Tris(trimethylsilyl)cyclopropenylium Cation: The First X-ray Structure Analysis of an α-Silyl-Substituted Carbocation[†]

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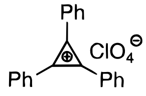
The X-ray crystal structure analysis of tris(trimethylsilyl)cyclopropenylium cation **2** is presented and compared with the structure and bonding properties obtained by quantum mechanical ab initio calculations. The calculated bond lengths for **2** are in good agreement with the experimentally determined ones. The effect of tris-silyl and tris-methyl substitution on the stability of the tris-substituted cyclopropenylium ions are calculated by using the isodesmic hydride transfer reaction 1. The pK_R+ value of **2** is predicted to be 4.

The cyclopropenylium cation is the smallest aromatic system, and ever since the first synthesis of triphenylcyclopropenylium perchlorate **1**,[1] this system has been the subject of numerous investigations.[2] The effect of various substituents on the relative stability of cyclopropenylium cations has been studied extensively,[3] and several crystal structure analyses have been reported to date.[4] Since trialkylsilyl groups are known to exert a destabilizing effect with respect to alkyl groups when directly attached to a carbenium ion center,[5] we were intrigued by the fact that tris(trimethylsilyl)cyclopropenylium hexachloroantimonate (**2**) could be prepared in a straightforward manner and that it appeared to be relatively stable.[6] We have therefore set out to investigate the crystal structure of **2** and to gain insight into its thermodynamic stability, its structure, and its bonding properties by quantum mechanical ab initio computational methods.

Synthesis and Crystal Structure Analysis

Tris(trimethylsilyl)cyclopropenylium hexachloroantimonate (**2**) was prepared from 1,2,3-tris(trimethylsilyl)cyclopropene-3-carboxylic acid according to the published procedure,[6] and good quality crystals were grown by slow diffusion of diethyl ether into a solution of **2** in acetonitrile at 0 °C.



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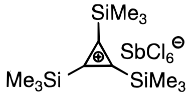

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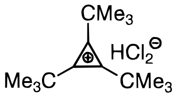

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The pale yellow crystals were monoclinic, space group $P2_1/c$. Diffraction data were collected both at 293 K and at 125 K. No phase transition was observed by DSC upon cooling. As expected, the accuracy of the low temperature study was better due to minimized thermal vibrations. The X-ray structure of **2** is shown in Figures 1a and 1b. The three silicon atoms are nearly coplanar with the central three-membered ring (see Figure 1). The ring is, however, significantly distorted from ideal D_{3h} symmetry due to the close vicinity of one of the chlorine atoms in the hexachloroantimonate anion to one of the ring carbon atoms. The shortest C···Cl distance is 3.460 Å (between C2 and Cl5, Figure 1b). Consequently, the C1−C2 (1.391(4) Å) and the C2−C3 bonds (1.384(4) Å) are longer than the C1−C3 bond (1.375(4) Å), and the Si2 atom bonded to C2 is bent out of the ring plane and away from the anion by 0.044 Å. A similar out of plane bending was observed for the tri-*tert*-butylcyclopropenylium cation **3**,[4b] and it was similarly attributed to the close contact between one ring carbon atom and a chlorine in the counterion. In contrast to **2**, all the ring C−C bond distances in **3** are equal at 1.372(1) Å. The C−C bond length in **3** is slightly shorter (by 0.012 Å) than the average in **2** (1.384(4) Å), but in view of the standard deviation of 0.004 Å for **2** this is hardly significant.

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[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1996.

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(2) For a recent review: Billups, W. In *The Chemistry of the cyclopropyl group*; Patai, S., Rappoport, Z., Eds.; Wiley Intersience: New York, 1987.

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(6) Maier, G.; Volz, D.; Neudert, J. *Synthesis* **1992**, 561.

