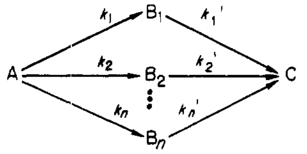
was distilled from NaOH. Methanol was purified by distillation from Mg activated with I_2.

Procedure. A reaction mixture consisting of allene (0.3 g), *p*-toluenesulfonylhydrazine (1.0 g), triethylamine (0.75 mL), an internal standard (0.1 g), and methanol (2 mL) was heated under reflux in a small flask equipped with a reflux condenser. At appropriate time intervals, the reaction mixture (0.05 mL) was withdrawn from the top of the condenser by use of a syringe with a long needle (20 cm), poured into a sample tube, and quenched by the addition of water (2 mL) and *n*-pentane (0.1 mL). The mixture was shaken vigorously, and the upper organic layer was subjected to VPC analysis. A gas chromatograph (Shimadzu 4APT) with a 4-m column of silicone XF-1150 was used. Only the expected peaks of the products were found along with those of the reactant allene and the internal standard. The peaks were assigned by comparing the retention times with those of authentic samples. The concentrations of reactants and products were determined by the internal standard method on the basis of the peak areas which were evaluated by integration on a Hitachi HITAC-10 computer. The internal standards used were cumene, anisole, *sec*-butylbenzene, and tetraline for the reactions of **1a–d**, respectively.

Kinetic Analysis. The distribution of various products was analyzed according to the reactions shown in Scheme I. The problem is essentially that of the consecutive, competitive first-order reactions as follows:



Integration of the relevant rate equations readily gives the molar fractions of A, B_1–B_n, and C at time *t* (eq 3a–c), where $[A]_0$ is the

$$\alpha \equiv [A]/[A]_0 = e^{-kt} \tag{3a}$$

$$\beta_i \equiv [B_i]/[A]_0 = \frac{k_i}{k_i' - k}\,(e^{-kt} - e^{-k_i't}) \tag{3b}$$

$$\gamma \equiv [C]/[A]_0 = 1 - \alpha - \sum_i \beta_i \tag{3c}$$

initial concentration of *A*, $i = 1, 2, ..., n$, and *k* is an overall first-order rate constant (eq 4).

$$k = \sum_i k_i \tag{4}$$

For our present purpose, we express β_i as the function of the extent of reaction x ($=1 - \alpha$) of A. The result is given in eq 5.

$$\beta_i = \frac{(k_i/k)}{(k_i'/k) - 1}[1 - x - (1 - x)^{k_i'/k}] \tag{5}$$

β_i attains a maximum when x reaches η_i such that

$$\eta_i = 1 - (k_i'/k)^{-1/[(k_i'/k) - 1]} \tag{6}$$

The value of β_i at the maximum is given in eq 7. Equations 6

$$\beta_{i,\max} = (1 - \eta_i)(k_i/k)/(k_i'/k) \tag{7}$$

and 7 greatly assist us in evaluating k_i/k and k_i'/k from the experimental curves. The curve fittings were accomplished by use of a Yokokawa-Hewlett-Packard Model 20 computer.

MO Computation. All calculations were performed within the framework of the ab initio restricted Hartree–Fock theory by employing a modified version of the GAUSSIAN 70 package.[23] The minimal STO-3G set was used with the suggested standard parameters.[24] As for the molecular geometries, standard bond lengths and angles proposed by Pople et al.[25] were employed.

Acknowledgment. We are indebted to Dr. Shigeru Nagase for his advice on MO calculations and to Kazumi Fujioka and Takeshi Sasajima for technical assistance.

Registry No. **1a**, 2327-99-3; **1b**, 22433-39-2; **1c**, 2327-98-2; **1d**, 2327-97-1; **2a**, 300-57-2; **2b**, 934-10-1; **2c**, 935-00-2; **2d**, 51795-73-4; **3c**, 15324-90-0; **3d**, 37549-95-4; **4a**, 873-66-5; **4b**, 768-00-3; **4c**, 1005-64-7; **4d**, 16002-93-0; **5a**, 766-90-5; **5b**, 767-99-7; **5c**, 1560-09-4; **5d**, 7642-18-4; **6a**, 103-65-1; **6b**, 135-98-8; **6c**, 104-51-8; **6d**, 538-68-1; ethylene, 74-85-1; propadiene, 463-49-0; 1,2-butadiene, 590-19-2; diimide, 3618-05-1.

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Geometries and Relative Energies of Some $C_6H_5^+$ and $C_5H_5Si^+$ Isomers. Pyramidal (Nido) vs. Planar, Cyclic Structures

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Ab initio molecular orbital calculations with geometry optimization at the STO-3G level have been carried out on pyramidal (**1**, **5**) and cyclic (**2**, **3**) $C_6H_5^+$ and $C_5H_5Si^+$ structures. Additional single-point calculations at the 4-31G ($C_6H_5^+$), 3-21G, and STO-3G* ($C_5H_5Si^+$) levels were performed to probe the effects of larger basis sets. Pyramidal structure **1**, with C_{5v} symmetry, places a carbon or a silicon atom in a position with a formal coordination number of five. Among the $C_6H_5^+$ isomers, the planar cyclic structures **2-C** and **3-C** are highly preferred over the pyramidal ones **1-C** and **5**, but there is a strong dependence of energies on the basis set employed. In contrast, the C_{5v} pyramidal $C_5H_5Si^+$ structure **1-Si** is favored over the planar, cyclic structures **2-Si** and **3-Si**. Whereas the phenyl cation **2-C** should have a singlet ground state, the silaphenyl cation **2-Si** is indicated to possess a triplet ground state. Analysis of the charge distributions illustrates the differences in electronic demands and bonding between C^+ and Si^+ species.

