

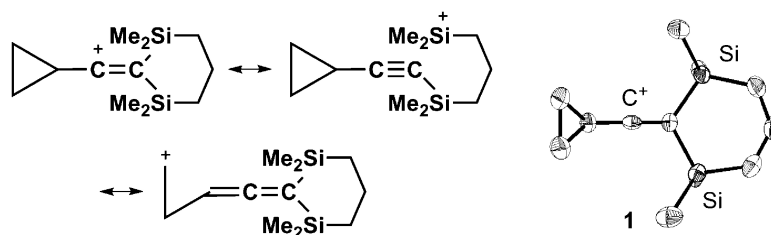
Communication

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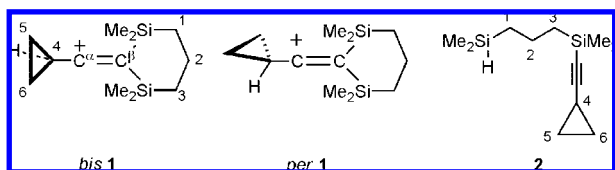
Molecular Structure of a Cyclopropyl Substituted Vinyl Cation

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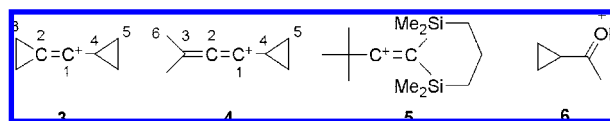
Most of the singular chemistry of cyclopropanes can be understood to arise from the uniquely strong donor character of the C–C σ -bonds in cyclopropane. The textbook example for the large electron-donating ability of the cyclopropyl ring is the unusual high stability of cyclopropylmethyl cations which are stabilized by interaction of the electron-deficient carbon atom with the Walsh-type orbitals of the cyclopropyl ring.¹ Cyclopropyl substituted cations have been the subject of numerous investigations over the past 60 years.² Many aspects of the intriguing structures of the parent $C_4H_7^+$ cation and of secondary and tertiary cyclopropylmethyl cations have been resolved by using NMR spectroscopy, in many cases combined with quantum mechanical computations.^{2,3} However, there have been no direct examinations of the experimental structure of these cations to gauge the theoretical data. The nearest approach to that goal is the work by Childs and co-workers, who obtained structural data of protonated α -cyclopropyl ketones from their hexafluoroantimonates.⁴ We present here the results of an X-ray structure investigation of a cyclopropyl substituted vinyl cation which clearly demonstrates the structural consequences of σ -delocalization involving the cyclopropyl substituent.



Vinyl cation **1** was prepared by reaction of the alkynylsilane **2** with trityl cation as described previously for related cations.⁵ As counterion, tetrakis(pentafluorophenyl)borate, $[B(C_6F_5)_4]^-$, was used. The salt $1[B(C_6F_5)_4]$ was isolated as a brown powder in 92% yield. Cation **1** was characterized in benzene solution by NMR spectroscopy (see Table S1). The appearance of a single ^{29}Si NMR signal at $\delta^{29}Si = 18.7$ indicates ring closure to a symmetric species. Characteristic for the $C=C^+$ unit of the vinyl cation are low field resonances at $\delta^{13}C = 204.5$ ($C(\alpha)$) and at $\delta^{13}C = 73.2$ ($C(\beta)$). These NMR chemical shifts are very close to those found for similar β -silyl substituted vinyl cations^{5,6} and are characteristic for the electronic situation found for a $C=C$ double bond formed from a positively charged dicoordinated carbon atom and an sp^2 -hybridized trigonal carbon center. In the solid state and in arene solution, the salt $1[B(C_6F_5)_4]$ is stable for weeks and this unusual stability is attributed to (i) the essentially non-nucleophilic reaction conditions and (ii) high thermodynamic stability due to the combined effect of two β -silyl substituents and one cyclopropyl ring directly attached to the positively charged $C(\alpha)$ atom.