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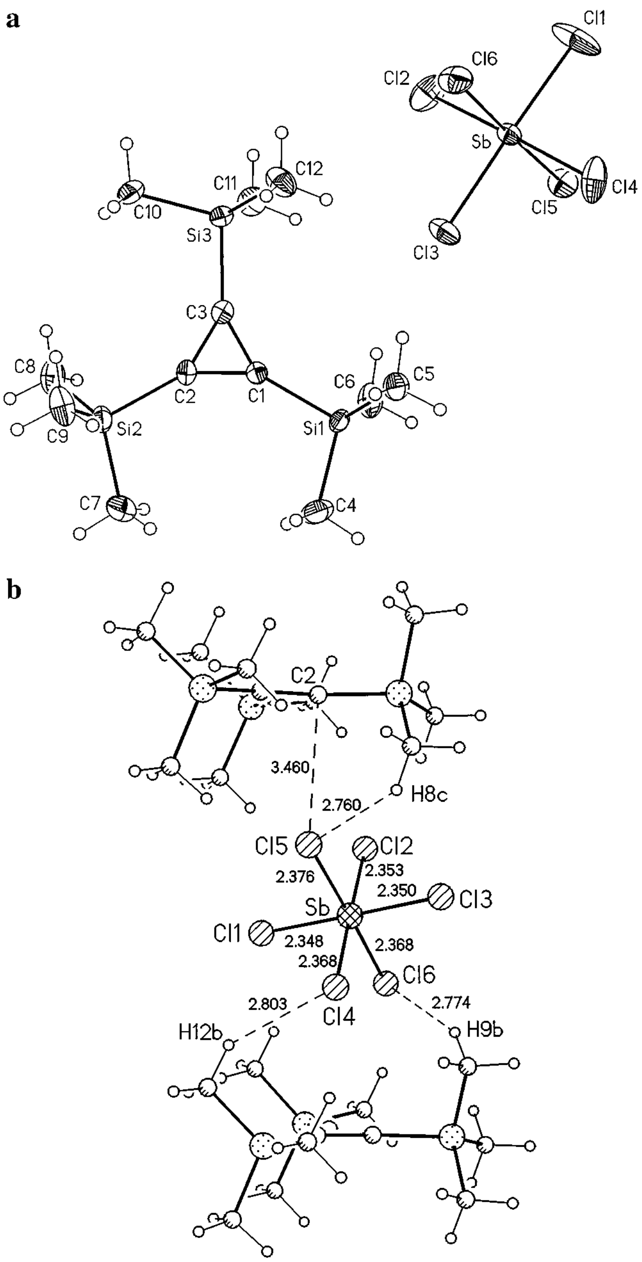


Figure 1. (a) ORTEP plot of the X-ray crystal structure of **2**. (b) Intermolecular distances (Å) in the crystal of **2**.

The Si−C$_{ring}$ bond lengths in **2** are all the same at (1.897(3) Å), but the Si−C$_{methyl}$ distances range between 1.844(4) and 1.866(4) Å. All the C$_{ring}$−C$_{ring}$−Si−C$_{methyl}$ torsional angles are different from 180° or 0°, and thus there is no methyl group located exactly in the ring plane. The relatively large differences between the Sb−Cl bonds can be attributed to the different contact distances between the chlorine atoms and the protons of the trimethylsilyl groups.

Computational Studies

Methods. All calculations were performed with the Gaussian 92 series of programs.[7] All structures were fully optimized initially at the HF-level using the polarized 6-31G* basis set,[8] and they were verified to be minima by subsequent frequency calculations.[7] The structures of the cyclopropenylium cations **4**−**6** were further optimized with inclusion of electron correlation using second order Møller-Plesset perturbation theory (MP2)[9] and the 6-31G* basis set. The core electrons were not included in the electron correlation (frozen core approximation, MP2(fc)). Energies for isodesmic reactions were evaluated at MP3(fc)/6-311G**//HF/6-31G* (i.e., MP3(fc)/6-311G**) single point calculations using HF/6-31G* optimized geometries. The calculated structures and total energies are given in the supporting information.

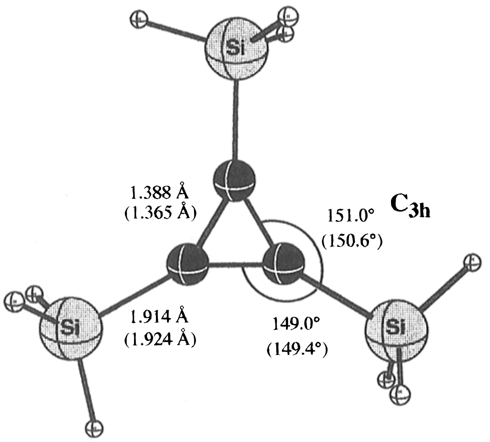
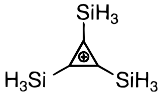


Figure 2. Calculated structures of **4** at MP2(fc)/6-31G* (in parentheses are given the optimized values at HF/6-31G*).



