^{1}J(SiC)=10.2$	$^{1}J(SiC)=50.3$				$^{1}J(SiC)=49.1$	

[a] In [D$_6$]benzene at 300 K. [b] In [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, $\sigma(^{13}C$, TMS $(T_d))=183.6$, $\sigma(^{29}Si$, TMS $(T_d))=329.1$). Nuclear chemical shift constants ^{n}J(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 ($C^{1/3}$, C^{SiMe_2}, C^{CH_3}), the mean values are given. [e] Coupling between Si and $C^{1/3}$, 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 $\tilde{\nu}=1987\,cm^{-1}$, which is assigned to the C=C$^+$ stretching vibration. This IR band is more intense than regular C=C stretch vibrations of C=C bonds and its position is strongly shifted to higher energy, which suggests a bond order of the C=C$^+$ bond in **1** significantly larger than 2.

Suitable crystals for X-ray analysis were obtained by recrystallization of **1** [$CB_{11}H_6Br_6$] 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 ($\Theta(SiC^{\beta}C^{\alpha}Si)=173.9°$). 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 $\alpha(C^{\beta}C^{\alpha}C)=178.8°$), which indicates an sp hybridization for C^{α} and, as a consequence, the C^{β}–C^{α} double bond is unusually short (122.1 pm) and approaches the length of a regular C–C triple bond. In addition, also the C^{α}–C single bond is short (144.9 pm). A quite remarkable feature of the molecular structure of **1** is the unusual length of the C^{β}–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 $\sigma(C^{\beta}Si)$ 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 C^{β}–Si single bonds markedly different from each other (by 3.8 pm) but also the $\alpha(Si\text{-}C^{\beta}\text{-}C^{\alpha})$ bond angles can be clearly distinguished (115.5° and 133.0°). The more acute bond angle is associated with the longer Si–C^{β} 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

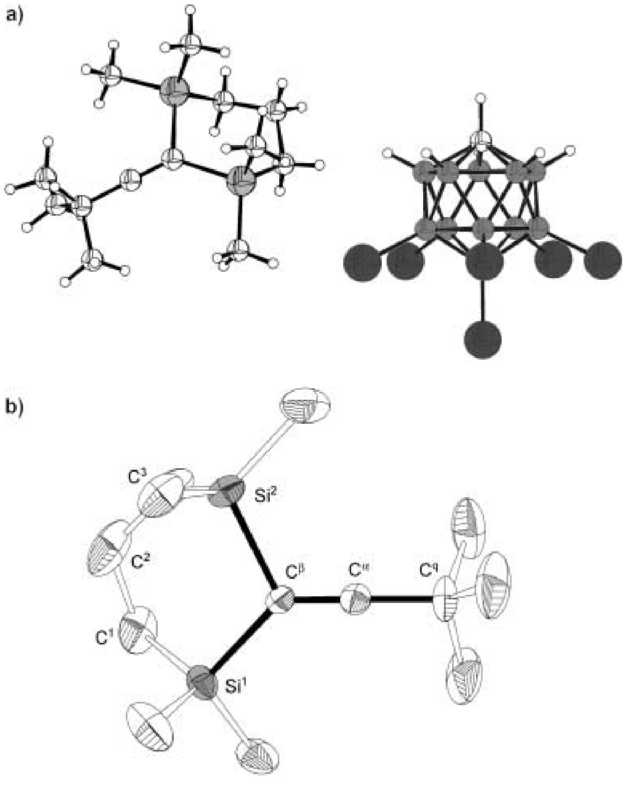


Figure 1. a) Perspective view of the asymmetric unit of the crystal structure of **1** [$CB_{11}H_6Br_5$] (black Br; dark gray B; white C; gray Si). b) Molecular structure of vinyl cation **1** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn at 30% probability level). Selected bond length [pm] and bond angles [°]: C^{β}-$C^{\alpha}=122.1$, C^{α}-$C^{q}=145.2$, Si^2-$C^{\beta}=198.4$, Si^1-$C^{\beta}=194.6$, C^{β}-C^{α}-$C^{q}=178.8$, Si-$^2C^{\beta}$-$C^{\alpha}=115.5$, Si-$^1C^{\beta}$-$C^{\alpha}=133.0$.

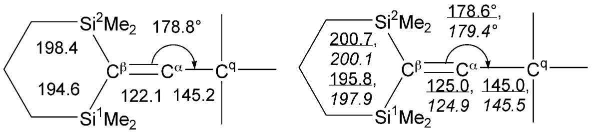
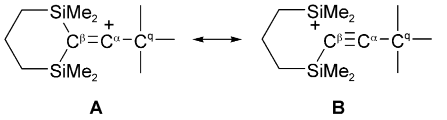


Figure 2. Comparison of experimental (left) and calculated (right; underlined, MP2/6-31G(d); italic, B3LYP6-31G(d)). Bond lengths [pm], bond angles [°], additional bond angles: Si-$^2C^{\beta}$-$C^{\alpha}=115.5$, *112.3*, *118.0*, Si^1-C^{β}-$C^{\alpha}=133.0$, 133.5, *127.6*.

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) + ΔZPVE), 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, $\delta^{29}Si = 31.8$ ppm[21] compared to the measured value of 28.9 ppm. At the applied level of theory, $\delta^{13}C$ 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 ($\Delta\delta^{13}C = 13.3$).[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 $^{1}J(SiC^{\beta})$ 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^{β} 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^{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**.

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