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Triphenylsilyl Perchlorate Revisited: ^{29}Si and ^{35}Cl NMR Spectroscopy and X-ray Crystallography Showing Covalent Nature in Both Solution and the Solid State. Difficulties in Observing Long-Lived Silyl Cations in the Condensed State[1a]

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Abstract: ^{29}Si and ^{35}Cl NMR spectroscopic and X-ray crystallographic study of triphenylsilyl perchlorate shows it to be a covalent perchloryl ester in both solution and the solid state. The results are in accord with earlier studies notably those of Wannagat but contrast the recent claim by Lambert et al. (*J. Am. Chem. Soc.* **1986**, *108*, 2482) for NMR observation of long-lived ionic triphenylsilyl perchlorate.

Although silicenium ions (trivalent sila cations) are well-known in the gas phase as high abundance fragments in the mass spectra of organosilicon compounds.[2] No analogous ions have been observed in solution or solid state. In contrast, long-lived carbenium ions (trivalent carbocations) can be readily prepared and studied as stable entities in solution.[3]

The reasons for this are many. Silicon has poor ability for pπ–pπ bonding. Whereas carbocations are readily stabilized by 2p–2p resonance, silicenium ions are more weakly stabilized through 2p–3p overlap over longer bonds with π-electrons or lone pairs on carbon, nitrogen, or oxygen centers.[4] In solution, silicenium ions have been proposed as reaction intermediates in many organosilicon reactions,[5] but attempts directed toward the observation of stable long-lived silicenium ions have been so far unsuccessful.[6] Under conditions developed for the preparation and study of stable carbocations[3] (low-nucleophilicity highly acidic systems, low temperatures), the high affinity of silicon for oxygen, fluorine, and chlorine usually results in the reaction of solvents (even SO_2, SO_2ClF) and/or reagents (Lewis acid halides, superacidic systems) with the developing electrophilic silicon center (i.e., to yield silyl fluorides, fluorosulfates, trifluoromethyl sulfonates, etc.).[1b,6a] The only exceptions are the recent claims of Lambert and co-workers for the ionic nature of tris(isopropylthio)silyl perchlorate[7] and triphenylsilyl perchlorate.[8]

Lambert et al. in their recent communication[8] reported the preparation and characterization of the triphenylsilyl cation in solution, a silicon analogue of the trityl cation. This claim is in contrast with previous studies[9] on triphenylsilyl perchlorte, including Lambert's own earlier work,[10] in which it was concluded that the perchlorate is a covalent ester (or tight ion pair) and no free triphenylsilyl cation can be observed.

In view of Lambert's report[8] and our long-standing interest and studies in silyl cations we report our findings including ^{29}Si and ^{35}Cl NMR spectroscopic studies as well as the X-ray crystal structure of the disputed triphenylsilyl perchlorate. In contrast to Lambert's results[8] our data, in accord with previous investigations notably those of Wannagat, conclusively show that both in solution and in the solid state the compound is a covalent silyl ester and not a free, ionized silyl cation salt.

Results and Discussion

Triphenylsilyl perchlorate was first prepared by Wannagat and Liehr[11] by reacting triphenylsilyl chloride with anhydrous silver perchlorate in benzene solution.[12] From solvolysis studies Wannagat concluded that the compound is a covalent perchloryl ester. The IR studies were also in accord with his conclusion.[12]

$$Ph_3SiCl + AgClO_4 \xrightarrow{\text{benzene}} Ph_3SiOClO_3 + AgCl$$

In 1975 J. Y. Corey reported[13a] the generation of 1-((dimethylamino)phenyl)-1-siladibenzodihydrotropylium ion by the hydride-transfer reaction of the corresponding silane with ionic triphenylmethyl perchlorate (a stable carbocation salt). The method was subsequently applied[13a] to prepare the purported ferrocenyldiphenylsilyl cation. Subsequently investigations by Mislow et al.,[14] however, concluded that the available evidence does not substantiate the ionic nature.

Lambert in his studies with Sun[10] and in recent studies with McConnell and Schultz[8] also used the same hydride-transfer method to prepare triphenylsilyl perchlorate. The latter work[8] based on interpretation of ^{1}H and ^{13}C NMR spectra as well as conductivity studies and cryoscopic molecular weight determination led Lambert et al. to reevaluate the structure of triphenylsilyl perchlorate as an ionic "sityl" salt and claim the first example of a stable organosilicon cation.

$$Ph_3SiH + Ph_3C^+ClO_4^- \rightarrow Ph_3CH + Ph_3Si^+ClO_4^- \text{ (?)}$$

The reported[8] ^{1}H and ^{13}C NMR data, however, are not diagnostic to differentiate the ionic structure from the covalent one.

