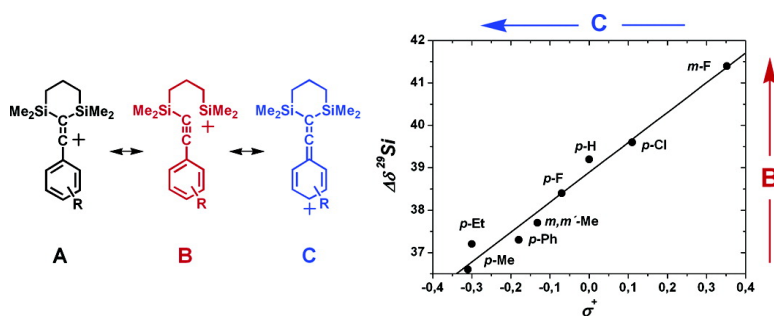Article

□-Delocalization versus □-Resonance in □-Aryl-Substituted Vinyl Cations

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σ-Delocalization versus π-Resonance in α-Aryl-Substituted Vinyl Cations

Thomas Müller,* Dominik Margraf, and Yvonne Syha

Contribution from the Institut für Anorganische und Analytische Chemie der Johann Wolfgang Goethe Universität Frankfurt, Marie Curie-Str. 11, D 60439 Frankfurt/Main, Federal Republic of Germany

Received March 16, 2005; E-mail: dr.thomas.mueller@chemie.uni-frankfurt.de

Abstract: The synthesis and isolation of 12 α-aryl, β, β'-disilyl-substituted vinyl cations **1b−l**, **7**, and **8** with the tetrakis(pentafluorophenyl)borate counteranion is reported. The vinyl cations are characterized by NMR spectroscopy and are identified by their specific NMR chemical shifts (δ ^{13}C(C$^+$) = 178.1−194.5; δ ^{13}C(C$^\beta$) = 83.3−89.9; δ ^{13}C(C^{ipso}) = 113.6−115.2; δ ^{29}Si = 25.0−12.0), supported by density functional calculations at the B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) level. All cations are found to be stable at room temperature in solution and in the solid state. The NMR chemical shifts as well as *J*-coupling data indicate for vinyl cations, **1b−l**, **7**, and **8**, the occurrence of substantial stabilization through π-resonance via the aryl substituents and through σ-delocalization via the β-silyl groups. For vinyl cation **8**, the free enthalpy of stabilization via π-resonance by the α-ferrocenyl substituent is determined by temperature-dependent ^{29}Si NMR spectroscopy to be $\Delta G^\ddagger$ = (48.9 ± 4.2) kJ mol^{-1}. A Hammett-type analysis, which relates the ^1J(SiC$^\beta$) coupling constant and the low-field shift of the ^{29}Si NMR signal upon ionization, $\Delta\delta$ ^{29}Si, with the electron-donating ability of the aryl group, indicates an inverse relation between the extent of Si−C hyperconjugation and π-donation. The computed structures (at B3LYP/6-31G(d)) of the vinyl cations **1a−l**, **7**, and **8** reveal the consequences of Si−C hyperconjugation and of π-resonance interactions with the aryl groups. The structures, however, fail to express the interplay between σ-delocalization and π-conjugation in that the calculated Si−C bond lengths and the C$^+$-C^{ipso} bond lengths do not vary as a function of the substituent.

Introduction

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-arylvinyl halides.[2] In the 1970s, numerous investigations established vinyl cations as transient 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 by Siehl and co-workers and provided important information about their electronic structure.[5−8] The major drawback of this conventional approach via superacids, like FSO$_3$H/SbF$_5$, is the high oxidation potential and the reactivity of the applied Lewis acids, SbF$_5$, which leads in the

case of vinyl cations to rearranged products or decomposition at temperatures higher than −100 °C.[8b] In the case of silyl-substituted carbocations, the omnipresence of sources for fluoride ions in the superacidic reaction media leads to facile desilylation.[5−8a] Although, this was ingeniously used for the generation of other vinyl cations,[6b] the thermodynamic stabilization by the β-silyl group, however, was lost. Recently, we were able to demonstrate that vinyl cations **1** can be obtained by intramolecular addition of transient silylium ions to alkynes in the presence of weakly coordinating anions, such as tetrakis-(pentafluorophenyl)borate, B(C$_6$F$_5$)$_4$$^-$ (TPFPB).[9] Solutions of these vinyl cation salts in aromatic hydrocarbons are persistent at room temperature, and the salts can be isolated as amorphous powders. With a brominated carborane anion,[10] crystalline material of the vinyl cation **1** (R = *t*-Bu) was obtained, and the X-ray structure was reported, which provided the first experimental structural evidence for the linear coordination of the positively charged carbon atom in vinyl cations and for the occurrence of SiC hyperconjugation.[11]
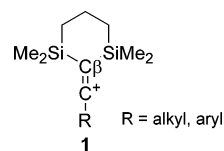
(1) For a recent monograph on vinyl cations: *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; Wiley: New York, 1997.
(2) (a) Grob, C. A.; Csapilla, J.; Cseh, G. *Helv. Chim. Acta* **1964**, *47*, 1590. (b) Grob, C. A. In ref 1, p 1.
(3) (a) Hanack, M. *Acc. Chem. Res.* **1976**, *9*, 364. (b) Kitamura, T.; Taniguchi, H.; Tsuno, Y. In ref 1, p 321.
(4) For a review, see: Lucchini, V.; Modena, G.; Pasquato, L. In ref 1, p 237.
(5) Siehl, H.-U. In ref 1, p 189.
(6) (a) Kaufmann, F.-P.; Siehl, H.-U. *J. Am. Chem. Soc.* **1992**, *114*, 4937. (b) Siehl, H.-U.; Kaufmann, F.-P.; Hori, K. *J. Am. Chem. Soc.* **1992**, *114*, 9343.
(7) (a) Siehl, H.-U. *Pure Appl. Chem.* **1995**, *67*, 769. (b) Siehl, H.-U. In *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Eds.; Wiley: New York, 1997; p 165.
(8) (a) Siehl, H.-U.; Kaufmann, F.-P.; Apeloig, Y.; Braude, V.; Danovich, D.; Berndt, A.; Stamatis, N. *Angew. Chem.*, *Int. Ed. Engl.* **1991**, *30*, 1479. (b) Siehl, H.-U.; Müller, T.; Gauss, J.; Buzek, P.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1994**, *116*, 6384.

1   R = alkyl, aryl

Scheme 1. Resonance Structures of α-Aryl-Substituted Vinyl Cations
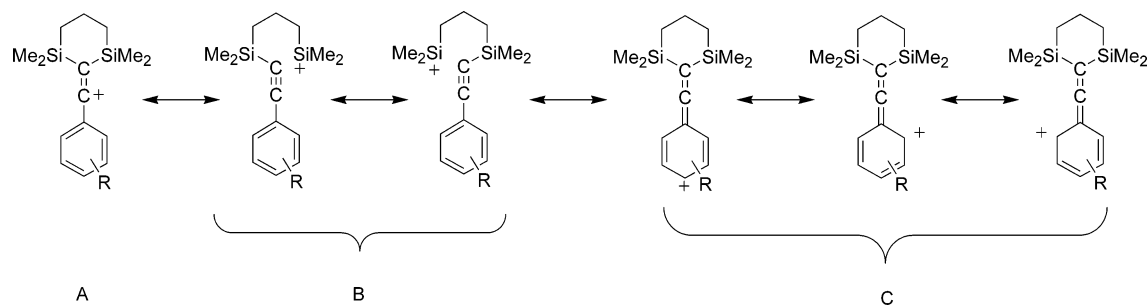
The unusual stability of the vinyl cations **1** is a result of (i) kinetic stabilization by the reaction conditions, that is, weakly coordinating anions and aromatic hydrocarbons as solvents, and (ii) the thermodynamic stabilization by hyperconjugational interaction between the dicoordinated carbon atom C^+ and the two β-silyl groups. It was already pointed out previously that the coplanar arrangement of the empty 2p-orbital at the positively charged carbon atom C^+ and the β-C—Si bond in β-silyl-substituted vinyl cations, in addition to the spatial proximity of the interacting orbitals in vinyl cations, leads to a very efficient electron delocalization from the σ-C^β—Si bond to the empty 2p-orbital of the dicoordinated carbon atom C^+.[12,13] The second substituent R at the carbon atom C^+ also provides stabilization either by inductive effects and/or by π-delocalization. As a consequence, the vinyl cation **1**, R = Ph, was calculated to be only 7.1 kJ mol^{-1} less stable than the trityl cation (Ph_3C^+).[9]