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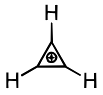

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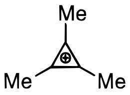

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Results and Discussion

(a) Structure. The tris-silyl-cyclopropenylium cation **4** in which the methyl groups in **2** have been replaced by hydrogen-atoms serves as a close model for **2** and similarly the trimethylcyclopropenylium cation **6** models cation **3**. The calculated structures of **4** at both MP2-(fc)/6-31G* and HF/6-31G* are shown in Figure 2. The calculated total energy of **2** along with those of other compounds of interest is given in Table 1. At both the HF/6-31G* and the correlated MP2(fc)/6-31G* levels the highly symmetric C_{3h} structure of **4** is a minimum. This clearly shows that the distortions apparent in the crystal structure of **2** are due to the influence of the counterion and/or to lattice effects. This conclusion is consistent with ^{13}C NMR measurements of **2** in solution which indicate that it has C_{3h} symmetry.[6] The calculated C−C bond length in the three-membered ring of **4** (1.388 Å at MP2(fc)/6-31G*, see Figure 2) is in excellent agreement (within the experimental error) with the average value found in the X-ray structure of **2** (1.384(4) Å). The calculated C$_{ring}$−Si bond distances in **4** of 1.914 Å (MP2-(fc)/6-31G*) are by 0.017 Å longer than the average measured C−Si bond length in **2**.

The calculated ring C−C bond length in **4** is by 0.019 Å longer (computed at the same level of theory) than that

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[7] *Gaussian 92/DFT*, Revision G.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Steward, J. J. P.; Pople, J. A.; Gaussian Inc., Pittsburgh PA, 1993.

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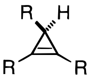
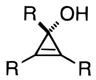
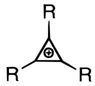
Table 1. Calculated Total Energies (au) and Zero-Point Vibrational Energies (ZPVE, kcal/mol) of Substituted Cyclopropenes, 3-Hydroxycyclopropenes, and Cyclopropenylium Cations (MP3(fc)/6-311G//6-31G*)**[a]

			
R = H	**7**	**8**	**5**[b]
E (a.u.)	–116.29703	–191.36904	–115.41897
ZPVE[c]	34.6	37.7	27.8
R = Me	**9**	**10**	**6**[d]
E (a.u.)	–233.93185	–309.00697	–233.10394
ZPVE[c]	86.2	89.0	79.3
R = SiH_3	**11**	**12**	**4**[e]
E (a.u.)	–986.96971	–1062.03996	–986.12694
ZPVE[c]	63.0	65.6	56.5

[a] H_2O: −76.26358 (MP3(fc)/6-311G**//6-31G*); H_3O^+: −76.55481 (MP3(fc)/6-311G**//6-31G*). [b] At MP2(fc)/6-31G*//MP2(fc)/6-31G*: −115.34935. [c] Calculated at HF/6-31G* and scaled by a factor of 0.91. [d] At MP2(fc)/6-31G*//MP2(fc)/6-31G*: −232.92107. [e] At MP2(fc)/6-31G*//MP2(fc)/6-31G*: −985.87696.

in the parent cyclopropenylium cation **5** (1.369 Å at MP2(fc)/6-31G*), and it is slightly elongated (by 0.008 Å, MP2(fc)/6-31G*) compared to that in the trimethyl-substituted cyclopropenylium cation **6**. The calculated ring C−C bond length in **6** (1.380 Å at MP2(fc)/6-31G*) is very close to the measured C−C ring distance in **3** (1.372 Å),[4c] demonstrating the good agreement between the calculations and the experiments. The Si−C bond length (1.914 Å at MP2(fc)/6-31G*, 1.924 Å at HF/6-31G*) in **4** is elongated by 0.063 Å compared to the Si−C(sp^2) bond in the tris-silyl-substituted cyclopropenol **12** (1.861 Å at HF/6-31G*) and by 0.069 Å compared to the Si−C(sp^2) bond in the tris-silyl-substituted cyclopropene **11** (1.855 Å at HF/6-31G*).