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(6) (a) Olah, G. A.; O'Brien, D. H.; Lin, C. Y. *J. Am. Chem. Soc.* **1969**, *91*, 701. (b) Brook, A. G.; Pannell, A. K. *Can. J. Chem.* **1970**, *48*, 3679. (c) Olah, G. A.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 4942. (d) Cowley, A. H.; Cushner, M. C.; Riley, P. E. *Ibid.* **1980**, *102*, 624.

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(9) For a review see: Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1.

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(12) Wannagat, U.; Brandmair, F. *Z. Anorg. Allg. Chem.* **1955**, *280*, 223.

(13) (a) Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *97*, 3727. (b) Corey, J. Y.; Gust, D.; Mislow, K. *J. Organomet. Chem.* **1975**, *101*, C-7.

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As a matter of fact the observed shift differences from known covalent triphenylsilyl derivatives are not significant and no reliable estimate is available for related shifts in the expected bona fide triphenylsilyl cation. ^{15}N NMR studies in methylene chloride solution with added acetonitrile solution showing no change in the nitrile nitrogen shift are also best in accord with a covalent ester. The conductivity studies showed little or no conductivity except in acetonitrile and sulfolane solvents under high dilutions, which, however, could be affected by low level impurities or hydrolysis to perchloric acid. The strongest evidence for the claimed ionic nature of triphenylsilyl perchlorate is the molecular weight determination reported in sulfolane solution which indicates an *i* factor of 2 and not 1 (the covalent form). It is indicated that in dilute sulfolane solution the ionization of triphenylsilyl perchlorate occurs or even an ionization equilibrium could exist, which is not detectable in higher concentration solutions used for NMR studies (vide infra). however, decomposition or impurities also could affect the data. It is recognized[11] that covalent triphenylsilyl perchlorate can decompose to give the corresponding hexaphenyldisiloxane and Cl_2O_7 and the latter could react with traces of water impurity to give perchloric acid.

We have prepared triphenylsilyl perchlorate both with Corey's hydride transfer method used by Lambert,[8] as well as with Wannagat's original method.[11] Both methods gave an identical product showing the ^{1}H and ^{13}C NMR parameters[15a,b] reported by Lambert.

In our preceding studies in search for the elusive trialkyl-(triaryl-) silyl cations, the chemical shift relationship developed for neutral tetrahedral silanes and carbon compounds was extended by Olah and Field[16] to the trigonal trivalent cations, and the chemical shifts for silicenium ions were predicted from their carbenium ion analogues. The $\delta(^{13}C^+)$ for the *tert*-butyl cation (330 ppm) leads to a predicted $\delta(^{29}Si^+)$ for the trimethylsilicenium ion (Me_3Si^+) within the range 225–275 ppm. Similarly, $\delta(^{13}C^+)$ for trityl cation leads to a predicted $\delta(^{29}Si^+)$ for triphenylsilicenium ion (Ph_3Si^+) within the range of 100–150 ppm.

Lambert et al.[8] were unable to obtain the ^{29}Si NMR shift for the purported triphenylsilyl cation. In our investigations the hydride-transfer experiment in CH_2Cl_2 solution (carried out on a 0.25-mmol scale) also gave poor ^{29}Si NMR spectrum, but after 20 000 pulses showed a weak signal at ~3 ppm (from external Me_4Si signal). On the other hand, the isolated compound prepared by Wannagat's method in dissolved in CH_2Cl_2/CH_3CN (1:1)[15b] (250 mg in 1-mL solvent mixture) gave a good ^{29}Si spectrum [Figure 1(i)] with the peak at $\delta(^{29}Si)$ 3.0 (thus reaffirming the validity of the related shift in the hydride-transfer experiment). We were also successful in obtaining the ^{29}Si NMR spectrum in the solid state by using CPA-MAS. A peak at δ 1.4 was observed (from Me_4Si) showing little difference of the chemical shift in solution from the solid state.