As shown previously for related carbocations,^{5b,c,7} the influence of the β -silyl substituents on the electron distribution in vinyl cation **1** is indicated by (i) the marked downfield shift of the ^{29}Si resonance at $\delta = 18.7$ compared to the precursor alkyne silane **2** ($\delta^{29}Si = -18.4$, $\Delta\delta^{29}Si = 37.1$)⁸ and (ii) by the strongly reduced $^1J(C-Si)$

coupling constant between the $C(\beta)$ atom and the silicon atoms ($^1J(C(\beta)-Si) = 19.2$ Hz, compared to $^1J(C-Si) \approx 60$ Hz in trialkylvinylsilanes).⁹ Similarly, the significant downfield shifts of the signals of the cyclopropyl carbon atoms compared to the precursor alkyne **2** ($\delta^{13}C(4) = 8.1$, $\Delta\delta^{13}C(4) = 7.2$, $\delta^{13}C(5,6) = 23.4$, $\Delta\delta^{13}C(5,6) = 14.7$)⁸ and their increased $^1J(C-H)$ coupling constants ($^1J(C(4)-H) = 186.6$ Hz and $^1J(C(5,6)-H) = 173.2$ Hz) suggest considerable delocalization of positive charge onto the cyclopropyl unit. Similar low-field shifts and enhanced $^1J(C-H)$ coupling constants were reported previously for cyclopropyl substituted vinyl cation **3** and allenyl cation **4** (**3**: $\delta^{13}C(4) = 21.2$, $^1J(C(4)-H) = 193.5$ Hz, $\delta^{13}C(5) = 43.9$, $^1J(C(5)-H) = 178.0$ Hz; **4**: $\delta^{13}C(4) = 25.7$, $\delta^{13}C(5) = 41.6$).¹⁰



The vinyl cation **1** is further characterized by a very intense band in the IR spectra at $\nu = 1958$ cm^{-1} , which is assigned to the $C=C^+$ stretching vibration. Similar strong absorptions were detected for related vinyl cations.^{5b,4} The unusual high energy shift of the $C=C^+$ stretching vibration indicates a bond order for the $C^\beta=C^\alpha$ bond in **1** markedly larger than 2.

Suitable crystals for X-ray single crystal analysis were obtained by recrystallization of $1[B(C_6F_5)_4]$ from 1,2,3,4-tetrafluorobenzene at room temperature.¹¹ The solid state structure of the salt reveals that the vinyl cation **1** is clearly separated from the borate anion; in particular no atom of the borate anion approaches the positively charged $C(\alpha)$ atom to a distance smaller than 344.7 pm. The molecular structure of vinyl cation **1** closely resembles in several aspects that of the *tert*-butyl substituted vinyl cation **5**.^{5b} The most remarkable features are the linearity of the $C(4)C(\alpha)C(\beta)$ unit ($\alpha(C(4)C(\alpha)C(\beta)) = 179.4(2)^\circ$) and the very short $C(\alpha)=C(\beta)$ bond (123.43(29) pm) which is actually closer to that of a $C\equiv C$ triple bond than to a $C=C$ double bond (see Figure 1a). Furthermore, the molecular structure of vinyl cation **1** illustrates the structural consequences of delocalization of positive charge into the σ -framework of this cation. The unusual length of the $C(\beta)-Si$ single bonds (193.20(19) and 194.64(19) pm) indicates the interaction of the $C(\beta)-Si$ σ -bond with the formally empty $2p(C(\alpha))$ orbital (i.e., β -silyl hyperconjugation).^{5b,7} In addition, the experimental molecular structure of cation **1** gives direct structural evidence for the hyperconjugative interaction of the strained C–C σ -bonds of the cyclopropyl unit with the formally empty $2p(C(\alpha))$ orbital. In particular, the bisected conformation of the cyclopropyl substituent found for vinyl cation **1** provides maximum overlap of the vacant $2p(C(\alpha))$ orbital with the $C(4)-C(5,6)$ bonds of the cyclopropyl substituent. Previously, NMR investigations have shown that this orientation of the cyclopropyl group is the ground-state conforma-

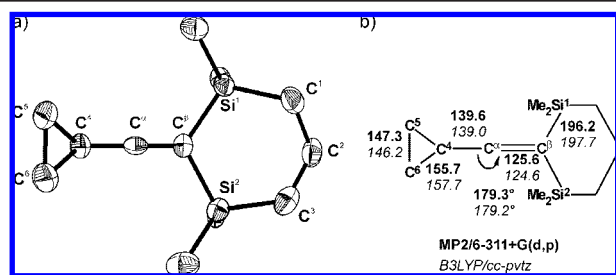
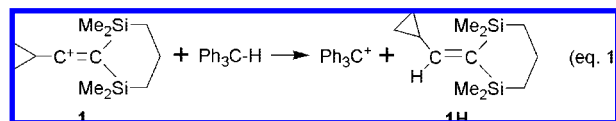