(b) Charge Distribution. The positive charge in all three investigated cyclopropenylium cations **4**−**6** is symmetrically distributed over all three carbon atoms. According to a NBO analysis[10] of the HF/6-31G* wave function the positive charge at the ring carbon atoms in **4**−**6** (+0.200 **6**, +0.026 **5**, −0.243 **4**) decreases with decreasing electronegativity of the substituent (CH_3(**6**) > H(**5**) > SiH_3(**4**)). For silyl substitution the ring carbons are actually negatively charged, although formally they represent the carbenium centers, and the positive charge resides on the silyl groups. Note that the charge on the substituents necessarily follow the reverse order, i.e., H_3Si (0.576 in **4**) > H (0.307 in **5**) > CH_3 (0.133 in **6**). As the Me_3Si group is probably a better σ-electron donor than H_3Si, the total negative charge at the ring carbons is expected to be even higher in the experimentally studied **2**. The occupation of the π-orbitals increase from 2 e in **5** to 2.04 e in **4** to 2.12 e in **6**. The smaller π-orbital occupation in **4** compared to **6** indicates the less effective hyperconjugative electron donation from the silyl group across the longer $Si-C^+$ bond, compared with methyl hyperconjugation in **6**.[11]

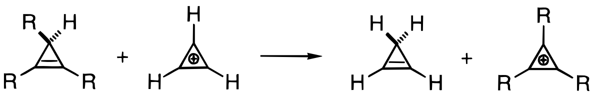
Table 2. Calculated Reaction Energies for Equations 1 and 5 in kcal/mol (MP3(fc)/6-311G//HF/6-31G*)**

ΔE	eq 1	eq 5
R = Me	31.5	29.5
R = SiH_3	22.1	23.2

It should also be noted that the calculated ^{13}C NMR chemical shift of **4** with 218.3 ppm (calculated at MP2(fc)/6-31G* using the IGLO method[12] and basis set II,[12] i.e. at IGLO/basis II/MP2(fc)/6-316*) agrees very well with the value measured experimentally for **2** (214.3 ppm[6]). This good experimental−theoretical agreement supports the reliability of the calculations also for other molecular properties.

(c) Thermodynamic Stability. Trialkylsilyl groups are known to destabilize trivalent carbenium ions compared to a methyl group.[5,13] Thus, in a hydride transfer reaction the tertiary α-silyl-substituted cation $H_3SiC^+Me_2$ is less stable than the *tert*-butyl cation Me_3C^+ by 8.6 kcal/mol (HF/6-31G*//HF/3−21G). In contrast, the silyl and the methyl groups have nearly the same stabilizing effect on vinyl cations; α-silyl and α-methyl substitution stabilize $H_2C{=}C{-}H^+$ by 25.0 and 23.9 kcal/mol (6-31G*//3−21G), respectively.[5e] Hopkinson and Lien found that the effect of substituents on the stability of carbocations is less pronounced in cyclopropenylium ions than in saturated carbenium ions.[14] Thus, they found that the amino-substituted cyclopropenylium ion is by 30.7 kcal/mol more stable than **5** (at 6-31G*//3-21G), while $Me_2C^+{-}NH_2$ is stabilized by 63.4 kcal/mol compared to Me_2CH^+. Hopkinson and Lien attributed the lower sensitivity of cyclopropenylium ions to substituent effects to the inherent higher stability of the 2π-Hückel aromatic system in these ions.[14]

We have calculated the effect of tris-silyl and tris-methyl substitution on the stability of tris-substituted cyclopropenylium ions by using the isodesmic hydride transfer reaction 1. The calculated total energies of the various species required to evaluate eq 1 are given in Table 1 and the energies of the isodesmic equations in Table 2.



(1)

According to eq 1 three silyl groups stabilize the parent cyclopropenylium cation **5** by 22.4 kcal/mol at MP3(fc)/6-311G**//6-31G*+ZPVE. Substitution with three methyl groups causes a significantly larger effect: **6** is more stable than parent **5** by 31.4 kcal/mol. This value is in good agreement with the value of 29 kcal/mol determined experimentally in the gas-phase from heterolytic bond dissociation energies.[15] The order of substituent stabiliz-

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(10) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (c) Glending, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.; NBO VERSION 3.1.