The observed ^{29}Si chemical shift at $\delta(^{29}Si)$ 3.0 in solution is compatible only with the covalent nature of the compound. As pointed out, a much more deshielded ^{29}Si chemical shift (around ~100–150 ppm) is expected[16] for a free triphenylsilyl cation. Attempts to obtain the ^{29}Si NMR spectrum at high dilution (0.0125 molar concentration) were unsuccessful. A similar shielded ^{29}Si shift (~11.5 ppm) was also observed for the related covalent diphenylmethylsilyl triflate in our earlier studies.[1b]

Further experimental proof for the covalent nature of triphenylsilyl perchlorate was obtained by ^{35}Cl NMR spectroscopy.

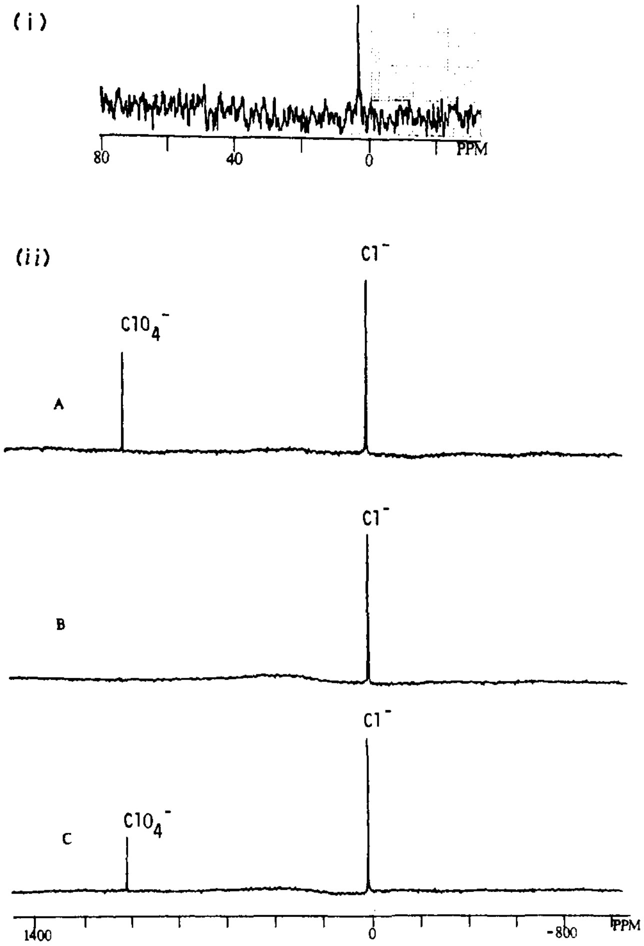

Figure 1. (i) 39.75-MHz ^{29}Si NMR spectrum of triphenylsilyl perchlorate in CH_2Cl_2/CH_3CN (1:1). (ii) 19.6-MHz ^{35}Cl NMR spectra: (A) 0.125 M solution of trityl perchlorate in CH_2Cl_2/CH_3CN (1:1); (B) equimolar amount of triphenylsilane and trityl perchlorate in CH_2Cl_2/CH_3CN (1:1)—0.125 M solution; (C) the solution in B hydrolyzed with 3 drops of water.

^{35}Cl is a quadrupolar nucleus with a nuclear spin of $^3/_2$ and a natural abundance of 75.5%. The ionic chloride and perchlorate anions have spherical symmetry and hence show sharp lines (line width <20 Hz) in their ^{35}Cl NMR spectra.[17] In contrast the ^{35}Cl signal of unsymmetrical covalent chlorine compounds (such as organochlorine compounds, covalent perchlorates, etc.) are very broad (typically 10 000 Hz).[17] Thus ^{35}Cl NMR spectroscopy is a convenient tool to distinguish ionic perchlorates from covalent ones. Figure 1(ii)A shows the ^{35}Cl NMR spectrum of trityl perchlorate in CH_2Cl_2/CH_3CN (1:1) solution (0.125 M) with respect to Cl^- ion in D_2O as external standard. The ^{35}Cl signal is very sharp (line width < 18 Hz) with a chemical shift of δ^{35}Cl) 1010 clearly indicating the presence of perchlorate anion attesting the ionic nature of trityl perchlorate. Addition of an equimolar amount of triphenylsilane to the solution (i.e., repeating Corey's hydride-transfer experiment[13a]) results in a dramatic change in the spectrum. Figure 1(ii)B shows the disappearance of perchlorate ion signal indicating the formation of only a covalent silyl perchlorate.[18a] This experiment[18b] further conclusively demonstrates that the triphenylsilyl perchlorate formed in the hydride-transfer experiment is covalent. Hydrolyzing the covalent silyl perchlorate generates ionized perchloric acid which is observed as a sharp peak at $\delta(^{35}Cl)$ 1003.0 [see Figure 1(ii)C]. When the in situ generated triphenylsilyl perchlorate or the independently prepared compound in CH_2Cl_2/CH_3CN is diluted further with acetonitrile up to 0.002 M concentration, the solution reveals in its ^{35}Cl NMR spectrum a reasonably sharp peak (line width ≈ 30 Hz) at $\delta(^{35}Cl)$ 1003.0. This is attributed to the hydrolysis product perchloric acid. Even very dry acetonitrile may have sufficient water impurity at these concentrations to effect hydrolysis. It is significant to note that at these high dilutions there