The stabilization mechanism operating in aryl-substituted vinyl cations **1** can be qualitatively depicted by the canonical resonance structures **A**–**C** (see Scheme 1). Hyperconjugation between the σ-C^β—Si bond and the empty 2p-orbital of the carbon atom C^+ is described by no-bond resonance structures **B**, and π-delocalization is indicated by structures **C**. An intriguing question which arises from this description of electron delocalization in aryl-substituted vinyl cations **1** is whether the extent of hyperconjugation through the β-SiC bonds depends on the electron-donating ability of the α-substituent or whether the stabilization arising from σ-delocalization effects is a constant term that adds to the stabilization which the α-substituent already confers on the vinyl cation **1**. A previous experimental study on α-mesityl-substituted vinyl cations **2** suggested, on the basis of chemical shift arguments, that the extent of π-delocalization in vinyl cations depends on the ability of the substituent at the C^β position to stabilize the positive charge at the carbon atom C^+.[5] In addition, mass spectroscopic studies have indicated that, for tricoordinated carbenium ions, the β-silyl stabilization (i.e., σ-delocalization) decreases significantly along the series primary, secondary, tertiary, and benzylic cations.[14] Similarly, high-pressure mass spectrometry data have shown that the thermodynamic stabilization by a

β-silicon substituent in the alkyl-substituted vinyl cation **3** is 8.4 kJ mol^{-1} more efficient than the phenyl-substituted cation **4**.[15]
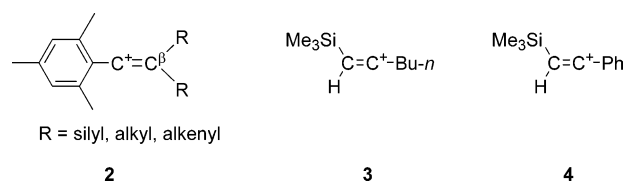
To probe the interplay between β-silyl stabilization and π-conjugation for stable vinyl cations of type **1** in detail, we synthesized a series of α-aryl-substituted vinyl cations and characterized these by NMR spectroscopy and identified spectroscopic parameters, which provide a measure for β-SiC hyperconjugation in these cations. These investigations were supported by density functional calculations of structure, energy, and NMR parameters of the experimentally observed cations.

Results and Discussion

Synthesis and Characterization of Vinyl Cations. The precursor alkynyl silanes **5**, **9**, and **10** were obtained from the reaction of 2-chloro-2,6-disila-2,6-dimethylheptane with the corresponding aryl alkynyllithium compound in satisfactory yield and characterized by standard techniques (see Scheme 2, and for details, see Experimental Part in the Supporting Information). Vinyl cations **1b**–**1l** were prepared by reaction of the corresponding alkynyl silanes **5** with trityl cation in benzene or toluene via transient silylium ions **6**, as described previously for cation **1a** and related cations (see Scheme 2).[9,11] For comparison, the α-naphthyl- and the α-ferrocenyl-substituted vinyl cations **7** and **8** were synthesized from the precursor alkynes **9** and **10**. The counteranion was, in all cases, tetrakis-(pentafluorophenyl)borate. The cation salts were isolated as red to brown oils or glassy amorphous solids in high yields.

The TPFPB salts of the vinyl cations **1a**–**1l**, **7**, and **8** are not soluble in hydrocarbons, and they form liquid clathrates with aromatic hydrocarbons.[16] These were prepared in C_6D_6 for NMR measurements. Previous studies[9,11] suggested that in these clathrates no sizable interactions between vinyl cations **1** and

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(10) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133.
(11) Müller, T.; Juhasz, M.; Reed, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1543.
(12) (a) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (b) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1985**, *107*, 5285.
(13) For recent reviews: (a) Apeloig, Y.; Müller, T. In ref 1, p 189. (b) Siehl, H.-U.; Müller, T. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. II, p 595.
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(16) (a) Lambert, J. B.; Yan, Z.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001. (b) Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Ed.; Academic Press: London, 1984; Vol. 1, Chapter 9. (c) Atwood, J. L. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; p 197. (d) Bond, D. R.; Jackson, G. E.; João, H. C.; Hofmeyer, M. N.; Modro, T. A.; Nassimbein, L. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1910. (e) Hunter, R.; Haueisan, R. H.; Irving, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 566–568. (f) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1996**, *15*, 3859.

Scheme 2. Synthesis of Vinyl Cations **1**
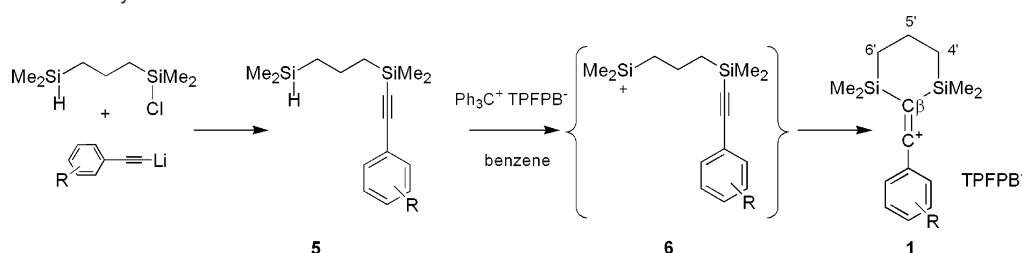
	a	b	c	d	e	f	g
R	H	4-methyl	4-ethyl	2,4-di-methyl	2,5-di-methyl	3,5-di-methyl	4-phenyl

	h	i	k	l	m	n	
R	2-fluoro	3-fluoro	4-fluoro	4-chloro	3-trifluoro-methyl	4-trifluoro-methyl	