Recently, Aylett and Colquhoun[2] observed the fragment ion $C_5H_5Si^+$ with high relative intensities in the mass spectra of $SiH_2[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ and $SiCl_2[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$. The analogous ions $C_5H_5Ge^+$ and $C_5H_5Sn^+$

are also known from the mass spectra of polynuclear metal carbonyl complexes;[3] structure types 1–3 have been proposed as being most likely for these ions.[2,3] Structures 2 and 3 were proposed for the $C_5H_5Ge^+$ ion,[3a] but Aylett and Colquhoun, recognizing the isoelectronicity of $C_5H_5Sn^+$ with C_5H_5In and the known η^5 (1, M^+ = In) structure of the latter in the gas phase,[4a] suggested that such half-sandwich geometries actually may be preferred for M = Sn, Ge, and Si. Jutzi et al.'s X-ray structure of nido cluster 4 provides direct support for this idea.[4b] Carbon as the apical atom would, of course, represent the first member of such a valence isoelectronic group 4A-cyclopentadienyl cation series. Pyramidal carbocations situating carbon in a position with a coordination number greater than 4 have received considerable interest since Winstein and Ordronneau considered (but rejected) a possible C_{6v} structure for the norbornadienyl cation $C_7H_7^+$,[5] the theoretical prediction by Williams and by Stohrer and Hoffmann of a stable C_{4v} $C_5H_5^+$ species,[6] and the experimental preparation by Hogeveen and Kwant of a C_{5v} $C_6(CH_3)_6^{2+}$ dication.[7]

If η^5-1-Si is the most stable structure for $C_5H_5Si^+$, significant bonding differences between Si and C would be indicated, since results of calculations for $C_6H_5^+$ do not indicate a preference for pyramidal structures. Extensive MINDO/3 calculations on $C_6H_5^+$ isomers predict the phenyl cation to be the most stable cyclic structure[8a] and probably the overall lowest energy isomer as well,[8b] but there is ample experimental evidence for the gas-phase formation of $C_6H_5^+$ ions other than the phenyl cation.[9] The ab initio calculations by Castenmiller and Buck[8a] on the singlet states of the nonclassical ion 1-C and the phenyl cation 2-C may be compared to those of Dill et al. and Vincent and Radom on the singlet and triplet states of the phenyl cation[10] and to independent calculations by us on 1-C. Minimal basis-set results indicate the singlet phenyl cation to be about 25 kcal/mol lower in energy than the pyramidal cation;[8a] however, as is discussed in detail below, this energy separation seems to be very basis set dependent. In this paper we examine calculationally the $C_5H_5Si^+$ isomers 1-Si, 2-Si, and 3-Si and compare them to the analogous $C_6H_5^+$ structures (1-C, 2-C, and 3-C) and an alternative pyramidal isomer, 5.

Methods

Ab initio molecular orbital calculations have been carried out on the molecules 1–3 (M = Si) and 1 and 3 (M = C) as well as 5 by utilizing modified versions of the GAUSSIAN 70[11a] and GAUSSIAN 76[11b] series of programs. The geometries were optimized under overall molecular symmetry constraints (C_{5v} for 1-Si and 1-C; C_{2v} for 2-Si, 3-Si, and 3-C; C_s and a planar carbon ring for 5) by using the minimal STO-3G basis set.[12a] Singlet states were examined with conventional restricted Hartree–Fock theory[13a] and a geometry optimization program based on the Davidon–Fletcher–Powell method;[14] triplet states were calculated with the unrestricted version (UHF) due to Pople and Nesbet[13b] using parabolic interpolation optimization. Calculations with the split valence 4-31G basis set[12b] were performed on the optimized geometries of 1-C, 3-C, and 5 (4-31G//STO-3G); the recently developed 3-21G basis sets[15] were employed on 1-Si, 2-Si, and 3-Si. Calculations with the STO-3G* basis set,[12c] which includes a set of d orbitals on Si, were carried out on 1-Si, 2-Si, and 3-Si (STO-3G*//STO-3G). The calculations of Dill et al.[10a] and Vincent and Radom[10b] on 2-C are quite similar to ours on the other $C_6H_5^+$ isomers and may thus be used for consistent comparison. The atom labeling is given in Figure 1, and the optimized geometries are listed in Table I. Table II gives the total and relative molecular energies; Table III gives pertinent results from the Mulliken electronic population analysis.[16]

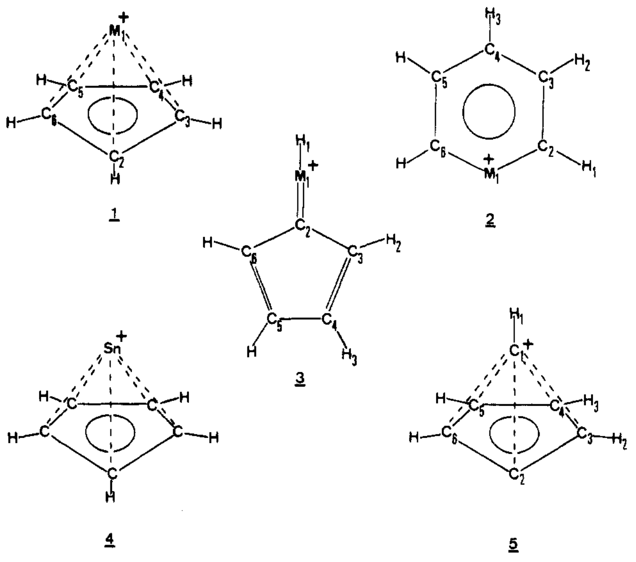

Figure 1. Atom labeling in structures 1–3 and 5.

