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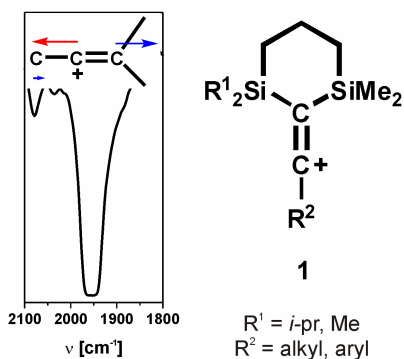


Hyperconjugation in β , β' -silyl substituted Vinylcations – Indications from IR Spectroscopy

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Vinyl cation salts **1**[B(C₆F₅)₄] have been analyzed using IR spectroscopy. The energy of the characteristic band assigned to the $\nu^{as}(\text{C}=\text{C}^+)$ was found to be very sensitive to the degree of hyperconjugational stabilization by the β -silyl groups.



Hyperconjugation in β, β' -silyl substituted Vinyl Cations – Indications from IR Spectroscopy

Andrea Klaer and
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Abstract.

Alkyl substituted vinyl cations **1a-c** have been synthesized in the form of their $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ salts and have been characterized by NMR and IR spectroscopy. The IR absorption bands detected for the $\nu^{\text{as}}(\text{C}=\text{C}^+)$ vibrations in vinyl cations are of great diagnostic value, due to their high intensity and due their relative isolated position in the IR spectra ($\tilde{\nu} = 1930\text{-}2020\text{ cm}^{-1}$). DFT calculations of the harmonic force constants at the B3LYP/cc-pvtz level of theory allowed for an unequivocal assignment of the band after scaling of the theoretical values to account for the anharmonicity of the experimental vibrational potential. A study on the energy of the $\nu^{\text{as}}(\text{C}=\text{C}^+)$ of alkyl (**1**) and aryl substituted vinyl cations, **2**, revealed a systematic trend, which indicates a decreasing stabilization of the vinyl cations by β -SiC-hyperconjugation when the electron donating ability of the substituent R^2 next to the positively charged carbon atom is increased.

Introduction

Vinyl cations are well established reaction intermediates in many synthetic transformations in organic chemistry.^[1] Direct spectroscopic evidence for vinyl cations in superacidic media was provided by low temperature NMR studies^[2] and recently significant progress in the synthetic methodology allowed the isolation of salts of stabilized vinyl cation, such as **1**[B(C₆F₅)₄], at room temperature^[3-8] and the experimental molecular structures of two examples were determined by X-ray diffraction methods.^[7,8] These recent advancements are a result of (i) kinetic stabilization by the reaction conditions, that is, weakly coordinating anions and aromatic hydrocarbons as solvents, and (ii) the thermodynamic stabilization by hyperconjugational interaction between the dicoordinated carbon atom C⁺ and the two β-silyl groups. The pronounced hyperconjugation or σ-delocalization in vinyl cations of type **1** are translated into characteristic NMR parameters^[3-5] and in specific structural features.^[7,8] In particular, NMR spectroscopy proved to be a valuable tool to study the interplay between σ-delocalization and π-resonance in aryl substituted vinyl cations **2**.^[4] In this report, we will show that also IR spectroscopy of vinyl cation salts provides a powerful method for the characterization of vinyl cations due to the very intensive absorption of the asymmetric C=C⁺ stretch vibration. In addition, it is demonstrated that the variation of the energy of this vibrational mode is a sensitive tool to study the effect of β-SiC hyperconjugation on the electronic structure of vinyl cations.

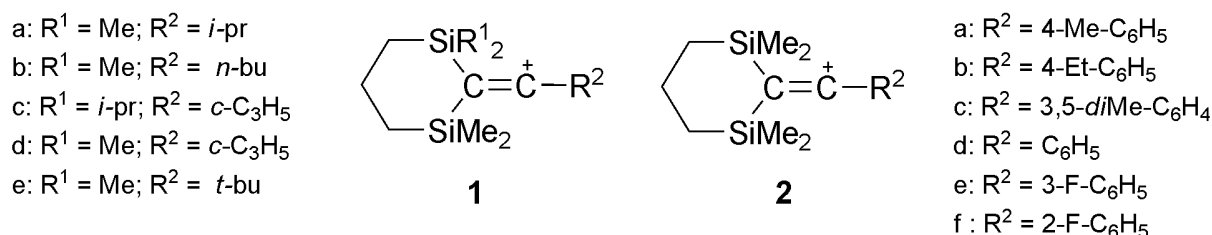
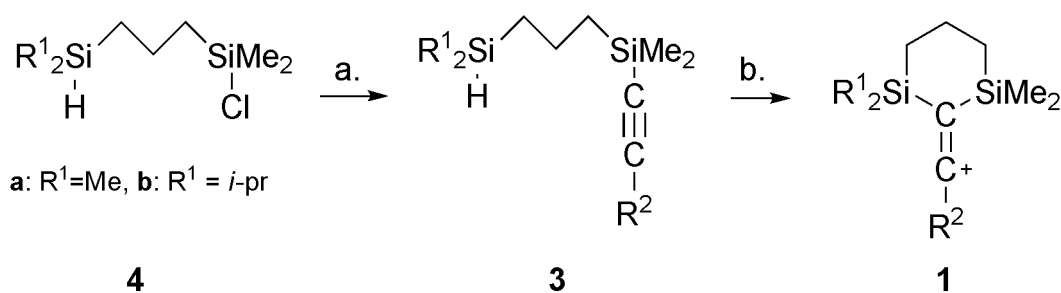


Chart 1.