9, R = 1-naphthyl   **11**, X = Cl
10, R = ferrocenyl   **12**, X = F
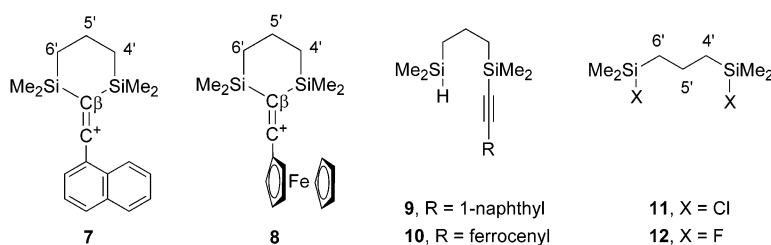
Table 1. Selected Experimental NMR Spectroscopic Data of Aryl-Substituted Vinyl Cations. NMR Chemical Shifts δ versus TMS, Coupling Constants ^1J (Hz) in Brackets[a]

compound	δ ^{29}Si	$\Delta\delta$ ^{29}Si [b]	δ ^{13}C($^+$)	δ ^{13}C($^\beta$)	δ ^{13}C(^{ipso})	δ ^{13}C(^{ortho})	δ ^{13}C(^{meta})	δ ^{13}C(^{para})	δ ^{19}F
1a[d]	22.8	39.2	185.8	84.1	113.7	141.6	130.9	143.0	
	[18.2, 55.0]			[18.2]	*−9.3*[c]	*9.8*[c]	*2.8*[c]	*14.7*[c]	
1a[d,e]	22.8	39.2	185.3	84.1	113.7	141.7	130.9	143.0	
1b	20.1	36.6	189.2	84.7	111.5	143.1	133.1	159.8	
	[19.8, 54.7]			[19.8]	*−8.6*[c]	*11.3*[c]	*4.2*[c]	*21.4*[c]	
1c	20.1	37.2	187.9	84.2	110.9	142.3	130.9	164.4	
	[20.2, 55.7]			[20.2]	*−9.5*[c]	*10.4*[c]	*3.2*[c]	*19.5*[c]	
1d	19.0	36.1	187.6	87.0	111.0	155.0, 142.8	133.1, 129.9	159.2	
	[20.7, 55.7]			[20.7]	*−9.0*[c]	*14.6*[c], *10.8*[c]	*2.9*[c], *3.7*[c]	*20.8*[c]	
1e	20.4	37.4	186.5	86.6	113.9	152.6, 142.1	139.3, 132.0	145.3	
	[19.5, 55.5]			[19.5]	*−8.8*[c]	*15.2*[c], *19.5*[c]	*3.5*[c], *2.8*[c]	*16.0*[c]	
1f	20.6	37.7	187.9	83.3	113.6	139.3	141.9	146.2	
	[18.8, 55.6]			[18.8]	*−9.2*[c]	*9.7*[c]	*8.5*[c]	*15.5*[c]	
1g	20.5	37.3	187.9	84.9	111.7	142.5	131.7	156.4	
	[19.5, 55.6]			[19.5]					
1h	24.9	41.2	178.1	89.9	104.0	169.6, 140.7	126.8, 117.6	146.6	−93.4
	[16.6, 55.2]			[16.6]	*−7.9*[c]	*6.5*[c], *16.9*[c]	*−7.0*[c], *2.1*[c]	*16.4*[c]	[273.3]
1i	25.0	41.4	182.0	84.7	115.2	137.8, 126.2	162.4, 133.0	130.2	−105.3
	[17.2, 55.5]			[17.2]	*−9.9*[c]	*10.0*[c], *13.9*[c]	*0.1*[c], *3.2*[c]	*7.5*[c]	[256.7]
1k	22.1	38.4	184.8	84.8	110.3	145.5	119.3	171.8	−78.5
	[18.8, 55.9]			[18.8]	*−9.1*[c]	*11.6*[c]	*3.5*[c]	*9.0*[c]	[276.2]
1l	23.0	39.6	184.3	85.3	111.8	142.3	131.7	152.1	
	[18.4, 55.7]			[18.4]	*−9.9*[c]	*9.1*[c]	*3.2*[c]	*17.6*[c]	
7	20.8	37.4	186.1	89.0					
	[19.9, 55.7]			[19.6]					
8	12.0	29.5	194.5	85.0					
	f			[24.6]					

[a] In benzene-d_6 at 303 K. [b] ^{29}Si NMR chemical shift difference between cation **1** and alkyne **5**; $\Delta\delta$ ^{29}Si = δ ^{29}Si(**1**) − δ ^{29}Si(**5**). [c] ^{13}C NMR chemical shift difference between cation **1** and alkyne **5**; $\Delta\delta$ ^{13}C = δ ^{13}C(**1**) − δ ^{13}C(**5**); negative values denote a high-field shift upon ionization. [d] Taken from ref 9. [e] In toluene-d_8 at 303 K. [f] The determination of ^1J(SiC$^\beta$) from ^{29}Si NMR data was not possible due to kinetic line broadening of the ^{29}Si signals.

solvent molecules take place; in particular, no Wheland-type intermediates are formed. Experimentally, this is shown by negligible solvent effects on the ^{13}C and ^{29}Si NMR chemical shifts when the solvent is changed from C_6D_6 to C_7D_8 (see Table 1).[9] Computationally, this is supported by relative small

calculated interaction energies, I(E), for vinyl cation **1a** and benzene (I(E) = 13.0 kJ mol^{-1}, at B3LYP/6-31G(d)),[9] and inclusion of thermal energy and entropy reveals that the association between **1a** and benzene is an endogonic process at 298 K (ΔG(298) = +16.3 kJ mol^{-1}). With all other common

organic solvents, rapid decomposition occurs; for example, with organic nitriles, the formation of silylated nitrilium ions can be observed.[9] After addition of methylene chloride to a solution of **1a** in toluene, a fast fragmentation reaction occurs even at temperatures as low as −50 °C, and the disilyldichloride **11** was detected by NMR spectroscopy as the final product. Similarly, the trifluoromethyl-substituted arylalkynyl silanes **5m,n** did not give the corresponding vinyl cations upon ionization with trityl cation, but the transient silylium ions **6m,n** underwent further degradation reactions and the only detectable product by NMR spectroscopy from both reactions was the disilyldifluoride **12** (see Experimental Part in the Supporting Information for details).[17] Both disilyldihalides, **11** and **12**, were identified by comparison of their NMR spectra with those of original samples.

Cations **1b−l**, **7**, and **8** were characterized in benzene solution by multinuclear NMR spectroscopy (see Table 1). The C═C$^+$ unit of the vinyl cations **1b−l** and **7** is readily identified by the low-field resonance of the positively charged C$^+$ carbon atom in the ^{13}C NMR spectra at δ ^{13}C = 178.1−189.2 and that attributed to the trigonal carbon atom C$^{\beta}$ at δ ^{13}C = 83.3−89.0. These ^{13}C NMR chemical shifts are very close to those observed for similar *β*-silyl-substituted 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.[5−9,11,13b] The relative high-field resonance of the aromatic *ipso* carbon atoms (δ ^{13}C^{ipso} = 104.0−115.2) is typical for the *ipso* C(sp^2)−C$^+$(sp) linkage in aryl-substituted vinyl cations.[5,6,9,13b] The ^{13}C NMR signals of the C^{ipso} atoms in **1b−l** and **7** appear at even lower frequencies than in the starting alkynes **5**, the chemical shift difference being $\Delta\delta$ ^{13}C^{ipso} = −7.9 to −9.9.[18] The symmetric structure of each vinyl cation **1b−l** and **7** in solution is apparent from one single line in the ^{29}Si NMR spectra at δ ^{29}Si = 19.0−25.0 and is further supported by the ^{1}H NMR and ^{13}C NMR data obtained for the disilacyclohexane moiety (see Experimental Part in the Supporting Information). The characteristic ^{13}C NMR spectroscopic data detected for the ferrocenyl-substituted vinyl cation **8** (δ ^{13}C(C$^{\alpha}$) = 194.5, δ ^{13}C(C$^{\beta}$) = 85.0, δ ^{13}C(C^1) = 52.6) are similar to those observed for vinyl cations **1b−l** and **7** and for other *α*-ferrocenyl-substituted vinyl cations,[5,19] and also for this cation, only one single resonance in the ^{29}Si NMR at δ ^{29}Si = 12.0 is detected at room temperature.[20]