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(15) (a) Following ^{13}C NMR shifts were observed for the triphenylsilyl perchlorate in CH_2Cl_2/CH_3CN (1:1) solution: $\delta(^{13}C)$ 136.7 (d), 133.0 (d), 129.4 (d), 128.7 (s). (b) The triphenylsilyl perchlorate was found sparingly soluble in either neat acetonitirle or sulfolane solutions. However, the compound went into solution by adding equal volume of dry dichloromethane.

(16) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485.

(17) Lindman, B.; Forsen, S. *NMR: Basic Princ. Prog.* **1976**, *12*.

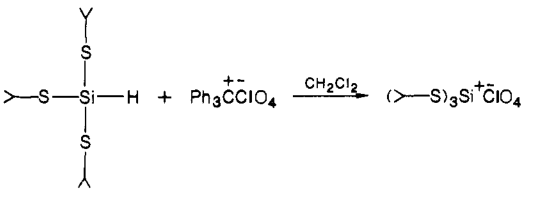
(18) (a) The ^{35}Cl signal of covalent perchlorate is extremely broad. (b) Similar observations were made in dichloromethane and dichloromethane/sulfolane solutions.

Table I. Final Atomic Coordinates for $Ph_3SiOClO_3$

	molecule 1			molecule 2		
	x	*y*	*z*	*x*	*y*	*z*
Cl	0.2135 (1)	0.6659 (1)	0.8286 (1)	−0.2983 (2)	0.4538 (2)	0.5417 (2)
Si	0.3078 (2)	0.8881 (1)	1.0532 (1)	−0.1878 (2)	0.2390 (2)	0.6440 (1)
O(1)	0.3208 (4)	0.7751 (4)	0.8835 (4)	−0.1796 (4)	0.3526 (4)	0.5348 (4)
O(2)	0.2202 (14)	0.5514 (7)	0.8777 (8)	−0.2681 (8)	0.4722 (8)	0.4067 (7)
O(3)	0.2613 (8)	0.6405 (7)	0.6826 (5)	−0.2719 (10)	0.5798 (6)	0.6363 (9)
O(4)	0.0795 (8)	0.7209 (15)	0.8981 (12)	−0.4278 (6)	0.3970 (9)	0.5975 (9)
C(1)	0.2165 (5)	1.1488 (5)	1.0626 (5)	−0.2880 (5)	0.0792 (5)	0.5753 (5)
C(11)	0.2272 (7)	1.0970 (6)	0.9398 (6)	−0.2880 (6)	0.0348 (6)	0.4316 (5)
C(12)	0.1697 (8)	1.2229 (7)	0.9488 (7)	−0.3563 (7)	−0.0876 (6)	0.3794 (6)
C(13)	0.1007 (7)	1.3106 (7)	1.0804 (7)	−0.4235 (7)	−0.1703 (6)	0.4688 (7)
C(14)	0.0865 (7)	1.2642 (7)	1.2010 (7)	−0.4254 (7)	−0.1301 (6)	0.6117 (6)
C(15)	0.1430 (7)	1.1375 (6)	1.1934 (6)	−0.3575 (7)	−0.0074 (6)	0.6637 (5)
C(2)	0.5038 (5)	0.9168 (5)	1.0358 (5)	0.0064 (6)	0.2041 (5)	0.6042 (5)
C(21)	0.5544 (6)	1.0534 (6)	1.0907 (6)	0.1130 (6)	0.3046 (6)	0.5795 (7)
C(22)	0.7001 (8)	1.0788 (7)	1.0746 (8)	0.2558 (7)	0.2740 (9)	0.5459 (8)
C(23)	0.7965 (7)	0.9723 (9)	1.0063 (8)	0.2887 (8)	0.1425 (10)	0.5383 (8)
C(24)	0.7501 (7)	0.8383 (8)	0.9534 (7)	0.1981 (8)	0.0395 (7)	0.5622 (7)
C(25)	0.6055 (6)	0.8124 (6)	0.9690 (6)	0.0531 (7)	0.0689 (6)	0.5953 (6)
C(3)	0.2133 (6)	0.7959 (5)	1.1921 (5)	−0.2705 (6)	0.3345 (5)	0.8332 (5)
C(31)	0.2925 (6)	0.7210 (6)	1.2473 (6)	−0.1841 (6)	0.4091 (6)	0.9190 (6)
C(32)	0.2246 (7)	0.6536 (7)	1.3505 (6)	−0.2431 (9)	0.4786 (7)	1.0589 (7)
C(33)	0.0762 (8)	0.6584 (7)	1.4026 (7)	−0.3888 (8)	0.4769 (7)	1.1170 (6)
C(34)	−0.0044 (7)	0.7314 (7)	1.3484 (7)	−0.4783 (7)	0.4040 (7)	1.0352 (6)
C(35)	0.0631 (6)	0.7983 (6)	1.2460 (6)	−0.4179 (6)	0.3349 (6)	0.8938 (6)