Results and Discussion

Synthesis

The precursor alkynyl silanes **3** were synthesized in high yields by reaction of disilaheptanes **4** with the corresponding metalated 1-alkynes. β,β-disilylsubstituted vinyl cations **1** were prepared by reactions of alkynyl silanes **3** with trityl cation in benzene or toluene as described previously for related cations.^[3-8] (Scheme 1). The counter ion was in all cases tetrakis(pentafluorophenylborate) ([B(C₆F₅)₄]⁻). The vinyl cation salts **1a-c** [B(C₆F₅)₄]⁻ were isolated as brown amorphous or microcrystalline solids in high yields (80-90%).



Scheme 1. Synthesis of vinyl cations **1**. a. $\text{BrMg-C}\equiv\text{C-R}^2$ / THF; b. $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ / C_6H_6 (For the numbering of compounds **1**, **3** see Chart 1).

The salts **1** $[\text{B}(\text{C}_6\text{F}_5)_4]$ form liquid clathrates of high salt concentrations with arene solvents which facilitate the NMR spectroscopic investigations. The thermal stability of the vinyl cation salts **1** $[\text{B}(\text{C}_6\text{F}_5)_4]$ strongly depends on the substituent R^2 . In the solid state and in arene solution, the cation salts **1a** $[\text{B}(\text{C}_6\text{F}_5)_4]$ and **1c** $[\text{B}(\text{C}_6\text{F}_5)_4]$ were stable for days and showed no sign of decomposition. In contrast, NMR spectroscopy indicated that cation salt **1b** $[\text{B}(\text{C}_6\text{F}_5)_4]$ started to decompose already after a few minutes in benzene solution at room temperature.

NMR spectroscopic characterization

The ^{13}C NMR spectroscopic parameter of the vinyl cations **1a**, **1b** and **1c** (see Table 1) closely resemble those reported previously for vinyl cations **1d** and **1e**.^[7, 8] Therefore, these cations clearly adopt a classical Y-shaped vinyl cation ground state structure. 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 $\delta^{13}\text{C}=190.8\text{--}201.0$ and that attributed to the trigonal C^β atom at $\delta^{13}\text{C}=70.5\text{--}78.0$. These NMR chemical shifts 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 sp^2 -hybridized trigonal carbon center.^[3-8] The unusual small $^1J(\text{C}^\beta\text{Si})$ coupling constant ($^1J(\text{C}^\beta\text{Si})=15.4$ Hz (**1a**)), is typical for the $\text{C}^\beta\text{--Si}$ bond in these cations and is a consequence of the reduced bond order due to delocalization of electron density from the $\sigma\text{-SiC}^\beta$ bond to the formally empty $2p$ orbital at the positively charged C^α atom.^[4-8] The ^{29}Si NMR chemical shifts of the vinyl cations **1a**, **1b** and **1c** (see Table 1) exhibited a marked downfield shift compared to the precursor alkynylsilanes **3a** ($\delta^{29}\text{Si} = -18.3$), **3b** ($\delta^{29}\text{Si} = -18.3$) and **3c** ($\delta^{29}\text{Si} = -18.4$). The deshielding of the β -silicon atoms is large ($\Delta\delta^{29}\text{Si} = 42.7\text{--}44.5$)^[9] and can be rationalized by the occurrence of $\beta\text{-SiC}$ hyperconjugation and therefore localization of positive charge at the β -silicon atoms.^[3-8]

Table 1. NMR chemical shifts δ for vinyl cations **1** in [D₆]benzene at 305 K.

Cpd	R ¹	R ²	$\delta^{13}\text{C}^{\alpha}$	$\delta^{13}\text{C}^{\beta}$	$\delta^{29}\text{SiMe}_2$	$\delta^{29}\text{Si-Pr}_2$	$\delta^{13}\text{C}(\text{CH}_2)$
1a ^[a]	Me	<i>i</i> -Pr	196.2	76.7	26.2	-	15.0, 15.9
1b	Me	<i>n</i> -Bu	190.8	78.0	24.4	-	15.0, 15.9
1c	<i>i</i> -Pr	<i>c</i> -C ₃ H ₅	201.0	70.5	24.8 ^[b]	26.8 ^[b]	8.2, 15.5, 16.2
1d ^[c, d]	Me	<i>c</i> -C ₃ H ₅	204.5	73.2	18.7	-	8.1, 14.9, 16.2
1e ^[c, e]	Me	<i>t</i> -Bu	202.4	75.3	29.1	-	15.0, 15.8

[a] At 297 K. [b] Assigned using ²⁹Si/¹H HMBC spectroscopy. [c] At 300 K. [d] From ref. 8.

[e] From ref. 7.