The ^{13}C NMR chemical shift pattern observed for the aryl carbon atoms in **1b−f,h−l** indicates, in each case, considerable charge transfer from the C$^+$ carbon atom to the *α*-aryl substituent, characteristic for *π*-delocalization, but the extent clearly depends on the individual substituent.[21] In all cases, the signals of the carbon atoms in *ortho* and *para* positions of the aryl substituent experience a marked low-field shift compared

Scheme 3. *π*-Delocalization in **1k**
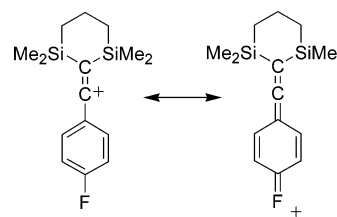
to that of the precursor alkynes in the ^{13}C NMR spectra ($\Delta\delta$ ^{13}C^{ortho} = 6.5−19.5, $\Delta\delta$ ^{13}C^{para} = 7.5−21.4), while the deshielding of the *meta* carbon atoms is much less pronounced, $\Delta\delta$ ^{13}C^{meta} = 0.1−8.5, in the case of *ortho* fluoro-substituted vinyl cation **1h**, even a shielding by $\Delta\delta$ ^{13}C^{meta} (**1h**) = −7.0 is observed (see also Table 1).[18] The delocalization of positive charge into the aryl substituent is also reflected by the ^{19}F NMR data for the fluoro-substituted vinyl cations **1h−k** (see Table 1). The fluorine atom in the *para*-substituted vinyl cation **1k** is strongly deshielded compared to the precursor aryl alkyne **5k** ($\Delta\delta$ ^{19}F (**1k**) = 32.5), and also for the *ortho*-substituted cation **1h**, a considerable low-field shift is detected ($\Delta\delta$ ^{19}F (**1h**) = 16.5).[18] The ^{19}F NMR signal of the *meta*-substituted cation **1i** is significantly less shifted to lower field ($\Delta\delta$ ^{19}F (**1i**) = 8.3). Similar deshielding effects have been previously observed for fluorinated arenium ions.[22] These deshielding effects on the ^{19}F NMR chemical shift for **1h−k** are paralleled by a significant increase of the ^{1}J(CF) coupling constant upon ionization in these cations (Δ^1J(CF) = 26.0 Hz, Δ^1J(CF) = 20.1 Hz, Δ^1J(CF) = 9.4 Hz, for **1k**, **1h**, and **1i**, respectively),[23] which is again markedly larger for the *ortho*- and *para*-substituted cations **1h** and **1k**.[24] Both factors, the deshielding of the fluorine atoms and the increase of the ^{1}J(CF) coupling constant, indicate significant involvement of the fluorine substituents in the *π*-delocalization in vinyl cations **1h,k**, as it is described for **1k** by the canonical resonance structures in Scheme 3.

Two NMR spectroscopic parameters in vinyl cations **1a−l** show the occurrence of *σ*-delocalization by interaction between the *β*-C−Si *σ*-bond and the empty 2p-orbital at the C$^+$ carbon atom as described by the no-bond resonance structures **B** (Scheme 1). That is, for all investigated vinyl cations, a significant low-field shift of the ^{29}Si NMR resonance compared to that of the precursor silylalkyne upon ionization is detected ($\Delta\delta$ ^{29}Si = 36.1−41.4 for **1a−l**, **7** and $\Delta\delta$ ^{29}Si = 29.5 for **8**, see Table 1).[18,25] This deshielding indicates localization of positive charge at the silicon atoms as a consequence of hyperconjugation between the *σ*-CSi bond and the 2p-orbital at C$^+$. The low-field shift of the ^{29}Si NMR silicon signal is largest for the *meta* fluoro-substituted vinyl cation **1i** and reaches its minimum value with the strongly electron-donating ferrocenyl substituent for vinyl cation **8**. In addition, the Lewis representations **B** of the vinyl cations **1** imply a reduced degree of bonding between the carbon atom C$^{\beta}$ and the two adjacent silicon atoms.

(17) Fluorine abstraction from benzylic CF$_3$ groups by transient silylium ions has been reported previously: Kira, M.; Hino, T.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6697.

(18) The NMR chemical shift differences $\Delta\delta^{XY}E$ is calculated according to: $\Delta\delta^{XY}E = \delta^{XY}E(\mathbf{1}) − \delta^{XY}E(\mathbf{5})$; $^{XY}E = {}^{13}$C, ^{19}F, ^{29}Si.

(19) Koch, E.-W.; Siehl, H.-U.; Hanack, M. *Tetrahedron Lett.* **1985**, *26*, 1493.

(20) For a tricoordinated ferrocenyl-substituted ethylsilyl cation, a ^{29}Si NMR chemical shift of δ ^{29}Si = 23.5 was observed. See: Siehl, H.-U.; Müller, B.; Malkina, O. In *Organosilicon Chemistry III*; Auner, N., Weis, J., Eds.; Wiley-VCH: New York, 1998; p 25.

(21) An unequivocal assignment of the carbon atom in the biphenyl-substituted alkyne **5g** was not possible; therefore, vinyl cation **1g** is excluded from this discussion.

(22) (a) Spear, R. J.; Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 2493. (b) Shteingarts, V. D.; Pozdnyakovich, Y. V.; Yakobson, G. G. *J. Chem. Soc., Chem. Commun.* **1969**, 1264. (c) Shtark, A. A.; Pozdnyakovich, Y. V.; Shteingarts, V. D. *J. Org. Chem. (USSR)* **1977**, *13*, 1544.

(23) The differences for the *J* coupling constants $\Delta^n J$ (E(1)E(2)) are calculated according: $\Delta^n J$ (E(1)E(2)) = $^n J$ (E(1)E(2)) (**1**) − $^n J$ (E(1)E(2)) (**5**); E(1), E(2) = C, Si, F, H.

(24) Similar increased ^{1}J(CF) coupling constants have been found in nitro-substituted fluorobenzenes. See: Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C NMR-Spektroskopie*: Thieme: Stuttgart, Germany, 1984; p 524.

(25) δ ^{29}Si of the alkynyl-substituted silicon atom was used for the calculation of $\Delta\delta$ ^{29}Si.
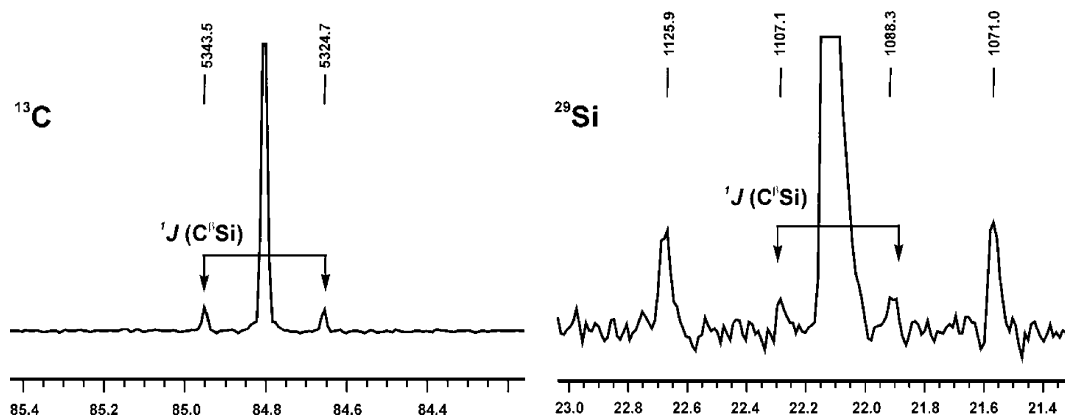
Figure 1. The 62.90 MHz ^{13}C NMR (left) and 49.69 MHz ^{29}Si NMR (right) spectra of **1k** in benzene-d_6 at 30 °C, which show the reduced $^1J(C^\beta Si)$ coupling constant (Hz).[28]