Results and Discussion

Geometries and Charge Distributions. (a) Pyramidal Structures. The general interaction diagram involving s and p orbitals, which account for the bonding in half-sandwich structures such as 1-Si, 1-C, and 5, has been well documented.[6,7,17] An sp hybrid on the apical group

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Table I. STO-3G Molecular Geometries of 1-Si, 2-Si, 3-Si, 1-C, 3-C, and 5[a]

molecule	electronic state	bond length	angle
η^5-cyclopentadienyl-Si^+ (1-Si)	$^1A_1$	$Si-C_2 = 2.126$ $C_2-C_3 = 1.426$ $Si-X = 1.745^c$ $C_2-H = 1.084$	$\tau_1 = 1.4^b$
silaphenyl cation (2-Si)	$^1A_1$	$Si-C_2 = 1.690$ $C_2-C_3 = 1.400$ $C_3-C_4 = 1.397$ $C_2-H_1 = 1.079$ $C_3-H_2 = 1.089$ $C_4-H_3 = 1.082$	$C_2SiC_6 = 128.2$ $SiC_2C_3 = 105.0$ $C_2C_3C_4 = 126.9$ $C_3C_4C_5 = 128.1$ $H_1C_2Si = 131.8$ $H_2C_3C_2 = 116.0$
	$^3B_1$	$Si-C_2 = 1.809$ $C_2-C_3 = 1.394$ $C_3-C_4 = 1.438$ $C_2-H_1 = 1.083$ $C_3-H_2 = 1.087$ $C_4-H_3 = 1.085$	$C_2SiC_6 = 110.6$ $SiC_2C_3 = 116.4$ $C_2C_3C_4 = 124.9$ $C_3C_4C_5 = 126.8$ $H_1C_2Si = 123.2$ $H_2C_3C_2 = 118.5$
	$^3A_2$	$Si-C_2 = 1.739$ $C_2-C_3 = 1.464$ $C_3-C_4 = 1.400$ $C_2-H_1 = 1.087$ $C_3-H_2 = 1.094$ $C_4-H_3 = 1.080$	$C_2SiC_6 = 109.7$ $SiC_2C_3 = 118.1$ $C_2C_3C_4 = 124.5$ $C_3C_4C_5 = 125.2$ $H_1C_2Si = 123.2$ $H_2C_3C_2 = 118.5$
silafulvenyl cation (3-Si)	$^1A_1$	$Si-C_2 = 1.649$ $C_2-C_3 = 1.501$ $C_3-C_4 = 1.329$ $C_4-C_5 = 1.511$ $Si-H_1 = 1.434$ $C_3-H_2 = 1.078$ $C_4-H_3 = 1.085$	$C_3C_2C_6 = 105.6$ $C_2C_3C_4 = 107.9$ $C_3C_4C_5 = 109.3$ $H_2C_3C_4 = 127.9$ $H_3C_4C_5 = 123.3$
η^5-cyclopentadienyl-C^+ (1-C)	$^1A_1$	$C_1-C_2 = 1.822$ $C_2-C_3 = 1.430$ $C_1-X = 1.357^c$ $C_2-H = 1.088$	$\tau_1 = 8.6^b$
fulvenyl cation (3-C)	$^1A_1$	$C_1-C_2 = 1.282$ $C_2-C_3 = 1.532$ $C_3-C_4 = 1.326$ $C_4-C_5 = 1.507$ $C_1-H_1 = 1.098$ $C_2-H_2 = 1.079$ $C_3-H_3 = 1.086$	$C_3C_2C_6 = 104.4$ $C_2C_3C_4 = 107.7$ $C_3C_4C_5 = 110.1$ $H_2C_3C_4 = 130.6$ $H_3C_4C_5 = 124.1$
5	$^1A_1$	$C_1-X = 1.444^c$ $C_2-C_3 = 1.507$ $C_3-C_4 = 1.460$ $C_4-C_5 = 1.439$ $C_2-X = 1.142^c$ $C_1-H_1 = 1.083$ $C_3-H_2 = 1.086$ $C_4-H_3 = 1.090$	$C_3C_2C_6 = 96.3$ $C_2C_3C_4 = 115.9$ $C_3C_4C_5 = 106.0$ $H_1C_1X = 175.0^c$ $H_1C_1XC_2 = 180.0^c$ $H_2C_3C_4 = 119.4$ $H_3C_4C_5 = 125.8$ $\tau_2 = 12.6^b$ $\tau_3 = 12.2^b$

[a] Distances in angstroms and angles in degrees. [b] The τ's indicate the hydrogen tilt angles with respect to the plane of the five-membered ring. Positive values signify that the hydrogens bend toward the apical group. [c] X is a "dummy" atom in the plane of the ring. In 1, X is in the center; in 5, C_1-X is orthogonal to the ring.