IR spectroscopic investigation

Previously, vinyl cations **1d** and **1e** were also characterized by a very intensive band in their IR spectrum at $\nu = 1958$ and 1987 cm^{-1} (see Table 2).^[7,8] Comparison with the results of density functional computations allowed in both cases the assignment of this strong band to the asymmetric stretch vibration of the C=C⁺ group, $\nu^{\text{as}}(\text{C}=\text{C}^+)$. Also for the newly synthesized vinyl cations **1a-c** and for aryl substituted vinyl cations **2a-f** IR spectra were recorded from their [B(C₆F₅)₄]⁻ salts in carefully dried and degassed nujol in an inert atmosphere. The aryl substituted vinyl cations **2** were prepared as described previously and their identity was confirmed by NMR spectroscopy.^[3,4] In each case strong IR bands assigned to the $\nu^{\text{as}}(\text{C}=\text{C}^+)$ were detected (see Table 2 and Figure 1 for an example). In order to confirm the assignment, the harmonic force constants of vinyl cations **1** and **2** were computed at the hybrid density functional B3LYP method using the extended cc-pvtz basis set.^[10] The values obtained for the $\nu^{\text{as}}(\text{C}=\text{C}^+)$ were multiplied by a global scaling factor of 0.9691 to account for the anharmonicity of the experimental vibrational potential, as suggested by Sinha et al..^[11] The energies, $\tilde{\nu}^{\text{as}}(\text{C}=\text{C}^+)^{\text{calc}}$, obtained by this procedure are very close to the experimental values with a maximum deviation of $\Delta\tilde{\nu} = -26\text{ cm}^{-1}$,^[12] which is well below the standard deviation of 35 cm^{-1} suggested for this model chemistry (see Table 2).^[11] For all cations **1**, **2** the $\nu^{\text{as}}(\text{C}=\text{C}^+)$ was predicted to be the most intense IR band and computed displacement vectors confirmed that the vibration is restricted to the linear R₃C-C(+) = C-Si₂ unit with the most prominent contributions from the asymmetric stretch of the C=C double bond (see Figure 2 for an example).

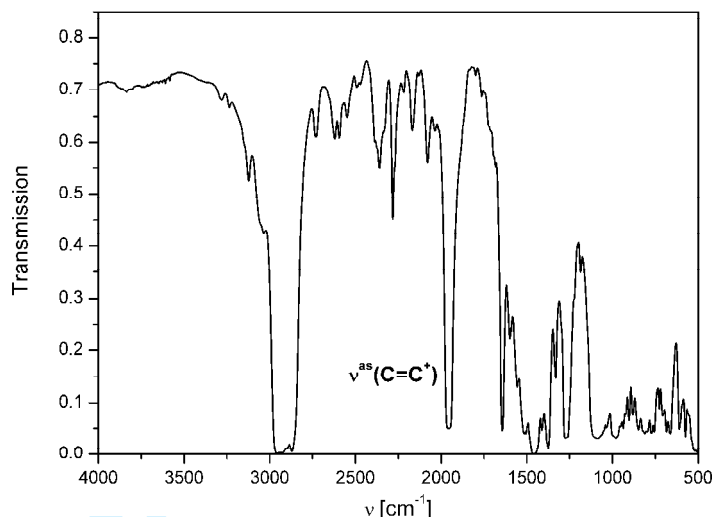


Figure 1. IR spectra of **1c**[B(C₆F₅)₄] (Nujol mull, NaCl plates).

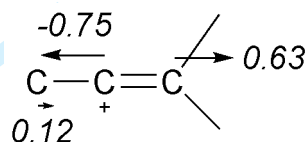
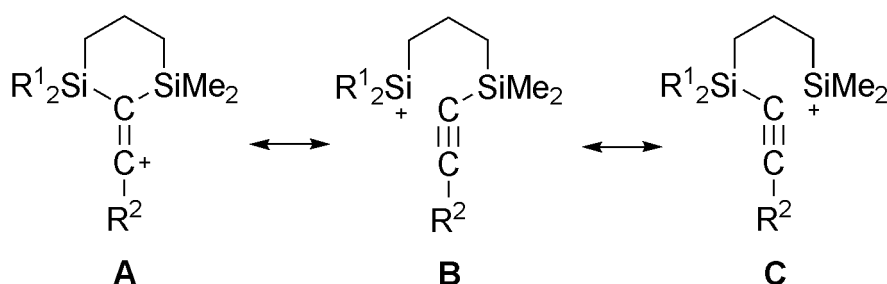


Figure 2. Schematic representation of $\nu^{\text{as}}(\text{C}=\text{C}^+)$ at 2042 cm^{-1} in vinyl cation **1a** as computed at B3LYP/cc-pvtz (size and direction of the displacement vectors in italic).