As a consequence, the $^1J(C^\beta Si)$ coupling constant in vinyl cations **1a−l**, **7**, and **8** are considerably smaller than regular coupling constants between sp²-hybridized carbon atoms and tetrahedral-coordinated silicon atoms ($^1J(=CSi) \approx 60$ Hz).[26,27] In this series, the extreme values are observed for the *ortho* fluoro-substituted vinyl cation **1h** ($^1J(C^\beta Si) = 16.6$ Hz) and for vinyl cation **8** ($^1J(C^\beta Si) = 24.6$ Hz; see Table 1, and for an example, see Figure 1).[28] A similar small $^1J(C^\beta Si)$ coupling constant has been detected in vinyl cation **1** (R = *t*-Bu).[11] In that case, the theoretical analysis revealed that the small coupling is a result of a strongly reduced Fermi contact term, which is attributed to the strongly reduced s-orbital contributions to the Si−C$^\beta$ bond.[11,29]

From the discussion of the NMR spectroscopic data, it is apparent that vinyl cations **1** are stabilized by π-delocalization via the α-aryl substituent and by σ-type interaction between the Si−C$^\beta$ bond and the 2p-orbital of the positively charged C$^+$ atom. The very similar structure of vinyl cations **1**, which differ among each other only in the substitution pattern of the aryl group, provides the unique opportunity to probe the influence of the aryl substituent on the β-silicon effect in vinyl cations. A well-established tool for quantifying the electron-donating ability of substituted aryl groups in reactions, which proceeds via benzylic carbocations, are Brown's substituent constants σ^+ for different *meta* and *para* substituents.[30−33] A plot of the σ^+ constants for the eight *meta* or *para* substituents[32,33] in vinyl cations **1a−c**, **f**, **g**, and **i−l** versus the deshielding $\Delta\delta$ ^{29}Si of the silicon atoms upon ionization[18,25] in these vinyl cations suggests a correlation between these parameters (see Figure 2a). The deshielding $\Delta\delta$ ^{29}Si clearly
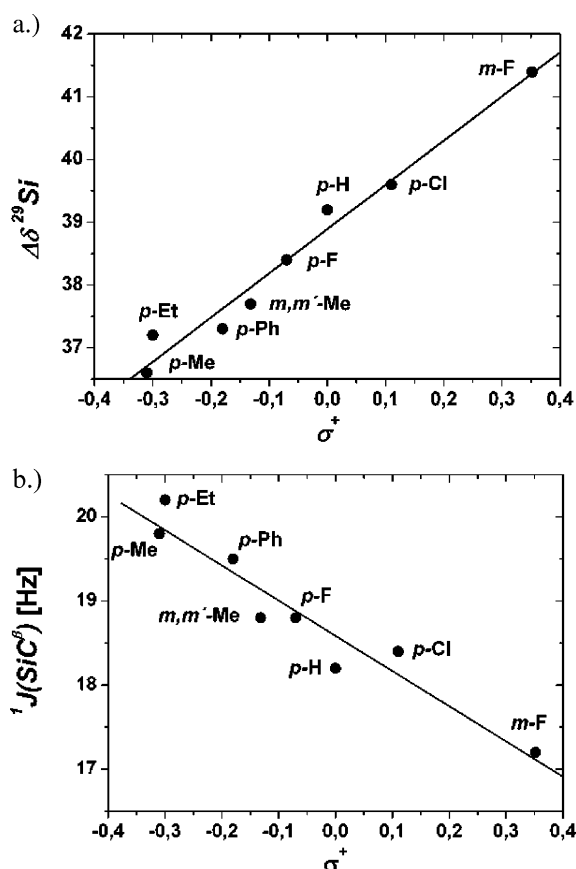
(26) Takeuchi, Y.; Takayama, T. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, p 267.
(27) A small $^1J(SnC)$ coupling constant was detected in a related distannylmethylene borane: Pilz, M.; Michel, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 409.
(28) The $^1J(C^\beta Si)$ constant was detected in both, the ^{29}Si and in the ^{13}C NMR spectra, with sufficient digital resolution to allow for a spectral resolution of 0.1 Hz; see Figure 1.
(29) This conclusion is fully supported by density functional calculations at the GIAO/B3LYP/6-311G(d,p) level of theory for **1i**, which predict $^1J(C^\beta Si)$ = 11.8 Hz (17.2 Hz, experimentally) with a significantly reduced Fermi contact contribution of 12.6 Hz. These values must be compared to the computed coupling constant between the methyl carbon atom and the silicon atom: $^1J(C^{Me}Si)$ = 48.7 Hz (55.5 Hz, experimentally) with Fermi contact contribution of 50.3 Hz.
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(31) (a) Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323. (b) Stock, M. L.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35.
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Figure 2. (a) Plot of σ^+ versus $\Delta\delta$ ^{29}Si for vinyl cations **1a−c,f,g,i−l**. The correlation is given by the following equation: $\Delta\delta$ ^{29}Si = (7.1 ± 0.5) σ^+ + (38.9 ± 0.1), R = 0.99. (b) Plot of σ^+ versus $^1J(C^\beta Si)$ for vinyl cations **1a−c,f,g,i−l**. The correlation is given by the following equation: $^1J(C^\beta Si) = (−4.2 ± 0.5) \sigma^+ + (18.6 ± 0.1)$, R = −0.96.

increases with decreasing π-donating ability of the aryl substituent. Similarly, the coupling constant $^1J(C^\beta Si)$ is reduced with the decreasing π-donating ability of the aryl substituent (see Figure 2b). Both correlations suggest that hyperconjugation in vinyl cations **1**, depicted by the resonance structure **B** (Scheme 1), becomes more important as the π-stabilization of the aryl substituent 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.

Table 2. Selected Computed Geometrical Parameter of α-Aryl-Substituted Vinyl Cations **1a-l**, **7**, and **8per**. Bond Lengths in Picometers, Bond Angles in Degrees (B3LYP/6-31G(d))