Figure 1. Molecular structure of vinyl cation **1**. (a) From X-ray crystal structure analysis (hydrogen atoms omitted for clarity, thermal ellipsoids drawn at 50% probability level). Important bond lengths (pm) and bond angles (deg). C(α)–C(β) 123.43(29); C(α)–C(4) 139.79(30); C(4)–C(5) 153.49(35); C(4)–C(6) 153.65(29); C(5)–C(6) 144.76(32); C(β)–Si(1) 193.20(19); C(β)–Si(2) 194.64(19); α (C(4)C(α)C(β)) 179.4(2). (b) From calculations.

tion for allenyl cation **4**^{10b} and for static α -cyclopropyl substituted carbocations in general.² Also protonated cyclopropyl ketones such as **6** appear to adopt the bisected conformation relative to the polarized CO π -bond.⁴

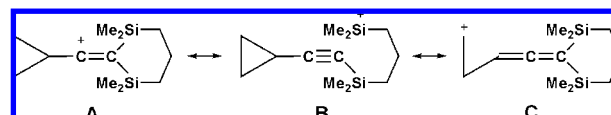
As a consequence of the interaction of the σ -framework of the cyclopropyl ring with the empty 2p-orbital at C(α), the three-membered ring is significantly distorted from the symmetric cyclopropane structure with very long C(4)–C(5,6) bond lengths (153.49(35) and 153.65(29) pm) and a considerably shortened C(5)–C(6) bond (144.76(32) pm) (CC in C₃H₆: 151.4 pm).^{12a} Furthermore, the C(4)–C(α) bond is very short (139.79(30) pm), shorter than the C(sp)–CH single bond in cyclopropylacetylene (144.0 pm).^{12b} This suggests for this formal single bond a bond order larger than 1.

Density functional (B3LYP/cc-pvtz) as well as correlated ab initio calculations¹³ (MP2/6-311+G(d,p)) predict very similar molecular structures for vinyl cation **1**, and these calculated gas-phase structures closely match its experimental solid-state structure (see Figure 1b). In particular, the computed structures of cation **1** show the same characteristics such as long C(β)–Si(1,2) bonds, a short C(α)–C(4) bond, long C(4)–C(5,6) bonds, and a short C(5)–C(6) bond, which indicate the extended σ -delocalization in vinyl cation **1**. The overall thermodynamic stability of cation **1** can be estimated relative to the trityl cation by the isodesmic hydride transfer reaction (eq 1), which suggests that it is by only 7.6 kJ mol^{−1} destabilized compared to the trityl cation.



The bisected isomer, *bis-1*, was found to be the most stable conformer while the perpendicular conformer, *per-1*, is the transition state for the rotation around the C(α)–C(4) bond and is 31.4 kJ mol^{−1} higher in energy than *bis-1* (at B3LYP/6-311+G(d,p)). This computationally determined rotational barrier provides an estimate for the stabilization of vinyl cation **1** by the cyclopropyl substituent. The unusual position of the C=C⁺ stretching vibration in the IR spectra of vinyl cation **1** is in agreement with the results of density functional calculations. Thus, determination of the force constants

Scheme 1. Resonance Structures of Vinyl Cation 1



of **1** at the B3LYP/cc-pvtz level of theory predicts for the C=C⁺ stretching vibration a very strong IR absorption at 1955 cm^{−1}, very close to the experimentally observed IR band at 1958 cm^{−1}.¹⁴

Thus, experimental and theoretical data clearly indicate the occurrence of σ -delocalization in vinyl cation **1** which involves both the C(β)–Si σ -orbitals and the Walsh type orbitals of the cyclopropyl ring. This interaction can be described as resonance between the canonical structures A, B, and C (see Scheme 1).

Acknowledgment. The Cluster for Scientific Computation (CSC) at the CvO University Oldenburg is thanked for providing computational resources.

Supporting Information Available: Experimental details; theoretical protocols; complete ref 13; tables of absolute energies and Cartesian coordinates, experimental and computed NMR chemical shifts, and computed IR frequencies; cif file of **1**[B(C₆F₅)₄]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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