The high intensity of the C=C stretch vibrations in vinyl cations **1**, **2** is intuitively explained by the significant change in the dipole moment during the vibrational motion of the two carbon atoms of the vinylic C=C⁺ moiety. The unusual high energy shift of the C=C⁺ stretching vibration indicates a bond order for the C=C⁺ bond markedly larger than 2. A notion which is supported by the results of X-ray diffraction measurements, which revealed extremely short formal C=C double bonds in the molecular structures of vinyl cations **1d,e** (123.4 pm (**1d**), 122.1 pm (**1e**)),^[7, 8] significantly closer to the standard length of a C≡C triple bond (120 pm) than to that of a C=C (132 pm) double bond. This high bond order of the C=C⁺ bond in vinyl cations **1**, **2** is partly due to hyperconjugation which involves the two β-silyl groups and increases the C=C bond order on cost of the C-Si bond order. The σ-delocalization is formally described by the *no-bond* resonance structures **B**, **C** which confers to the C=C⁺ linkage a triple bond character (Scheme 2). The strong IR band of the $\nu^{\text{as}}(\text{C}=\text{C}^+)$ is not only suitable for the identification of vinyl cations by IR spectroscopy, the determination of its exact position might also serve as a gauge for the extent of stabilization of this cation by hyperconjugation. As shown previously, the contribution of the canonical structures **B**, **C** depends on the electron donating ability of the substituent R² next to the positively charged

carbon atom.^[4] Electron donating substituents R^2 significantly decrease the electron deficiency at the positively charged carbon atom and thereby minimize the need for additional hyperconjugational stabilization by the β -SiC bond. In this context, it is interesting to note that this gradual reduction of σ -delocalization will be immediately noticeable in the position of the $\nu^{\text{as}}(\text{C}=\text{C}^+)$ band in the IR spectrum. Therefore, IR spectroscopy seems to be well suited to study subtle changes in the electronic situation of vinyl cations of type **1** and **2**.



Scheme 2. Resonance structures for vinyl cations **1** and **2**.

Comparison of the positions of the $\nu^{\text{as}}(\text{C}=\text{C}^+)$ band in the IR spectra of the alkyl substituted vinyl cations **1a**, **b**, **d** and **e** reveals an interesting trend. There is a strictly monotonic decreasing of the energy of $\nu^{\text{as}}(\text{C}=\text{C}^+)$ when the values for vinyl cations substituted with primary (**1b**), secondary (**1a**) and tertiary (**1e**) substituents R^2 are compared (see Table 2). For cation **1d** with the strongly stabilizing cyclopropyl group, a bathochromic shift of 57 cm^{-1} compared to the *n*-butyl substituted cation **1b** is detected. This indicates a growing force constant and thereby an increasing bond order for the $\text{C}=\text{C}^+$ bond in vinyl cations **1** along the series **1d** ~ **1c** < **1e** < **1a** < **1b** (see Table 2). Since the above series clearly reflects decreasing electron donating ability of the alkyl group R^2 , this comparison confirms qualitatively the idea that with decreasing electron donation of the substituent R^2 the β -silyl hyperconjugation in vinyl cations **1** becomes more important.

A more quantitative basis is provided by the analysis of the data for the aryl substituted vinyl cations **2** (see Table 2). Due to the electron donating ability of the aryl substituents, an additional low energy shift of $\nu^{\text{as}}(\text{C}=\text{C}^+)$ in the IR spectra of vinyl cation salts **2** $[\text{B}(\text{C}_6\text{F}_5)_4]$ compared to the alkyl substituted vinyl cations **1a,b,e** was detected. In the series of aryl substituted vinyl cations **2** the largest wave number was found for vinyl cation **2e** with the electron withdrawing 3-fluoro-phenyl substituent. For the electron donating 4-ethylphenyl substituted vinyl cation **2b** the most bathochromic shifted IR band was detected. Moreover, a plot of $\nu^{\text{as}}(\text{C}=\text{C}^+)$ versus Brown's substituent constants σ^+ ^[13, 14] for the five different *meta* or *para* aryl substituents in vinyl cations **2a-e** suggests a correlation between these parameters (see Figure 2). This correlation indicates that hyperconjugation in vinyl cations **2**, depicted by

the resonance structures **B**, **C** (Scheme 2), becomes more important as the π -stabilization by the aryl substituent R^2 is diminished. Therefore, the contribution of β -SiC hyperconjugation to the overall thermodynamic stability of vinyl cations is not constant, but it is determined by the electron demand at the electron-deficient dicoordinated carbon atom.

The qualitative comparison in the case of the alkyl substituted vinyl cations **1a-e** and the correlation valid for the aryl substituted vinyl cations **2a-e** demonstrate that the energy of the $\nu^{\text{as}}(\text{C}=\text{C}^+)$ absorption is a sensitive probe for the extent of σ -delocalization in vinyl cations as described in Scheme 2. It is interesting to note that the observed and computed changes in the energy of the $\nu^{\text{as}}(\text{C}=\text{C}^+)$ is expressed only much less significantly in the computed $\text{C}=\text{C}^+$ bond lengths.¹⁵ That is, the computations predict a change in $r(\text{C}=\text{C}^+)$ of merely 1.2 pm when vinyl cation **1b** ($R^2 = n\text{-Bu}$) is compared with cation **2a** ($R^2 = 4\text{-Me-C}_6\text{H}_4$) while the energy of the $\nu^{\text{as}}(\text{C}=\text{C}^+)$ changes by 80 cm^{-1} . This fact suggests that the influence of β -SiC hyperconjugation on the $\nu^{\text{as}}(\text{C}=\text{C}^+)$ stretch vibrations is more pronounced on its force constants (that is the shape of the potential curve) than on the actual equilibrium distances (as expressed in the computed $\text{C}=\text{C}^+$ bond lengths).