Table II. Total and Relative Molecular Energies for Structures 1–3 and 5[a]

molecule	electronic state	*E*(STO-3G)	rel *E*	*E*(3-21G or 4-31G//STO-3G)	rel *E*	*E*(STO-3G*//STO-3G)	rel *E*
1-Si	$^1A_1$	−475.343 96	0.0	−478.311 55^b	0.0	−475.411 60	0.0
2-Si	$^1A_1$	−475.193 24	94.6	−478.197 30^b	71.7	−475.241 54	106.7
	$^3B_1$	−475.292 01	32.6	−478.276 24^b	22.2	−475.340 24	44.8
	$^3A_2$	−475.195 26	93.3	−478.201 83^b	68.8	−475.239 43	108.0
3-Si	$^1A_1$	−475.158 57	116.3	−478.164 30^b	92.4	−475.194 42	136.3
1-C	$^1A_1$	−226.948 06	40.7	−229.326 61^c	67.1		
2-C	$^1A_1$	−226.988 78^d	15.1	−229.425 40^{c,d}	5.1		
		−226.983 88^e	18.2	−229.421 58^{c,e}	7.5		
	$^3B_1$	−227.012 90^e	0.0	−229.433 57^{c,e}	0.0		
	$^3A_2$	−226.999 96^e	8.1	−229.429 25^{c,e}	2.7		
3-C	$^1A_1$	−226.936 76	47.8	−229.375 97^c	36.1		
5	$^1A_1$	−226.879 95	83.4	−229.266 23^c	105.0		

[a] Total energies in hartrees and relative energies in kilocalories per mole. [b] 3-21G basis. [c] 4-31G basis. [d] Reference 10b. [e] Reference 10a.

Table III. STO-3G Mulliken Population Data for Optimized Structures 1–3 and 5

molecule	1-Si($^1A_1$)	2-Si($^1A_1$)	2-Si($^3B_1$)	2-Si($^3A_2$)	3-Si($^1A_1$)	1-C($^1A_1$)	3-C($^1A_1$)	5($^1A_1$)
				π-Charge[a]				
Si	0.547	0.947	0.294	0.820	1.021			
C_1						0.698	1.268	0.959
C_2	0.954	1.101	0.961	0.843	0.985	0.870	0.779	0.430
C_3		0.918	0.947	0.718	1.090		1.107	0.817
C_4		1.043	0.932	1.088	0.919		0.870	0.812
				Total Charge				
Si	+0.710	+1.000	+0.979	+0.733	+0.905			
C_1						+0.120	+0.216	−0.063
C_2	−0.092	−0.260	−0.220	−0.198	−0.182	−0.004	+0.042	+0.088
C_3		−0.023	−0.038	+0.061	−0.070		−0.032	−0.007
C_4		−0.090	−0.034	−0.097	−0.018		+0.009	+0.027
H_1	+0.150	+0.139	+0.118	+0.123	+0.051	+0.180	+0.247	+0.205
H_2		+0.132	+0.114	+0.138	+0.089		+0.130	+0.172
H_3		+0.114	+0.110	+0.115	+0.111		+0.140	+0.193

[a] Population of p orbitals parallel to the C_5 axis (1), of p orbitals perpendicular to the molecular plane (2, 3), or of p orbitals parallel to the symmetry plane (5).

has the correct symmetry to interact with the lowest π MO of a cyclopentadienyl cation, Cp^+ (1-Si, 1-C), or a cyclopentadienylidene ring (**5**). The p orbitals on the apical group parallel to the ring plane can interact with the next set of π MO's (degenerate in Cp^+ and nearly so in cyclopentadienylidene), and these three stabilized molecular orbitals form a pseudo-6-π-electron aromatic system. The remaining sp hybrid contains either a lone pair (1-Si, 1-C) or forms a bond to hydrogen (**5**). The ring-cap bonding thus occurs almost exclusively between p orbitals; as a matter of fact, all overlap populations involving the apical Si(3s) or C(2s) orbital and the ring orbitals in 1-Si and 1-C, respectively, are negative. The apical–basal distance is, as expected from simple arguments based on atomic size, considerably larger in $CpSi^+$ (1.745 Å) than in CpC^+ (1.357 Å); this results in a Si–C distance of 2.126 Å in 1-Si and a C_1–C_2 distance of 1.822 Å in 1-C, distances which are 15–20% longer than typical single bonds between these elements.[18] The ring dimensions in 1-Si and 1-C are very similar (C–C distances of 1.426 Å in 1-Si and 1.430 Å in 1-C) and correspond well to the bond lengths observed or calculated in, e.g., CpLi,[19a] CpBeH,[19b] CpIn,[4a] and $(Me)_5CpSn^+$.[4b]

The two systems 1-Si and 1-C differ in the calculated charge distributions (Table III). We do not agree that the positive charge in 1-C is indicated to be delocalized only over the capping atom and the hydrogens.[8a] Even in neutral hydrocarbons the STO-3G basis predicts polarized carbon–hydrogen bonds from a Mulliken population analysis, $C^{\delta-}$–$H^{\delta+}$, with δ typically of the order 0.1. A total of 0.35 e is donated from the unique carbon C_1 into the 2p(π) orbitals of the ring, but this is accompanied by a back-donation from the σ system of 0.23 e, so that the overall net charge on the apical carbon is only +0.12. The electron distribution among the atomic orbitals on C_1 is 1.88 e in the 2s orbital, 0.65 e in each of the 2p orbitals lying parallel to the ring plane, and 0.70 e in the 2p orbital along the symmetry axis, indicating a high percentage of 2s character in the lone-pair orbital. The carbon atoms in the ring skeleton are calculated to be essentially neutral although negative values ($C^{-0.1}$) are usual; the hydrogens carry a net charge of +0.18, larger than usual. The surplus positive charge is thus distributed surprisingly uniformly among *all* the atoms in the molecule. In 1-Si, however, the major part of the positive charge is on silicon (+0.71), clearly illustrating its lower electronegativity (0.7 units less than carbon on the Pauling scale). The net charges on the carbons have typical negative values. The electron density increase on the ring carbons in 1-Si over 1-C is almost solely related to the extra charge in the 2p(π) orbitals (0.86 in 1-C, 0.95 in 1-Si), which brings about increasing π-bonding and slightly decreasing C–C distances in 1-Si relative to 1-C. A total π donation from Si of 0.77 e takes place, with only 0.06 e returning from the σ system. Si has still almost 2 electrons (1.89 e) in the 3s orbital, but only 0.49 e in each of the 3p orbitals perpendicular to the symmetry axis and 0.55 e in the 3p orbital along the axis; again, large s character in the lone-pair orbital is indicated.