(11) Similarly the population of the 2p(C^+) orbital (using the NBO procedure[10] and the 6-31G* basis set) in $CH_3CH_2^+$ (0.178 e) or in $(H_3C)_3C^+$ (0.272 e) is significantly higher than in $H_3SiCH_2^+$ (0.054 e) or in $(H_3Si)(CH_3)_2C^+$ (0.258 e), respectively. Furthermore, in $(H_3C)_3C^+$ the populations of the C−H and Si−H bonds, which are coplanar with the 2p(C^+) orbital are 1.915 e and 1.968 e, respectively, pointing to the fact that 2p(C^+)−CH hyperconjugation is stronger than 2p(C^+)−(SiH) hyperconjugation. The corresponding second order perturbation energies of 31.5 kcal/mol for the 2p(C^+)−σ(CH) interaction and 7.4 kcal/mol for the 2p(C^+)−σ(SiH) interactions point to the same conclusion. See: Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1291 and ref 5c,e.

(12) Kutzelnigg, W.; Fleisher, U.; Schindler, M. In *NMR Basic Principles and Progress*; Springer-Verlag: New York, 1991; Vol. 23, pp 167−262.

(13) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.

(14) Hopkinson, A. C.; Lien, M. H. *J. Am. Chem. Soc.* **1986**, *108*, 2843.

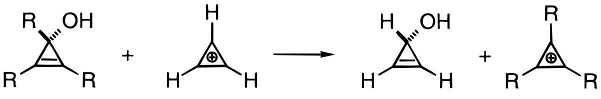
ing abilities of Me > Si ≫ H found for the cyclopropenylium ions **4**−**6** is the same as that for the corresponding alkyl cations, i.e. $MeC^+Me_2 > (H_3Si)C^+Me_2 \gg HC^+Me_2$.[13,5c,5e] However, the magnitude of the stabilizing effect in the cyclopropenylium ions is smaller than that in ordinary carbenium ions, in agreement with an earlier study on the effect of amino-substitution.[14]

Table 3. Calculated Free Energies for Reaction 4 (MP3(fc)/6-311G//HF/6-31G*)**

	ΔH[a]	$T\Delta S$	ΔG	$\Delta\Delta G$[b]	$\Delta(pK_R^+)$[c]	pK_R^+
R = H	−13.4	−2.4	−11.0	0	0	−7.2[d]
R = Me	−42.7	−3.2	−39.5	−28.5	20.8	7.4[e]
R = SiH_3	−36.5	−3.4	−33.1	−22.1	16.1	4.1

[a] ΔH calculated using total energies at 298 K and scaled ZPVE's. [b] $\Delta\Delta G = \Delta G(R) - \Delta G(H)$. [c] Calculated using eq 5. [d] Experimental from ref 17. [e] Experimental from ref 19.

Note that the difference between R = CH_3 and SiH_3 in eq 2 which involves a hydroxide exchange of 5.7 kcal/mol is smaller than found in eq 1 (i.e. 9.0 kcal/mol) which involves hydride transfer. This difference is due to a destabilization of the silyl-substituted cyclopropenol **12** relative to the methyl-substituted cyclopropenol **10**. Similar ground state effects were found in other silyl vs alkyl substituted alcohols.[18]



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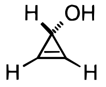

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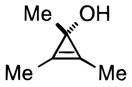

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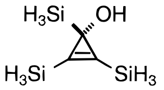

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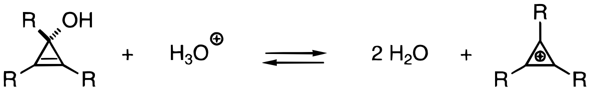
A frequently used quantitative measure of the stability of persistent carbocations in solution is its pK_R^+ value[16] defined in eq 3 where C_R^+ and C_{ROH} are the equilibrium concentrations of the carbocation and the corresponding alcohol for reaction 4.

$$pK_R^+ = H_R + \log [C_R^+/C_{ROH}] \qquad (3)^{17}$$



(4)

The pK_R^+ values of the cations **4** or **6** *relative* to the parent **5** (ΔpK_R^+), which are of interest here, are defined by eq 5, where R = SiH_3 or CH_3, respectively. The calculated ΔpK_R^+ values are given in Table 3. These values were calculated using the calculated ΔG values (these are not very different from the ΔH values as the ΔS values associated with eq 4 are small) and eq 5.