Table 2. Experimental ($\nu^{\text{as}}(\text{C}=\text{C}^+)^{\text{exp}}$) and computed wavenumbers ($\nu^{\text{as}}(\text{C}=\text{C}^+)^{\text{calc}}$) of the $\text{C}=\text{C}^+$ stretching vibration for vinyl cation salts **1**[$\text{B}(\text{C}_6\text{F}_5)_4$] and **2**[$\text{B}(\text{C}_6\text{F}_5)_4$] (in cm^{-1}) and computed $\text{C}=\text{C}^+$ bond lengths (in pm) in these vinyl cations.

Cpd.	R^1	R^2	$\nu^{\text{as}}(\text{C}=\text{C}^+)^{\text{exp}}$	$\nu^{\text{as}}(\text{C}=\text{C}^+)^{\text{calc. [a]}}$	$r(\text{C}=\text{C}^+)^{[b]}$
1a	Me	<i>i</i> -Pr	1996	1979	123.7
1b	Me	<i>n</i> -Bu	2015	1989	123.7
1c	<i>i</i> -Pr	<i>c</i> -C ₃ H ₅	1955	1954	124.5
1d ^[c]	Me	<i>c</i> -C ₃ H ₅	1958	1955	124.6
1e ^[d,e]	Me	<i>t</i> -Bu	1987	1968	123.9
2a ^[f]	Me	4-Me-C ₆ H ₄	1935	1939	124.9
2b	Me	4-Et-C ₆ H ₄	1936	1938	125.0
2c	Me	3,5-di-Me-C ₆ H ₃	1943	1940	124.9
2d	Me	C ₆ H ₅	1951	1947	124.7
2e	Me	3-F-C ₆ H ₄	1962	1955	124.5
2f	Me	2-F-C ₆ H ₄	1956	1955	124.6

[a] Calculated at B3LYP/cc-pvtz using a global scaling factor of 0.9691 [11]. [b] Calculated at B3LYP/cc-pvtz. [c] From ref. 5. [d] From ref. 7. [e] The $[\text{CB}_{11}\text{HBr}_6]$ salt was used. [f] From ref.4.

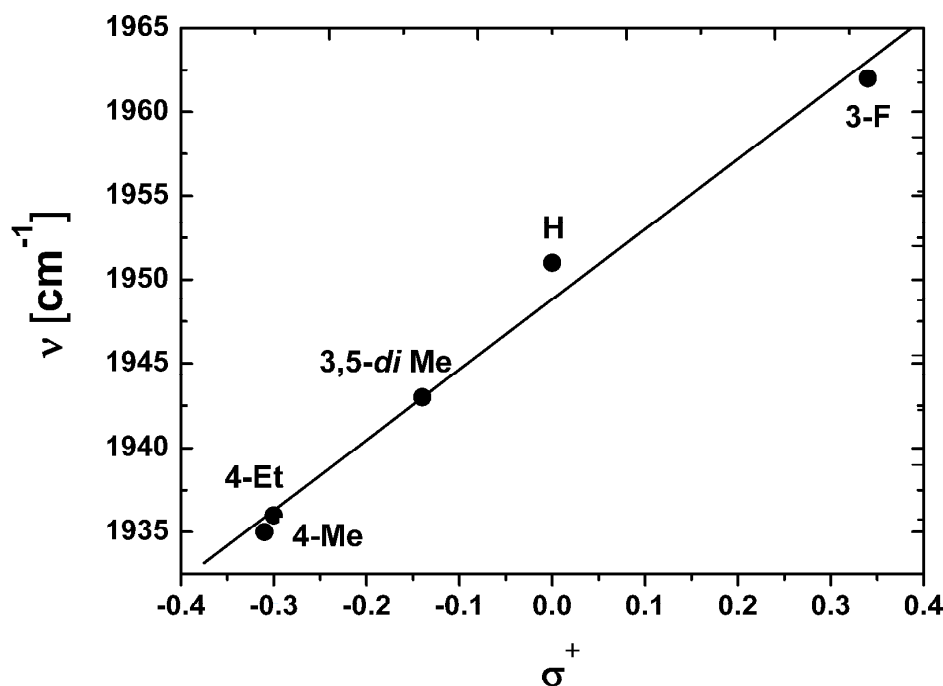


Figure 2. Plot of σ^+ versus $\tilde{\nu} [\text{cm}^{-1}]$ for aryl substituted vinyl cations **2a-e**. The correlation is given by the following equation: $\tilde{\nu} = (1948 \pm 0.70) \text{ cm}^{-1} + (41.8 \pm 2.8) \text{ cm}^{-1} \sigma^+$, $R = 0.9935$.

Conclusion.