The cap-ring bonding appears to be quite strong. The total overlap population between the apical carbon and all ring carbons is 0.72;[20] that between two neighboring carbons in the ring is 0.89. The total overlap population in 1-Si between Si and the ring carbons is 0.56.

The bonding in **5** and alternative pyramidal $C_6H_5^+$ structures is less satisfactory. The distance from the carbon atom in the CH^+ group of **5** to the plane of the ring (1.444 Å) is a little larger than the corresponding distance in 1-C, but the CH^+ group is placed asymmetrically with respect to the carbon atoms of the ring. The C_1–C_2 distance is 1.841 Å (similar to the C_1–C_2 in 1-C) while the C_1–C_3 (C_1–C_6) and C_1–C_4 (C_1–C_5) distances are equal and considerably shorter at 1.660 Å. This is in accordance with the considerably higher π-electron density at these centers and indicates a tendency toward η^4 coordination. The bond lengths in the ring are unequal with C_4–C_5 as the shortest bond (1.439 Å), followed by the formal double bond C_3–C_4 at 1.460 Å and C_2–C_3 at 1.507 Å. The bonding from the apical carbon is stronger to C_3 (overlap population of 0.34) than to C_4 (0.24) with almost no bonding at all to C_2 (0.06). Since we have not investigated deviations from nonplanarity of the ring carbon skeleton, it is quite possible that **5** does not represent a minimum within C_s symmetry.

A common feature to all three pyramidal structures is the bending of the ring hydrogens *toward* the apical group. As explained in detail elsewhere,[21] the direction and magnitudes of the tilt vary in a systematic manner with

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(17) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179.

(18) The Si–C distance in H_3SiCH_3 is 1.867 Å: Kilb, R. W.; Pierce, L. *J. Chem. Phys.* **1957**, *27*, 108. The calculated STO-3G value is 1.866 Å.[12c]

(19) (a) Alexandratos, S.; Streitwieser, A., Jr.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1976**, *98*, 7859. (b) Jemmis, E. D.; Alexandratos, S.; Schleyer, P. v. R.; Streitwieser, A., Jr.; Schaefer, H. F. *Ibid.* **1978**, *100*, 5695.

(20) All overlap populations given in ref 8a appear to be a factor of 2 too low.

(21) Jemmis, E. D.; Schleyer, P. v. R.; Pople, J. A., to be submitted for publication. Jemmis, E. D. Ph.D. Thesis, Princeton University, 1978.

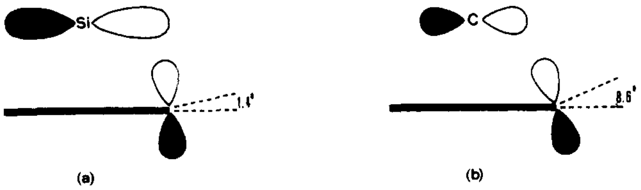
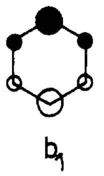
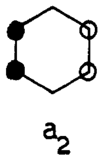


Figure 2. Schematic representation of the hydrogen bending in 1-Si (a) and 1-C (b).

the size of the orbitals on the apical group, the size of the ring, and the apex–base distance. Since the size of the ring is essentially the same in 1-Si and 1-C, the hydrogen tilt is considerably smaller with the larger Si as the apical atom (Figure 2a) than with C (Figure 2b). In Me_5CpSn^+ and C_5H_5In, the orbitals on the isoelectronic Sn^+ and In atoms apparently are even larger and more diffuse. This results in the methyl groups in Me_5CpSn^+ and the hydrogens in CpIn tilting *away* from the capping atom by about 4°.[4] The shorter apical carbon–ring carbon distances in **5** result in an even greater hydrogen tilt to more than 12° toward the CH cap. This orients the C 2p orbitals to allow for maximum overlap. The apical hydrogen in **5** bends toward the C_4–C_5 bond by 5.0°, orienting the 2p orbitals on the CH cap for improved overlap with those of the ring.

(b) Planar Structures. We have studied three electronic states of the silaphenyl cation **2-Si**, namely, the 6-π-electron singlet and two triplets with 5-π-electron configurations ($^3B_1$, $^3A_2$). These triplets have one electron in the silicon lone-pair orbital and one electron in the b_1 or a_2 π orbitals, respectively. The LUMO in the singlet state is almost exclusively the silicon lone-pair orbital, but it is also weakly Si–C antibonding. The optimized silaphenyl cation structures show features similar to the corresponding states of the phenyl cation,[10] but the relative changes between silabenzene[22] and the silaphenyl cation, although parallel, are generally smaller than those between benzene and the phenyl cation.[10] In the singlet silaphenyl cation the internal angle at Si widens to 128.2° (a change of 17.9° from silabenzene[22]) in order to increase the population of the formally empty σ orbital on Si by hyperconjugation; for similar reasons the angle at C_2 (C_6) narrows by 12.4° from silabenzene to 105.0°. The corresponding angles and differences between benzene and the singlet phenyl cation are 144.9° (24.9°) and 103.6° (16.4°). The carbon–silicon distance is shortened considerably from 1.722 Å in silabenzene to 1.609 Å in singlet **2-Si**. The smaller geometrical distortions in **2-Si** indicate the electronic demands of Si^+ to be significantly less than those of C^+ in **2-C**. In accordance with the nodal pattern of the b_1 orbital, the Si–C bond length increases considerably in the $^3B_1$ state to 1.809 Å, accompanied by a decrease of the internal angle at Si to 110.6°. Since the a_2 orbital has a node on Si and C_4, a smaller lengthening of the Si–C bond is predicted in the $^3A_2$ state (0.05 Å); the C_2–C_3 bond (1.464 Å) has lengthened significantly by 0.06 Å. The angles in the $^3B_1$ and $^3A_2$ states are rather similar.