compound	$C^+{=}C^\beta$	C^β–Si	C^+–C^{ipso}	C^{ipso}–C^{ortho}	C^{ortho}–C^{meta}	C^{meta}–C^{para}	$C^\beta{=}C^+{-}C^{ipso}$	$Si{-}C^+{=}C^\beta$
1a[a]	125.7	197.3; 197.3	139.6	142.1; 142.1	138.6; 138.6	140.6; 140.6	179.7	122.3, 122.3
1b	126.0	196.8; 196.8	139.1	142.1; 142.2	138.3; 138.2	141.1; 140.0	179.6	122.1, 122.2
1c	126.0	196.6; 196.8	139.0	142.2; 142.2	138.2; 138.2	141.0; 141.0	179.6	122.5, 121.8
syn- **1d**	126.2	196.5; 196.4	138.7	143.3; 142.5	140.0; 137.8	140.7; 141.0	178.8	122.2, 122.1
*anti-***1d**	126.2	196.5; 196.5	138.7	142.5; 143.4	137.8; 139.0	140.6; 141.6	179.3	122.3, 122.2
syn- **1e**	126.0	196.7; 196.6	139.1	143.1; 142.5	139.4; 138.7	139.6; 140.9	179.3	122.2, 122.1
*anti-***1e**	126.0	196.8; 196.6	139.1	143.0; 142.5	138.6; 139.5	141.0; 139.6	178.6	123.4, 121.0
1f	125.9	196.8; 196.8	139.3	141.9; 141.9	139.1; 139.1	140.7; 140.7	179.6	122.2, 122.1
1g	126.2	196.4; 196.2	138.6	142.4; 142.4	137.8; 137.9	141.8; 137.9	179.5	121.4, 122.6
*anti-***1h**	125.6	197.4; 197.4	139.1	142.3; 142.0	138.3; 138.4	140.6; 139.7	178.5	121.9; 121.9
syn- **1h**	125.6	197.4; 197.4	139.1	142.0; 142.4	138.4; 138.3	139.7; 140.6	179.0	122.2; 122.3
*anti-***1i**	125.6	197.8; 197.8	139.9	141.9; 141.8	138.9; 138.3	139.8; 139.8	179.8	122.3; 122.3
syn- **1i**	125.6	197.7; 197.7	139.9	141.9; 141.8	138.3; 138.9	139.8; 139.8	180.0	122.3; 122.3
1k	125.9	197.2; 197.2	139.2	142.3; 142.3	138.2; 138.2	140.0; 140.0	179.7	122.3; 122.3
1l	125.9	197.3; 197.3	137.7	142.1; 142.1	138.3; 138.3	140.5; 140.5	179.7	122.3; 122.3
anti- **7**	126.2	196.5; 196.5	138.6				179.2	122.1; 122.1
syn- **7**	126.2	196.4; 196.4	138.6				179.5	122.0; 121.9
8per	126.5	197.8; 194.4	137.7				174.1	114.6; 130.0

[a] Data for **1a** were reported previously; see ref 9.

Computational Results: Density functional calculations[34] at the B3LYP/6-31G(d)[35] level of theory (for technical aspects, see Computational Details in the Supporting Information) predict for the α-aryl-substituted vinyl cations **1b**−**l** similar structures as reported previously for **1a**[9] and found also experimentally for the α-*t*-butyl-substituted vinyl cation **1**, R = *t*-butyl.[11] The computed structural data are summarized in Table 2. The sp-hybridization of the positively charged carbon atom C^+ is indicated for all cations by a bond angle $\alpha(C^\beta C^+ C^{ipso})$ close to 180° ($\alpha(C^\beta C^+ C^{ipso}) = 178.5{-}180°$) and the very short $C^\beta{=}C^+$ formal double bond, which is actually closer to that of a $C{\equiv}C$ triple bond ($r(C^\beta{=}C^+) = 125.6{-}126.2$ pm). Long $Si{-}C^\beta$ bonds ($r(Si{-}C^\beta) = 196.2{-}197.8$ pm), which exceed regular single bond lengths between (sp^2)-hybridized carbon atoms and tetracoordinated silicon atoms (187.8 pm)[36] by ca. 9−10 pm, suggest considerable interaction between the $\sigma(C{-}Si)$ bond and the empty 2p-orbital at the dicoordinated carbon atom. The $Si{-}C^\beta$ bonds in **1a**−**l** are shorter than those calculated at the same level of theory for **1**, R = *tert*-butyl ($r(Si{-}C^\beta) = 200.1$, 197.9),[11] and in each cation, both $Si{-}C^\beta$ bonds are practically of identical length. The α-aryl groups in **1a**−**l** are oriented almost perpendicular to the plane spanned by the two silicon atoms and the C^β atom, thereby providing maximum overlap between the empty $2p(C^+)$-orbital and the π-system of the aryl substituent (see Figure 3 for the computed structure of *anti-***1d**). The π-delocalization is also apparent from the very short formal $C^+{-}C^{ipso}$ single bond ($r(C^+{-}C^{ipso}) = 137.7{-}139.9$ pm), which reveals the importance of the allenic resonance description **C** (see Scheme 1). As a result, the C−C bond lengths in the aryl rings follow in all vinyl cations the expected long−short−middle sequence (see Table 2). This bond lengths pattern is slightly modified by the actual electronic situation caused by the substituents. The most striking fact arising from the computed structures of the cations **1a**−**l** is that all important
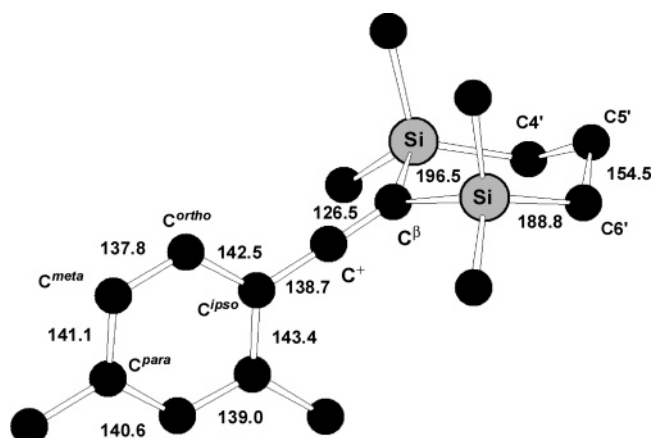
(34) All computations were done with *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.
(35) (a) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (d) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612.
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Figure 3. Computed structure of *anti-***1d**,[37] calculated at B3LYP/6-31G-(d), bond lengths in picometers. Hydrogen atoms are omitted for clarity.

geometrical parameters which indicate β-SiC hyperconjugation or π-conjugation (i.e., $r(Si{-}C^\beta)$ and $r(C^+{-}C^{ipso})$, respectively) are almost not influenced by the variable substituents at the aryl group (see Table 2). The α-aryl groups in vinyl cations **1**, **7**, and **8** obviously reduce the electron deficiency of the dicoordinated carbon atom C^+ significantly, and therefore, the geometrical consequences of σ-delocalization are less pronounced than as found in **1**, R = *tert*-butyl,[11] and predicted by computations for simple β-silyl-substituted vinyl cations.[12,13] As a consequence, subtle effects which distinguish the electronic structure of the vinyl cations **1**, **7**, and **8** and are clearly detected by NMR spectroscopy are not shown by the computed geometries. This indicates that NMR spectroscopic parameters are better suited to monitor the intriguing interplay between π-conjugation and σ-delocalization in vinyl cations of type **1**, **7**, and **8**.