$$\Delta\Delta G(R,H) \equiv \Delta G(R) - \Delta G(H) = 2.303RT\Delta pK(R^+) \qquad (5)$$

According to the calculations (Table 3) the pK_R^+ value of the trimethylcyclopropenylium cation **6** is by 20.8 units ($\Delta\Delta G$ = 28.5 kcal/mol) more positive than that of the parent cyclopropenylium cation **5**. This calculated value is higher than the experimentally derived (in solution) ΔpK_R^+ of 14.6 (i.e. $\Delta\Delta G$ = 20.0 kcal/mol) between **5**[19] and **6**.[20] The difference between the experimental (solution) and calculated (gas-phase) $\Delta\Delta G$ probably results from solvation effects,[21] although other reasons such as deficiencies in the computational methods may also contribute.

Table 4. Experimental Data of the X-ray Crystal Structure Determination of 2

measurement	**1a**	**1b**
formula	$C_{12}H_{27}Si_3^+SbCl_6^-$	$C_{12}H_{27}Si_3^+SbCl_6^-$
molecular mass	590.06	590.06
temperature (K)	293	125
crystal size (mm)	0.80 × 0.50 × 0.50	0.35 × 0.35 × 0.35
crystal color	pale yellow	pale yellow
space group	$P2_1/c$	$P2_1/c$
a (Å)	10.710(1)	10.437(2)
b (Å)	16.288(2)	16.224(4)
c (Å)	15.736(2)	15.481(3)
α (deg)	90	90
β (deg)	95.57(2)	97.69(2)
γ (deg)	90	90
V (Å^3)	2732.1(5)	2597.9(9)
D_x (g cm^{-3})	1.435	1.509
Z	4	4
refl independent	3537	5877
refl observed [$F_0 \geq 4\sigma(F)$]	3536	5258
R	0.0481	0.0423
R_w	0.0545	0.0512
μ (mm^{-1})	1.72	1.81
2θ range measured (deg)	7−45	3−60
no. of parameters	199	208

The gas-phase calculated $\Delta\Delta G$ value (22.1 kcal/mol) of the tris-silyl-substituted cyclopropenylium cation **4** is by 6.4 kcal/mol smaller than for **6**. Consequently, the ΔpK_R^+ value of **4** in the gas-phase is predicted to be smaller, 16.1. Assuming that in solution ΔpK_R^+ of **4** is reduced by the same factors as that of **6** we estimate that in solution ΔpK_R^+ of **4** is 11.3 units. Thus, the pK_R^+ value for tris-silyl cyclopropenylium cation **2** is predicted to be around 4.

In conclusion, we have presented the first crystal structure of an α-trialkylsilyl-substituted carbocation (**2**). The destabilizing effect of the silyl groups is significantly smaller than in vinyl cations or in tricoordinated carbenium ions. This is due to the higher stability of the aromatic cyclopropenylium cation. The pK_R^+ value of **2** is predicted to be 4.

Experimental Section

Crystal Structure Determinations. The X-ray data at 293 K were collected on an Stoe-Siemens diffractometer, Mo K_α radiation.[22] The calculations were done using the SHELX-TL program. The X-ray data at 125 K were collected on an automated diffractometer Nicolet R 3m/v, graphite monochro-

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[18] H_R is a measure of the acidity of the solvent and approches pH at low concentrations of acid.

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[21] It is often found that energy differences between ions are larger in the gas-phase than in solution; see for example: (a) Aue, D. H.; Webb, H. M.; Davidson, W. R.; Toure, P.; Hopkins, H. P., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1170 and references therein. (b) Aue, D. H.; Webb, H. M.; Bowers, M. J. *Ibid.* **1976**, *98*, 318. (c) Arnett, E. M.; Hofelich, T. C. *Ibid.* **1983**, *105*, 2889. (d) Arnett, E. M.; Petro, C.; Schleyer, P. v. R. *Ibid.* **1979**, *101*, 522.

[22] The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

mator, Mo K_α radiation, Wyckoff scan. The calculations were done with the SHELXTL-PLUS program.

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Supporting Information Available: X-ray crystal structure data (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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