b_1


a_2

The geometrical distortions in singlet **2-Si** result only in a population of 0.15 e in the formally vacant in-plane 3p Si orbital, and with only 1.21 e in the 3s orbital a large σ deficiency is present. Whereas charge polarization of the π cloud in the phenyl cation[10] is able to alleviate part of the similar electron deficiency, the smaller electronegativity of Si defeats this mechanism, and less than 1 π electron resides on Si (0.95 e) and more than 1 e on the ortho (1.10 e) and para (1.04 e) positions in singlet **2-Si**. Overall, C_2 is thus negatively charged, while Si carries a deficiency of +1.00. In the $^3B_1$ state the population of the Si 3p orbital increases to 0.69 and the 3s population to 1.40; however, the π-electron population on Si is strongly diminished, so almost no decrease in net charge results. The π distribution as well as the overall distribution appears more homogenous in the $^3B_1$ state than in the singlet state of **2-Si**. A very uneven distribution in the π system is noticeable in the $^3A_2$ state, with a large concentration on C_4. The net charges show a less positive Si (+0.73) than in the $^1A_1$ and $^3B_1$ states with alternating charges along the carbon ring.

In the fulvenyl cation **3-C**, the external C_1–C_2 bond is quite short (1.282 Å), reflecting the sp hybridization at C_1, but the ring bonds have nearly normal single and double bond lengths. The Si–C_2 bond in **3-Si** of 1.649 Å is even shorter than that calculated in the singlet **2-Si**, although it is not quite as short as the calculated double bond in singlet silaethylene (1.637 Å).[22]

The charge distributions provide rationalizations for the small ring geometrical differences. The π part of the external double bond in **3-C** is strongly polarized toward C_1 (2p(π) population of 1.27 e), and there is 0.18 e in the formally empty, perpendicular 2p orbital on C_1. In **3-Si** the external Si–C bond is not nearly as strongly polarized in the π part (3p(π) population of 1.02 e), making more π-electron density available for bonding in the ring near C_2; hence, the C_2–C_3 distance is shorter in **3-Si** than in **3-C**. The population of the perpendicular 3p orbital is only 0.11 e; thus, while C_1 and H_1 carry together about half of the excess charge in **3-C**, Si and H_1 together have 95% of the positive charge in **3-Si**.

Energies. As seen in Table II, **1-C**, **3-C**, and **5** appear to be less stable than the phenyl cation **2-C**. Through semiempirical corrections of the calculated singlet–triplet splitting, the singlet state in **2-C** was concluded to be the ground state, with the $^3B_1$ state lying some 20 kcal/mol higher in energy.[10a] Compared to singlet **2-C**,[10b] the pyramidal C_{5v} structure **1-C** is 25.6 kcal/mol higher in energy at the STO-3G level (Table II). The vinylic isomer **3-C** is 32.6 kcal/mol and the other capped isomer **5** is 68.3 kcal/mol above **2-C** at this basis set level. With the split valence basis set (4-31G//STO-3G), however, the capped, closed structures are severely destabilized relative to the open, planar ones. The separation between the singlet states of **1-C** and **2-C** increases to 62.0 kcal/mol, and **5** is now 99.9 kcal/mol higher in energy than **2-C**, while the separation to **3-C** remains about the same, 31.0 kcal/mol. A similar minimal-split valence basis set effect has been noticed, e.g., in the calculations on $C_5H_5^+$ isomers by Hehre and Schleyer[23a] and by Köhler and Lischka[23b] and in several calculations by us comparing capped and planar isomers. The addition of d functions to the basis set should favor the capped structures relative to the planar ones,[23b] but it is unlikely that the ordering would be reversed. Estimates of correlation energy also should reduce the energy difference between **1-C** and **2-C**.[23b] It might be noted, though, that **3-C** is lower in energy than any alternative cyclic $C_6H_5^+$ isomers considered by Castenmiller and Buck.[8a]

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(22) Schlegel, H. B.; Coleman, B.; Jones, M., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 6499.

(23) (a) Hehre, W. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 5837. (b) Köhler, H.-J.; Lischka, H. *Ibid.* **1979**, *101*, 3479.