was no observable ^{29}Si NMR absorption in the silicon spectrum.

We have also restudied Lambert's reported work[7] on the hydride exchange of tris(isopropylthio)silane with trityl perchlorate in dichloromethane using ^{35}Cl NMR spectroscopy. No sharp ^{35}Cl NMR signal was observed for the claimed[7] ionic tris(isopropylthio)silyl perchlorate. This can again indicate covalent or partially covalent nature. However, we were unable to obtain a discernible ^{29}Si NMR spectrum of the species because of its poor solubility, nor was it possible to isolate crystals. Therefore, ^{35}Cl and ^{29}Si NMR studies failed to affirm the reported ionic silyl cation structure.



We need to point out that regretfully in Lambert's published work[7,8] no sufficient experimental details were given, including concentrations of studied solutions (and their dilutions) for the observation of long-lived silyl cations. Under our high dilution conditions, however, no ^{29}Si NMR observation of a long-lived silyl cation was so far possible.

X-ray Crystallographic Study. To further ascertain the structure of triphenylsilyl perchlorate, we succeeded to isolate crystals and carried out X-ray diffraction studies. A good crystal of triphenylsilyl perchlorate was obtained from CH_2Cl_2/*n*-hexane (1:1) solution by the layering method under dry nitrogen. The solving of the X-ray structure was a difficult crystallographic task. Numerous attempts with the more common space group *P*1 revealed tantalizing fragments of the structure but ultimately resulted in failure. It was then decided to try the rare noncentric space group *P*1, with two independent molecules in the unit cell. The correct structure was finally revealed via a combination of exhaustive MULTAN[19] trials (which located the $C_3SiOClO_3$ cores of the two molecules), followed by expansion of the structure by tangent refinement using the program DIRDIF,[20] and finally refined to completion by using the program SHELX-76.[21] Crystal data: $C_{18}H_{15}SiClO_4$; triclinic; $a = 9.590$ Å, c 10.033 Å, $\alpha = 105.6°$, $\beta = 74.4°$, $\gamma = 94.4°$; space group *P*1. The final *R* factor for 1859 reflections is 0.0388. Data collection was performed at room temperature on a Syntex $P2_1$ diffractometer.

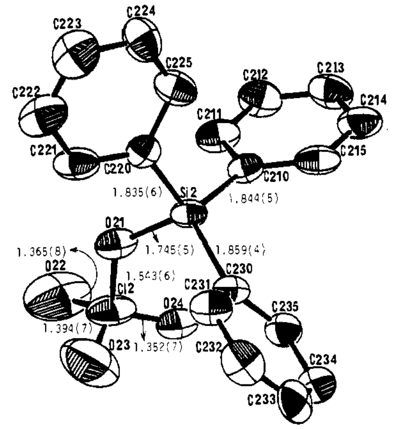


Figure 2. ORTEP drawing of the structure of triphenylsilyl perchlorate. For clarity no hydrogen atoms are shown. Average bond distances and angles: Si–C = 1.846 (5) Å, Si–O(b) = 1.744 (4) Å, Cl–O(b) = 1.535 (4) Å, Cl–O(t) = 1.368 (7) Å, Si–O–Cl = 128.9 (2)°, O–Si–C = 104.9 (2)°, C–Si–C = 113.5 (2)°, O(b)–Cl–O(t) = 105.5 (4)°, O(t)–Cl–O(t) = 113.1 (7)°.