The six-membered disilacycle in all vinyl cations **1a**−**l** adopts a regular chair conformation (see Figure 3). As a result of the perpendicular ground state conformation of the aryl substituent relative to the Si_2C^β plane, the unsymmetrical substituted vinyl cations **1d,e,h,i** may exist as *syn*- or *anti*-conformers.[37] The energy difference between both conformers is for all unsymmetrical substituted vinyl cations **1d,e,h,i** negligible (at most
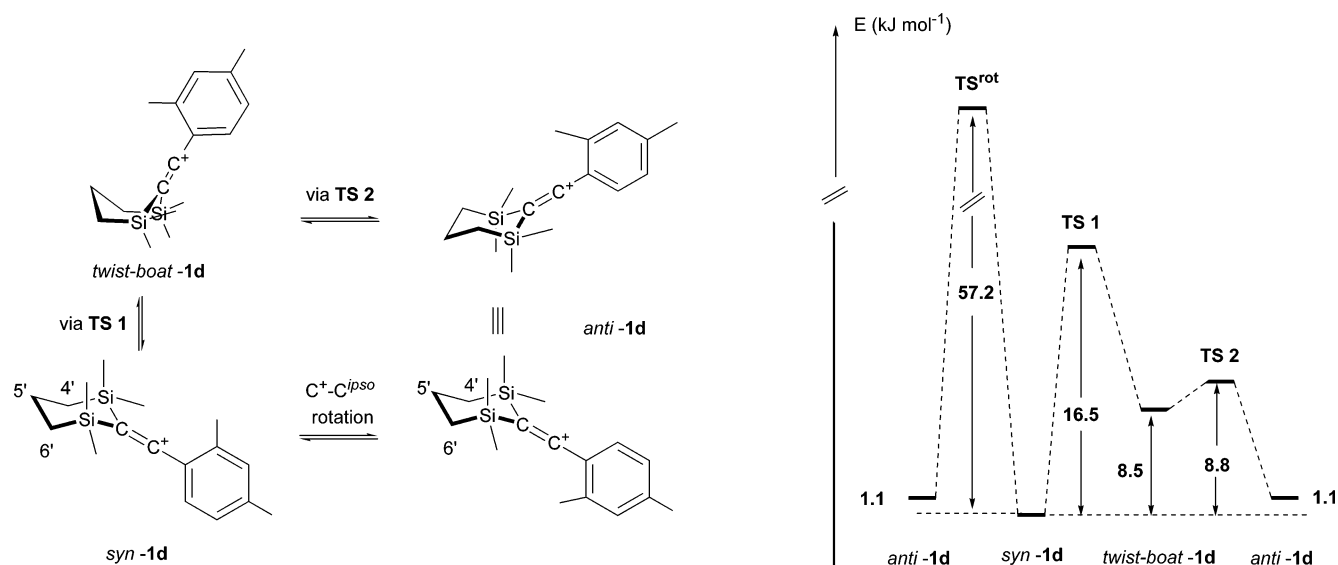
Figure 4. (a) The *syn*/*anti* isomerization of vinyl cation **1d** via its twist boat conformer and by rotation around the $C-C^{ipso}$ bond. (b) Energy profile for both competing isomerization pathways as computed at B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) + ΔZPVE.

1.1 kJ mol^{-1} for the *ortho*- and *para*-dimethyl-substituted vinyl cation **1d**, at B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) + ΔZPVE).

The barrier for internal rotation around the $C^{+}-C^{ipso}$ bond is, however, substantial, due the partial double bond character of this bond and due to steric crowding in the transition state for rotation; that is, for vinyl cation **1d**, a barrier of 57.2 kJ mol^{-1} is predicted (B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) + ΔZPVE). A two-step ring flip process of the disilacyclohexane ring via the twist boat conformer of **1d**, as it is shown in Figure 4a, can however equilibrate the *syn* and *anti* isomers without rotation around the $C^{+}-C^{ipso}$ bond. This alternative isomerization pathway was investigated computationally in detail for **1d**, and it involves a maximal barrier of merely 16.5 kJ mol^{-1}, and the second step is nearly barrierless (0.3 kJ mol^{-1} at B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) + ZPVE, see Figure 4b and Supporting Information for further details). Similar or somewhat smaller barriers can be expected for vinyl cations **1e,h,i**. This computational result is in qualitative agreement with the experimental finding that only one signal for the equatorial and axial methyl groups at silicon in vinyl cations **1d,e,h,i** is observed in the ^{1}H and ^{13}C NMR spectra recorded at 30 °C. This indicates equilibrium between the *syn* and *anti* isomers, which is fast on the NMR time scale at room temperature.

For the α-naphthyl-substituted vinyl cations *syn*/*anti*-**7**, a situation quite similar to that of **1a–l** is predicted by the calculations, that is, structural features indicating (i) considerable interaction between the π-system of the naphthyl substituent and the 2p(C^{+}) (i.e., short $C^{+}C^{ipso}$ bonds: $r(C^{+}-C^{ipso}) = 138.6$ pm) and (ii) significant SiC^{β} hyperconjugation (i.e., relatively long $C^{\beta}Si$ bonds: $(r(C^{\beta}Si) = 196.4$ and 196.5 pm). In addition, the energy difference between the *syn* and *anti* isomer is negligible ($\Delta E = 0.1$ kJ mol^{-1}, with the *anti* isomer being more stable). In vinyl cation **8**, however, the particular geometry of the ferrocenyl substituent leads to the unsymmetrical ground

state conformation **8per**. In **8per**, the substituted cyclopentadienyl ring is oriented perpendicular to the plane spanned by the C^{β} carbon atom and the two silicon substituents. This conformation guarantees maximum overlap between the π-system of the cyclopentadienyl ring and the empty 2p-orbital at the C^{+} carbon atom, and it lends a nonequivalent environment of the two silicon atoms in **8**. This contrasts the observation of only one ^{29}Si NMR signal at room temperature. The only equilibration mode capable of interconverting the two silicon atoms is the internal rotation around the $C^{+}-C^{1}$ single bond via the planar transition state conformation, **8plan**, for which the π-interaction between the ferrocenyl substituent and the formally empty 2p(C^{+})-orbital is switched off. The theoretical activation free enthalpy for the rotation, the free enthalpy difference between **8plan**, and the perpendicular ground state conformation **8per** are relatively high, $\Delta G^{\ddagger}(298) = 47.7$ kJ mol^{-1}.[38] This indicates strong conjugative interaction between the vinyl cation moiety and the ferrocenyl substituent in **8per**.

8 per   **8 plan**
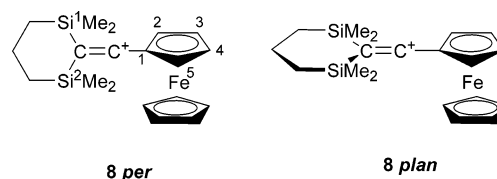
Experimentally, this barrier for internal rotation in vinyl cation **8** could be verified by temperature-dependent ^{29}Si NMR measurements, which showed that the single line at δ ^{29}Si $= 12.0$ disappears in the baseline at $T = -15$ °C and is replaced at $T = -30$ °C by two relatively broad signals at δ ^{29}Si $= 15.3$ and 7.6 for the two nonequivalent silicon atoms in the ground state of vinyl cation **8per**. This process is reversible and can be explained by the internal rotation around the $C^{+}-C^{1}$ single bond, which equilibrates both silicon atoms in **8**. The activation parameters for the hindered rotation as determined by a line

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(37) We define the *syn* isomer as the isomer for which the substituent in *meta* or *ortho* position of the aryl substituent is on the same side of a plane spanned by the dicoordinated carbon atom and the two methylene carbon atoms $C^{4'}$ and $C^{6'}$, as the methylene carbon atom $C^{5'}$. Similarly, for the *anti* isomer, the substituent in *meta* or *ortho* position is on the opposite side of this plane; see Figure 3.

(38) The free enthalpy of activation for the internal rotation around the $C^{+}-C^{1}$ bond is computed from the electronic energy difference between **8plan** and **8per** at B3LYP/6-311G(2d,p), corrected by the thermal corrections to the free enthalpy as obtained at the B3LYP/6-31G(d) level.