The situation is quite different with the $C_5H_5Si^+$ isomers. The STO-3G calculations indicate the η^5 form **1**-Si to be the most stable conformer; the $^3B_1$ state of the silaphenyl cation **2**-Si is 32.6 kcal/mol higher in energy. The singlet and the other triplet state ($^3A_2$) of the silaphenyl cation and **3**-Si all lie about 100 kcal/mol higher in energy than the η^5 state of **1**-Si and do not seem to be competitive. As with the carbon analogues, use of the split valence basis (3-21G//STO-3G) results in the relative destabilization of the η^5 form (between 10 and 25 kcal/mol). However, with the inclusion of d orbitals on Si, the relative energies further favor the η^5 form by about 12–20 kcal/mol (STO-3G*//STO-3G vs. STO-3G//STO-3G). The $^1A_1$–$^3B_1$ separation in **2**-Si (62.0 kcal/mol) is considerably larger than that in **2**-C (18.2 kcal/mol at the STO-3G level),[10a] while the $^1A_1$–$^3A_2$ energy difference in **2**-Si is only 1.2 kcal/mol (10.1 kcal/mol in **2**-C)[10a]; in both cases the triplets are the lower lying states (STO-3G). A large part of the difference in energy between the two triplets in **2**-Si may be traced back to the orbital energy difference of 41.2 kcal/mol present between the b_1 and the a_2 orbital in the singlet silaphenyl cation. Since accurate multiplet separations are difficult to obtain theoretically, it is often convenient to attempt an empirical calibration of the separations by means of documented data from smaller, related systems. The singlet–triplet separation in silylene is calculated to be 15.7 kcal/mol at the STO-3G level with the singlet state as the ground state.[24] A far more extensive calculation by Meadows and Schaefer[25] gave 18.6 kcal/mol (empirically corrected to 10.0 kcal/mol) for this energy difference, while a photolysis experiment[26] produced a maximum value of 0.6 eV (13.8 kcal/mol). The STO-3G basis set may thus underestimate the stability of the $^3B_1$ state in SiH_2 relative to the singlet by a few kilocalories per mole. The unrestricted Hartree–Fock method applied here to the triplets mixes in states of higher spin multiplicities (quintets, heptets, ...), thus implicitly including some correlation energy and artificially lowering the triplets relative to the singlet. Unfortunately, the $^3B_1$ state of **2**-Si is heavily contaminated from such higher spin states ($\langle S^2 \rangle = 2.63$) as opposed to the $^3A_2$ state ($\langle S^2 \rangle = 2.16$) or the $^3B_1$ state in SiH_2 ($\langle S^2 \rangle = 2.003$).[24] The value of this added correlation energy would seem easily to exceed a few kilocalories per mole, making the $^1A_1$–$^3B_1$ separation of 62.0 kcal/mol in **2**-Si an upper bound. This implies that the calculated 32.6 kcal/mol separation between **1**-Si and the $^3B_1$ state of **2**-Si is a lower limit, but we must consider the expected basis-set dependence in the relative stability of pyramidal vs. planar structures. The relative destabilization of **1**-Si at a split valence basis set level is smaller than that of **1**-C, because of the larger apical–ring distance involved. Ahlrichs and Heinzmann[27] argued that the "mismatch" of p(π) orbitals on C and Si, present at a minimal basis set level and responsible for the claimed weakness of the Si–C double bond,[28] may be substantially relieved with extended basis sets. The gain in energy from the use of a more flexible valence basis roughly follows the double bond character in the Si–C and C–C bonds, i.e., **3**-Si $\approx$ **2**-Si($^1A_1$) $\approx$ **2**-Si($^3A_2$) > **2**-Si($^3B_1$) > **1**-Si. The addition of d functions preferentially stabilizes the pyramidal isomer **1**-Si relative to planar **2**-Si and **3**-Si. The ground state of the silaphenyl cation thus appears to be the $^3B_1$ state, and we expect this state to lie considerably above the singlet state of **1**-Si. This supports the suggestion of Aylett and Colquhoun.[2]

The binding energies for the half-sandwich structures may be estimated from eq 1 and 2. Using ground-state

$$C_6H_5^+ \ (\mathbf{1}\text{-C}) \rightarrow C_5H_5^+ + C \qquad (1)$$

$$C_5H_5Si^+ \ (\mathbf{1}\text{-Si}) \rightarrow C_5H_5^+ + Si \qquad (2)$$

energies calculated with molecular scaling factors for the dissociation products,[29] we find a binding energy for **1**-C (eq 1) of 73.3 kcal/mol at the STO-3G level but of only 28.3 kcal/mol at 4-31G. The inclusion of d functions in the basis set would preferentially lower the energy of **1**-C and increase the energy of eq 1.[23b] The binding energy in the silicon pyramid (eq 2) is calculated to be considerably larger, 153.7 kcal/mol at the STO-3G level and 192.9 kcal/mol at the STO-3G* level.

Conclusions

Two factors seem to be very important in determining the most stable isomer: (1) the efficient distribution of the excess charge to achieve overall maximum bonding and (2) the relative preference for double vs. single bonds. Molecules containing a Si–C double bond are chemically unstable.[27,28,30] Inspection of the different $C_6H_5Si^+$ isomers illustrates how strongly Si prefers to be bonded to C by single or even partially single bonds; the stabilities of the isomers and states follow closely the degree of double bond character in the Si–C bonds. Since carbon–carbon double bonds are considerably stronger than silicon–carbon double bonds (bond energies of 63 and 46 kcal/mol, respectively),[27] the electron deficiency is best associated with the weaker bonds in order to maintain efficient bonding elsewhere in the molecule. The electropositive Si can accommodate a large portion of excess charge with little reorganization of the remainder of the molecule. Carbon also prefers to be singly bonded, but the 6-π-electron aromaticity in **2**-C seems to be far better than the multicenter bonding in **1**-C. The more electronegative element, carbon, does not accommodate positive charge on one atom (e.g., the capping atom in **1**) satisfactorily, and significant geometrical changes are needed to distribute the charge optimally. This is observed especially in **5**.