The crystal data clearly show covalent bond between silicon and the perchlorate oxygen. The silicon–oxygen bond distance of 1.744 Å is slightly longer (by 0.11 Å) than that observed[22] in siloxanes (~1.63 Å). The other important bond distances are shown in the ORTEP drawing in Figure 2. The X-ray structure of triphenylsilyl perchlorate irrefutably shows its covalent nature in the crystal. Final atomic coordinates and selected bond distances and angles are given in Tables I and II, respectively. Also available, as supplementary material, are (a) the final anisotropic thermal parameters, (b) the calculated hydrogen positions, and (c) the observed and calculated structure factors for triphenylsilyl perchlorate (see paragraph at end of paper for ordering details). We are aware that the structure of the crystalline perchlorate could differ from that in dilute solutions. Regardless the X-ray structure

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(19) MULTAN: a system of computer programs for the automatic solution of crystal structures for X-ray diffraction data (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.*, **1971**, *A27*, 368).

(20) DIRDIF: Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van Den Hark, T. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G. and Parthasarathi, V. Crystallography Laboratory, Netherlands, 1981.

(21) SHELX-76: Sheldrick, G. M.; University of Cambridge, 1976.

(22) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981.

Table II. Selected Bond Distances (Å) and Angles (deg) for $Ph_3SiOClO_3$

	molecule 1	molecule 2
	Bond Distances	
Cl–O(1)	1.526 (4)	1.543 (5)
Cl–O(2)	1.354 (8)	1.365 (8)
Cl–O(3)	1.371 (5)	1.394 (7)
Cl–O(4)	1.360 (8)	1.362 (7)
Si–O(1)	1.742 (4)	1.745 (5)
Si–C(1)	1.830 (6)	1.844 (5)
Si–C(2)	1.847 (5)	1.835 (6)
Si–C(3)	1.859 (5)	1.859 (4)
	Bond Angles	
O(1)–Cl–O(2)	107.2 (5)	104.5 (4)
O(1)–Cl–O(3)	103.8 (3)	104.3 (4)
O(1)–Cl–O(4)	106.1 (5)	106.9 (4)
O(2)–Cl–O(3)	113.7 (4)	109.5 (5)
O(2)–Cl–O(4)	105.0 (8)	119.8 (5)
O(3)–Cl–O(4)	120.2 (6)	110.6 (5)
Si–O(1)–Cl	130.2 (2)	127.5 (2)
O(1)–Si–C(1)	107.4 (2)	107.4 (2)
O(1)–Si–C(2)	97.3 (2)	98.8 (2)
O(1)–Si–C(3)	109.6 (2)	109.0 (2)
C(1)–Si–C(2)	112.1 (2)	111.7 (2)
C(1)–Si–C(3)	113.8 (2)	114.3 (2)
C(2)–Si–C(3)	115.0 (3)	114.2 (2)

is in full accord with the solution NMR studies.

Conclusions

In conclusion, ^{29}Si and ^{35}Cl spectroscopic and X-ray crystallographic studies conclusively reaffirm that triphenylsilyl perchlorate, as originally suggested by Wannagat[11] and since concluded by other investigators,[10] is a covalent perchloryl ester and not an ionic silicenium ion both in the solid state and in the solution studies. Due to the high affinity of silicon for oxygen and halogen donors as well as limited Si–C 3pπ–2pπ overlap long-lived stable trivalent organosilicon cations, R_3Si^+, have not yet been observed in solution. The reported results of Lambert[8] on triphenylsilyl perchlorate concerning conductivity and cryoscopic molar weight measurements are significant, but questions remain as to the true nature of the species involved. There is indeed the possibility that in highly dilute solutions of sufficient dielectric constant and low nucleophilicity the covalent silyl perchlorates would undergo ionization.[23] Experimental evidence including proper spectroscopic (particularly ^{29}Si NMR) identification so far, however, is unavailable to substantiate the existence of long-lived silyl cations in solution. The present NMR spectroscopic and X-ray crystallographic data under the reported conditions found no evidence for long-lived silyl cations in solution or in the crystalline state. We would like, however, to emphasize that intermediate formation of silyl cations in solution is indicated not only in hydride-transfer reaction but also in other S_N1-type reactions and rearrangements. Silyl cations are further well-studied in the gas phase. It is not the lack of thermodynamic stability but kinetic instability which renders their observation as long-lived species in solution so far unsuccessful. Our studies are continuing to obtain and observe long-lived organosilicon cations with possible lower nucleophi gegenions and solvent systems utilizing the criteria and methods developed for their characterization and differentiation. It is necessary, however, to exercise great care in this field to avoid claims to the observation of long-lived silyl cations based on insufficient data.