Table 3. Selected Computed NMR Chemical Shifts δ of Aryl-Substituted Vinyl Cations[a]

R	δ ^{29}Si[b]	δ ^{13}(C$^+$)	δ ^{13}(C$^\beta$)	δ ^{13}C^{ipso}	δ ^{13}C^{ortho}	δ ^{13}C^{meta}	δ ^{13}C^{para}
1a	26.3	199.9	93.4	117.9	151.2; 151.2	137.3; 137.2	152.9
1b	23.2	201.1	93.5	114.7	151.0; 150.4	138.0; 137.9	172.2
1c	22.9	201.3	93.4	114.7	151.0; 151.0	137.5; 137.5	179.2
syn-**1d**	21.3	199.5	96.7	115.2	166.1; 152.4	139.1; 135.3	172.4
anti-**1d**	22.3	199.4	96.4	115.1	166.6; 152.0	139.0; 135.5	172.5
syn-**1e**	23.1	199.3	96.0	118.1	165.1; 151.9	148.8; 138.0	154.8
anti-**1e**	24.2	199.5	95.7	118.0	164.9; 151.8	149.0; 137.9	154.7
1f	23.6	201.9	92.2	117.6	148.3; 148.3	151.3; 151.3	156.2
1g	21.0	202.8	94.2	114.2	150.8; 150.8	134.6; 134.6	168.0
syn-**1h**	28.2	192.7	99.9	108.8	183.2; 149.7	132.7; 123.4	156.3
anti-**1h**	28.1	193.0	99.8	108.8	183.0; 149.8	132.8; 123.4	156.3
syn-**1i**	29.0	197.8	93.4	119.6	146.8; 135.8	172.4; 139.0	141.0
anti-**1i**	29.2	197.8	93.4	119.6	146.9; 135.7	172.4; 139.0	141.0
1k	25.2	198.6	94.6	114.0	154.7; 154.7	125.5; 154.7	183.9
1l	26.1	198.7	94.9	115.3	150.7; 150.7	138.4; 138.4	173.1
syn-**7**	21.5	200.0	98.1	114.7			
anti-**7**	23.3	199.8	98.2	114.5			
8per	19.5[c]	209.4	91.4	93.3			

[a] Computed at GIAO/B3LYP/6-311G(2d,p)//B3LYP/6-31G(d), relative to calculated TMS (PG: T_d; σ ^{29}Si(TMS) = 328.5; σ ^{13}C(TMS) = 182.8. [b] Mean value of two ^{29}Si NMR chemical shifts. For vinyl cations **1a**–**l** and **7**, the computed ^{29}Si NMR chemical shift difference for both silicon nuclei was smaller than 0.3. [c] Mean value from δ ^{29}Si(1) = 23.7 and δ ^{29}Si(2) = 15.2.

shape analysis are: $\Delta H^{\ddagger} = (52.2 \pm 2.0)$ kJ mol^{-1}, $\Delta S^{\ddagger} = (12 \pm 8)$ J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}(T^{av} = 268$ K$) = (48.9 \pm 4.2)$ kJ mol^{-1} (see Supporting Information for details), which compares favorably with the results of density functional calculations at the B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) level of theory.

Quantum mechanical methods for the calculation of NMR chemical shifts have been extensively applied in carbo-[39] and silyl-cation[40,41] chemistry, and the validity of theoretical structures is frequently established by comparing the computed NMR chemical shifts with the experimental data. Characteristic ^{29}Si and ^{13}C NMR chemical shifts calculated at GIAO/B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) for **1a**−**l**, **7**, and **8** are summarized in Table 3.[42] The agreement between the calculated ^{29}Si NMR chemical shifts δ ^{29}Si^{calcd} and the experimental data for the vinyl cations **1a**−**l**, **7**, and **8** is convincing; that is, the deviation $\Delta\delta$ ^{29}Si^{calcd} is small ($\Delta\delta$ ^{29}Si^{calcd} = δ ^{29}Si^{calcd} − δ ^{29}Si^{exp} = 0.5−4.1). Thus, the ^{29}Si NMR chemical shift calculations corroborate the validity of the computed structures. The performance of this specific theoretical model for the calculations of ^{13}C NMR chemical shifts is much less satisfactory. Although the general trend of the experimental ^{13}C NMR chemical shifts is faithfully reproduced by the computations, the individual errors between computed and experimental ^{13}C chemical shifts are large. In general, all characteristic carbon nuclei of the aryl-substituted vinyl cations **1a**−**l** are calculated to be too deshielded, for example, for **1a**, by 4.2−14.1 ppm. In particular, the deviations for the sp-hybridized C$^+$ carbon atom are large: $\Delta\delta$ ^{13}C^{calcd} = +11.9−15.8. However, experimental and calculated ^{13}C NMR chemical shift data are linearly correlated.[43] This indicates that the deviations are due to a systematic error, for example, deficiencies of the applied method

and basis set. DFT-based methods, such as GIAO/DFT calculations, are known to overestimate paramagnetic contributions to the chemical shielding, giving overly deshielded chemical shifts in critical cases for molecules with small HOMO/LUMO separations.[41a,44] It has been demonstrated that the accurate calculation of the magnetic properties of dienyl cations requires high correlated methods, such as CCSD(T).[45,46] The size of the cations studied and the extent of the present investigation, however, prevent the use of these highly accurate methods. The overall agreement between the experimental and the theoretical data (see Tables 1 and 3) is, however, satisfying when the reduced accuracy of the ^{13}C NMR chemical shift calculations is taken into account.

Conclusions

The α-aryl-substituted vinyl cations **1b**−**l**, **7**, and **8** have been synthesized by treatment of alkynyl silanes with trityl cation and TPFPB as counteranion in benzene as solvent. The vinyl cation salts have been isolated and characterized by NMR spectroscopy, supported by density functional calculations on their structures, energies, and NMR parameters. The analysis of the ^{13}C and ^{19}F NMR data reveals in all investigated cases the delocalization of positive charge into the aryl substituent. For the α-ferrocenyl-substituted vinyl cation **8**, the extent of π-delocalization could be quantified by the determination of the free enthalpy barrier for internal rotation around the C$^+$C^{ipso} bond to be $\Delta G^{\ddagger} = (48.9 \pm 4.2)$ kJ mol^{-1}. In addition, the ^{29}Si NMR data give clear evidence for the occurrence of β-Si−C hyperconjugation in these cations. Hammett-type analyses for eight *meta*- or *para*-substituted α-arylvinyl cations suggest that the extent of σ-delocalization by β-Si−C hyperconjugation is

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determined by the electron demand of the positively charged C^+ carbon atom, which is controlled by the electron-donating ability of the aryl group. As a result, the contribution of σ-delocalization to the electronic structure of **1** is depressed with increasing electron-donating ability of the aryl substituent in vinyl cations **1**.

The consequences of π-conjugation and σ-delocalization are clearly visible in the computed structures of cations **1a−l**, **7**, and **8**. The short C^+C^{ipso} bond predicted for all investigated vinyl cations demonstrates the importance of π-resonance in α-arylvinyl cations, and the long $C^\beta Si$ bond indicates considerable electron transfer from the occupied β-SiC σ-bonds to the formally empty $2p(C^+)$-orbital. The subtle interplay between π-conjugation and σ-delocalization, which is clearly evident from the analysis of the magnetic properties of vinyl cations **1**, is however not apparent from their computed structures, which are all very similar. That is, all computed $Si−C^\beta$ bond lengths are predicted to fall in a very narrow range between 196.2 and 197.8 pm, and also, the prominent structural indicator for π-conjugation in vinyl cations **1**, the C^+C^{ipso} bond length, is computed to be very similar for all vinyl cations **1** (137.7−

139.0 pm). Considering the reliability of the computed structures at the applied level of theory,[11] this result suggests that although the NMR data indicate the effects of σ-delocalization and π-conjugation in vinyl cations **1**, intriguingly, this effect is not apparent from the structural results.

Supporting Information Available: Computational details and experimental procedures, the description of dynamic NMR studies, table of calculated absolute energies of vinyl cations **1a−l**, **7**, and **8**, computed geometries of vinyl cations **1b−l**, **7**, and **8** in *xyz* coordinates, description of the NMR computations, NMR spectra of vinyl cations **1b−l**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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