The synthesis of three alkyl or cycloalkyl substituted β, β' substituted vinyl cations **1a-c** using the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ counter anion and their characterization by NMR spectroscopy was reported. In addition, the IR data of eleven $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ salts of alkyl (**1**) and aryl substituted vinyl cations, **2**, were analyzed. The very intense band of the asymmetric stretch vibration of the $\text{C}=\text{C}^+$ unit of vinyl cations, $\nu^{\text{as}}(\text{C}=\text{C}^+)$, is located in a characteristic region of the IR spectra ($\tilde{\nu} = 1930\text{--}2020 \text{ cm}^{-1}$) and proved to be well suited for the straight forward identification of vinyl cations. This position of the $\nu^{\text{as}}(\text{C}=\text{C}^+)$, while unusual for the stretch vibration of a $\text{C}=\text{C}$ double bond, indicates the strong CC linkage in vinyl cations **1**, **2** and suggests a bond order which is markedly higher than 2. This high bond order in vinyl cations **1**, **2** is partly due to the occurrence of β -silyl hyperconjugation which confers on the $\text{C}=\text{C}^+$ bond considerable triple bond character. In addition, the exact energy of $\nu^{\text{as}}(\text{C}=\text{C}^+)$ is found to depend significantly on the electron donor ability of the substituent R^2 directly attached to the positively charged carbon atom. Strongly electron donating substituents R^2 repress β -silyl hyperconjugation and lead consequently to a bathochromic shift of the IR band, while a high energy shift is found for electron withdrawing substituents. This dependence is also shown by the linear correlation

of the energy of the asymmetric $C=C^+$ vibration and the σ^+ substituent constants, which is found for five *meta* and *para* aryl substituted vinyl cations **2**.

For Peer Review

Technical Section

Computations All molecular structure optimizations were done using the Gaussian03 Rev. D.01 package of programs.^[10] The molecular structures of the vinyl cations **1a-e**, and **2a-f** were optimized using the nonlocal DFT level of theory and Becke's three-parameter hybrid functional and the LYP correlation (B3LYP)^[16] along with the cc-pvtz basis set.^[17] Subsequent frequency calculations at the B3LYP/cc-pvtz level of theory verified these structures as minima on the potential energy surface (PES). The asymmetric C=C⁺ stretch vibration was identified by analysis of the computed displacement vectors and in order to correct for the anharmonicity of the experimental molecular vibrations a global scaling factor of 0.9691 was applied.^[11]

Experimental, general considerations. All procedures were carried out under inert argon atmosphere using Schlenk techniques. Benzene, benzene-*d*₆, toluene, THF and pentane were distilled from sodium. Ph₃C⁺ [B(C₆F₅)₄]⁻ was prepared according to reported methods^[18, 19]. IR spectra were recorded on a Bruker Vector 22 spectrometer. The preparations of the IR samples were performed in a nitrogen filled glove box (H₂O, O₂ < 0.1ppm). High resolution mass spectra were carried out on a Finnigan-MAT95 spectrometer with electron impact ionization (EI). NMR spectra were recorded on a Bruker DRX 500 spectrometer. ¹H spectra were calibrated using residual solvent signals: δ ¹H(benzene-*d*₅) = 7.20, δ ¹H(toluene-*d*₇) = 2.03. ¹³C spectra were calibrated using solvent signals: δ ¹³C(benzene-*d*₆) = 128.0, δ ¹³C(toluene-*d*₈) = 20.4. ²⁹Si NMR spectra were calibrated using external Me₂SiHCl (δ ²⁹Si = 11.1 vs TMS). ²⁹Si NMR spectra were recorded using the INEPT pulse sequence. The assignment of the signals resulted from DEPT 135, proton coupled ¹³C NMR and 2D C, H- and Si, H correlated measurements.

Synthesis of alkynes 3. Ethylmagnesium bromide was prepared by reaction of 1 eq ethyl bromide and 1eq. magnesium in THF (15 mL). 1 eq of the corresponding 1-alkyne was added at room temperature and the resulting mixture was stirred for 1 h. Then 1 eq. 2-chloro-2,6-disila-2,6-dimethylheptane, **4a** or 2-chloro-2,6-disila-2-dimethyl-6-diisopropylheptane, **4b**, was added at 0 °C and the solution was stirred over night. The solvent was removed, the residue was dissolved in *n*-pentane, and the salts were removed by filtration. After evaporation of *n*-pentane under reduced pressure the alkynes **3** were obtained.

3a: Yield 57%. ^1H NMR (500.133 MHz, 300 K, $[\text{D}_6]\text{benzene}$): δ 0.10 (d, 6H, $^3J(\text{HH}) = 3.4$ Hz; $\text{Si}(\text{CH}_3)_2\text{H}$), 0.24 (s, 6H; $\text{Si}(\text{CH}_3)_2\text{C}\equiv\text{C}$), 0.73-0.81 (m, 4H; H1/3), 1.09 (d, 6H; $^3J(\text{HH}) = 7.0$ Hz; H5), 1.63-1.70 (m, 2H; H2), 2.45 (sept, 1H; H4), 4.18 (sept, 1H; $^1J(\text{SiH}) = 180.1$ Hz; HSi); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.758 MHz, 300 K, $[[\text{D}_6]\text{benzene}]$): δ -4.3 ($\text{SiH}(\text{CH}_3)_2$), -1.1 ($\text{Si}(\text{CH}_3)_2\text{C}\equiv\text{C}$), 18.6 (C3), 19.4 (C2), 20.7 (C1), 21.8 (C4), 23.0 (C5), 82.5 (C^α), 113.9 (C^β); ^{29}Si NMR (99.362 MHz, 300 K, $[\text{D}_6]\text{benzene}$): δ -18.3 ($\text{Si}(\text{CH}_3)_2\text{C}\equiv\text{C}$), -14.3 ($\text{Si}(\text{CH}_3)_2\text{H}$). EI HRMS: Calc For $[\text{C}_{12}\text{H}_{26}\text{Si}_2]$ m/z 226.1573, found m/z 226.1571.