Experimental Section

Triphenylsilane, triphenylsilyl chloride, and trimethylsilyl chloride were purchased from Petrarch Systems and purified before use (either by recrystallization or by distillation). Tris(isopropylthio)silane was prepared from purified trichlorosilane (Petrarch) and 2-propanethiol (Aldrich) following the published procedure.[24] All other materials used in the study were commercially available highest purity samples. All the solvents used in the study were rigorously dried (CH_2Cl_2 over P_2O_5 and CH_3CN over P_2O_5) by reflux, doubly distilled into flame dried all glass apparatus, and stored under dry argon. All manipulations were carried out in drybox under a blanket of dry argon. Trityl perchlorate was prepared from trityl alcohol and perchloric acid in the presence of acetic anhydride.[25] Triphenylsilyl perchlorate as well as trimethylsilyl perchlorates were prepared following Wannagat's published procedure[12] with slight modifications.

Triphenylsilyl Perchlorate. Silver perchlorate hydrate (Alfa) (2.5 g, 11.1 mmol) was dissolved in 50 mL of benzene in a three-necked 100-mL round-bottom flask equipped with Dean-Stork condenser, and the solution was refluxed under a blanket of dry argon over a period of 16 h to remove the water of hydration from silver perchlorate. After the dehydration the benzene solution was cooled to room temperature followed by dropwise addition of a solution of triphenylsilyl chloride 3.13 g (10.6 mmol) in 20 mL dry benzene over a period of 5 min. The resulting mixture was stirred for 16 h at room temperature. After the reaction the benzene was evaporated under vacuum, the residue extracted with 50 mL of dry dichloromethane, and the isoluble silver chloride discarded. The dichloromethane extract on evaporation provided triphenylsilyl perchlorate as a gray powder, 2.5 g (66% yield). The material was further purified by recrystallization from CH_2Cl_2/*n*-hexane solvent system and stored at 0 °C under dry argon.

Hydride-Transfer Experiments. To a suspension of 86 mg (0.25 mmol) of trityl perchlorate in 1.5 mL of dry dichloromethane in a flame-dried 10-mm NMR tube under a blanket of dry argon is added a solution of triphenylsilane (65 mg, 0.25 mmol) in 1 mL of dry dichloromethane with various stirring. The hydride exchange was instantaneous as indicated by the color change (yellow to colorless). Similar procedure was employed with other solvents.

X-ray Studies. The single crystal of triphenylsilyl perchlorate for X-ray analysis was grown from 5% (by wt) solution in 1:1 dry dichloromethane/*n*-hexane solvent mixture. The X-ray data were collected at room temperature by using a Nicolet/Syntex $P2_1$ diffractometer.

NMR Spectra. The ^1H, ^{13}C, ^{35}C, and ^{29}Si NMR spectra were obtained on a Varian Associates Model XL-200 NMR spectrometer equipped with a broad-band probe. Additional ^{29}Si NMR work was carried out on a Bruker 500-MHz NMR spectrometer equipped with a broad-band probe. Solid-state ^{29}Si work was carried on a JEOL-90 spectrometer equipped with solid-state broad-band probe equipped with CPAMS accessory.

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Supplementary Material Available: The final anisotropic thermal parameters, (Table A) and the calculated hydrogen positions (Table B) of triphenylsilyl perchlorate (2 pages); the observed and calculated structure factors (Table C) of triphenylsilyl perchlorate (8 pages). Ordering information is given on any current masthead page.

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(23) Some of the referees suggested this possibility.

(24) Wolinki, L.; Tieckelmann, H.; Post, H. W. *J. Org. Chem.* **1951**, *16*, 395.

(25) Dauben, H. J., Jr.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442.