3b: Yield 96%. ^1H NMR (500.133 MHz, 300 K, $[\text{D}_6]\text{benzene}$): δ 0.10 (d, 6H, $^3J(\text{HH}) = 3.8$ Hz; $\text{Si}(\text{CH}_3)_2\text{H}$), 0.25 (s, 6H; $\text{Si}(\text{CH}_3)_2\text{C}\equiv\text{C}$), 0.73-0.77 (m, 3H; H7), 0.79-0.82 (m, 4H; H1/3), 1.30-1.41 (m, 4H; H5/6), 1.65-1.71 (m, 2H; H2), 2.10 (t, 2H, $^3J(\text{HH}) = 6.8$ Hz; H4), 4.19 (sept, 1H, $^1J(\text{SiH}) = 180.8$ Hz; HSi); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.758 MHz, 300 K, $[\text{D}_6]\text{benzene}$): δ -4.3 ($\text{SiH}(\text{CH}_3)_2$), -1.2 ($\text{Si}(\text{CH}_3)_2\text{C}\equiv\text{C}$), 13.7 (C7), 18.6 (C3), 19.5 (C2), 19.5 (C4), 20.7 (C1), 22.1 (C6), 31.0 (C5), 82.8 (C^α), 108.4 (C^β); ^{29}Si NMR (99.362 MHz, 300 K, $[\text{D}_6]\text{benzene}$): δ -18.3 ($\text{Si}(\text{CH}_3)_2\text{C}\equiv\text{C}$), -14.3 ($\text{Si}(\text{CH}_3)_2\text{H}$). EI HRMS: Calc For $[\text{C}_{13}\text{H}_{28}\text{Si}_2]$ m/z 240.1730, found m/z 240.1732.

3c: Yield 96%. ^1H NMR (500.133 MHz, 297 K, $[\text{D}_6]\text{benzene}$): δ 0.24 (s, 6H; $\text{Si}(\text{CH}_3)_2\text{C}\equiv\text{C}$), 0.37-0.39 (m, 2H; H5a), 0.63-0.65 (m, 2H; H5b), 0.80-0.83 (m, 4H, H1; H3), 0.99-1.03 (m, 2H; $\text{Si}(\text{CH}(\text{CH}_3)_2)$), 1.05-1.07 (m, 1H; H4), 1.09-1.13 (m, 12H; $\text{Si}(\text{CH}(\text{CH}_3)_2)$), 1.69-1.76 (m, 2H; H2), 3.75-3.78 (m, $^1J(\text{SiH}) = 177.6$ Hz, 1H; SiH); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.772 MHz, 297 K, $[\text{D}_6]\text{benzene}$): δ -1.1 ($\text{Si}(\text{CH}_3)_2$), 0.9 (C4), 8.7 (C5), 10.9 ($\text{Si}(\text{CH}(\text{CH}_3)_2)$), 13.0 (C1), 19.0 ($\text{Si}(\text{CH}(\text{CH}_3)_2)$), 19.4 ($\text{Si}(\text{CH}(\text{CH}_3)_2)$), 20.4 (C2), 21.2 (C3), 79.0 (C^β), 111.3 (C^α); ^{29}Si NMR (99.357 MHz, 297 K, $[\text{D}_6]\text{benzene}$): δ -18.4 ($\text{Si}(\text{CH}_3)_2\text{C}\equiv\text{C}$), 5.5 ($\text{Si}(\text{CH}(\text{CH}_3)_2)$). EI HRMS: Calc For $[\text{C}_{16}\text{H}_{32}\text{Si}_2]$ m/z 280.2043, found m/z 280.2039.

Synthesis of vinyl cations 1. 1 eq. alkynylsilane **3** (0.5 mmol) was added to a vigorously stirred solution of $\text{Ph}_3\text{C}^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ (461 mg, 0.5 mmol) in benzene or toluene (2 mL) at room temperature. The mixture was stirred for 10 min. Stirring was stopped and the two phases were allowed to separate. The upper phase was removed and the lower phase was washed with *n*-pentane (3×2 mL). The solvent was removed and the product was obtained as brown powder in good yields (80- 90%).

1a TPFPB: ^1H NMR (499.873 MHz, 297 K, $[\text{D}_6]\text{benzene}$): δ 0.17 (s, 12H; $\text{Si}(\text{CH}_3)_2$), 0.45-0.47 (m, 4H; H1/3), 0.86 (d, 6H, $^3J(\text{HH}) = 7.0$ Hz; H5), 1.47 (m, 2H; H2), 2.29 (sept, 1H; H4); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.706 MHz, 297 K, $[\text{D}_6]\text{benzene}$): δ 0.2 ($\text{Si}(\text{CH}_3)_2$), 15.0 (C1/3), 15.9 (C2), 18.3 (C5), 26.7 (C4), 76.7 (C^β), 196.2 (C^α); ^{29}Si NMR (99.305 MHz, 297 K, $[\text{D}_6]\text{benzene}$): δ 26.2 ($\text{Si}(\text{CH}_3)_2$); ^1H NMR (499.873 MHz, 303 K, $[\text{D}_8]\text{toluene}$): δ 0.01 (s, 12H; $\text{Si}(\text{CH}_3)_2$), 0.29-0.30 (m, 4H; H1/3), 0.71 (d, 6H, $^3J(\text{HH}) = 7.0$ Hz; H5), 1.30 (m, 2H; H2), 2.16 (sept, 1H; H4); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.706 MHz, 303 K, $[\text{D}_8]\text{toluene}$): δ 0.4 ($\text{Si}(\text{CH}_3)_2$), 15.3 (C1/3), 16.2 (C2), 18.6 (C5), 27.0 (C4), 77.0 ($^1J(\text{SiC}) = 15.4$ Hz; C^β), 196.6 (C^α); ^{29}Si NMR (99.305 MHz, 303 K, $[\text{D}_8]\text{toluene}$): δ 26.3 ($\text{Si}(\text{CH}_3)_2$). IR: $\tilde{\nu} = 1996\text{ cm}^{-1}$ (nujol)

1b TPFPB: ^1H NMR (499.873 MHz, 305 K, $[\text{D}_6]\text{benzene}$): δ 0.06 (s, 6H; $\text{Si}(\text{CH}_3)_2$), 0.36 (m, 4H; H1/3), 0.67 (m, 3H; H7), 0.99 (m, 2H; H6), 1.13 (m, 2H; H5), 1.36 (m, 2H; H2), 2.03 (m, 2H; H4); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.706 MHz, 305 K, $[\text{D}_6]\text{benzene}$): δ -0.3 (CH_3), 12.6 (C7), 15.0 (C1/3), 15.9 (C2), 22.1 (C6), 24.6 (C4), 27.4 (C5), 78.0 (C^β), 190.8 (C^α); ^{29}Si NMR (99.305 MHz, 305K, $[\text{D}_6]\text{benzene}$): δ 24.4 ($\text{Si}(\text{CH}_3)_2$). IR: $\tilde{\nu} = 2015\text{ cm}^{-1}$ (nujol)

1c TPFPB: ^1H NMR (499.873 MHz, 305 K, $[\text{D}_6]\text{benzene}$): δ 0.06 (s, 6H; $\text{Si}(\text{CH}_3)_2$), 0.32-0.36 (m, 4H; H1/3), 0.75 (m, 14H; $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.08-1.11 (m, 1H; H4), 1.15-1.16 (m, 4H; H5), 1.34-1.39 (m, 2H; H2); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.706 MHz, 305 K, $[\text{D}_6]\text{benzene}$): δ -0.3 (CH_3), 7.9 (C4), 8.2 (C1), 14.3 ($\text{CH}(\text{CH}_3)_2$), 15.5 (C3), 16.2 (C2), 17.0 ($\text{CH}(\text{CH}_3)_2$), 23.8 (C5), 70.5 (C^β), 201.0 (C^α); ^{29}Si NMR (99.305 MHz, 305 K, $[\text{D}_6]\text{benzene}$): δ 24.8 ($\text{Si}(\text{CH}_3)_2$), 26.8 ($\text{Si}(\text{CH}(\text{CH}_3)_2)_2$); ^1H NMR (499.873 MHz, 305 K, $[\text{D}_8]\text{toluene}$): δ 0.00 (s, 6H; $\text{Si}(\text{CH}_3)_2$), 0.24-0.29 (m, 4H; H1/3), 0.67 (m, 14H; $\text{Si}(\text{CH}(\text{CH}_3)_2)_2$), 1.05-1.08 (m, 1H; H4), 1.12-1.15 (m, 4H; H5), 1.32 (m, 2H; H2); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.706 MHz, 305 K, $[\text{D}_8]\text{toluene}$): δ -0.2 (CH_3), 8.1 (C4), 8.4 (C1), 14.6 ($\text{CH}(\text{CH}_3)_2$), 15.7 (C3), 16.5 (C2), 17.2 ($\text{CH}(\text{CH}_3)_2$), 24.0 (C5), 70.8 (C^β), 201.3 (C^α); ^{29}Si NMR (99.305 MHz, 305 K, $[\text{D}_8]\text{toluene}$): δ 24.9 ($\text{Si}(\text{CH}_3)_2$), 26.8 ($\text{Si}(\text{CH}(\text{CH}_3)_2)_2$). IR: $\tilde{\nu} = 1955\text{ cm}^{-1}$ (nujol)

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