If we classify the valence molecular orbitals with respect to the common C_s symmetry plane, we find that the singlet states of **2**-Si and **2**-C have eight symmetric and six antisymmetric orbitals,[31] while **1**-Si, **3**-Si, **1**-C, **3**-C, and **5** all have nine symmetric and five antisymmetric orbitals. Interconversions between the set of homomers[32] **1**-C, **3**-C, and **5** (or **1**-Si and **3**-Si) are therefore "allowed", but conversion from any of these to **2**-C (or **2**-Si) is "forbidden", involving a HOMO–LUMO crossing.[32] The rearrangement of **5** to **3**-C would seem to occur without too large a barrier, whereas **1**-C rearranging to **3**-C looks far more improbable with the necessary insertion of the apical carbon into the

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[24] Krogh-Jespersen, M.-B., unpublished data.

[25] Meadows, J. H.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1976**, *98*, 4383.

[26] Kasdan, A.; Herbst, E.; Lineberger, W. C. *J. Chem. Phys.* **1975**, *62*, 541.

[27] Ahlrichs, R.; Heinzmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7452.

[28] Damrauer, R.; Williams, D. R. *J. Organomet. Chem.* **1974**, *66*, 241. Curtis, M. D. *Ibid.* **1973**, *60*, 63.

[29] Planar $C_5H_5^+$: E(STO-3G) = −189.632 83 au, E(4-31G//STO-3G) = −191.646 48 au. Hehre, W. J. In "Modern Theoretical Chemistry"; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 4. C(^{3}P): E(STO-3G) = −37.198 39 au, E(4-31G) = −37.635 05 au. Si(^{3}P): E(STO-3G) = −285.466 23 au.

[30] Barton, T. T.; Wulff, W. D.; Arnold, E. V.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 2733. Elsheikh, M.; Pearson, N. R.; Sommer, L. H. *Ibid.* **1979**, *101*, 2491.

[31] Our count differs from that of ref 8a, which lists **2**-C as having seven symmetric and seven antisymmetric valence orbitals.

[32] Dewar, M. J. S.; Kirschner, S.; Kollmar, H. W. *J. Am. Chem. Soc.* **1974**, *96*, 5240.

carbon-hydrogen bond. Although **3**-C is indicated to be the lowest energy conformer among its set of homomers (31 kcal/mol below 1-C, 4-31G//STO-3G), the apparent lack of an easy pathway for rearrangement might lend some kinetic stability to 1-C, if it can be formed. A possible precursor is the pyramidal Hogeveen dication[7] $C_6R_6^{2+}$ which might dissociate to $C_6H_5^+$ and R^+ to reduce electrostatic repulsion. This process would be favorable if R^+ is a stable cation (e.g., *tert*-butyl). The $C_6R_5^+$ thus formed might be expected to retain the pyramidal structure of this dication.

We have not proven that 1-Si is the most stable $C_5H_5Si^+$ isomer, but this seems likely. It would seem imperative to place as much of the excess positive charge as possible on Si, but in alternative noncyclic structures this must lead to a structure with unfavorable Si-C multiple bonding. Although the energy estimates provided here may be only qualitatively correct, the geometries obtained should be reasonably reliable[33] and will be useful as starting points for higher level calculations (e.g., those combining split valence and d basis sets), when these become feasible.

Acknowledgment. We gratefully acknowledge the cooperation provided by the Regional Computation Center in Erlangen and the availability of an efficient geometry optimization program written by D. Poppinger and a single-precision version of GAUSSIAN 70 for the TR440 computer written by H.-U. Wagner. We thank M.-B. Krogh-Jespersen and E. D. Jemmis for valuable discussions and W. J. Hehre and J. A. Pople for supplying the 3-21G basis sets prior to publication. This work was supported by the Fonds der Chemischen Industrie at Erlangen and by a Merck Junior Faculty Development Grant at Rutgers.

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Gaseous Anion Chemistry. Negative Chemical Ionization of Acyl Chlorides, Diacyl Chlorides, and Perfluorodiacyl Chlorides

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We report here reactions of OH^- and $O^-\cdot$ in the gas phase with seven acyl chlorides, three diacyl chlorides, and two perfluorodiacyl chlorides through examination of negative chemical ionization mass spectra. With OH^- as the reactant, formation of the acetylenic alkoxide ion, $RC{\equiv}CO^-$, is favored. Reactions with $O^-\cdot$ typically are simpler than those with OH^- and show Cl^- as the most intense ion. In neither case are $(M-1)^-$ ions or ions containing chlorine seen. The intensity of $O^-\cdot$ spectra varies widely with structure. The reactions of perfluorosuccinyl and perfluoroglutaryl chloride are quite different from their nonfluorinated analogues, and loss of the elements of phosgene is an important process. There is some evidence for occurrence of intramolecular hydrogen transfer with $O^-\cdot$ as the reactant ion.

In recent years there have appeared the first reports of OH^- negative chemical ionization mass spectra of various types of organic compounds, including simple esters, ketones, and alcohols,[1] essential oils,[2] steroids,[3] methadone and its metabolites,[4] and both cyclic[5] and open-chain[6] diols. In the present study we have examined both the OH^- and the $O^-\cdot$ spectra of seven simple acyl chlorides, three straight-chain diacyl chlorides, and two perfluorodiacyl chlorides. Our studies have served to identify interesting chemical transformations brought about by anions in the gas phase, and these are discussed below.

When OH^- was used as the ionizing reagent, it was produced by reactions of $O^-\cdot$ from N_2O (eq 1) with either hydrogen or methane, following eq 2 or 3. The same methods have been used in previous studies in this laboratory.[1-3,6]

$$N_2O + e \rightarrow N_2 + O^-\cdot \tag{1}$$

$$O^-\cdot + H_2 \rightarrow OH^- + H \tag{2}$$

$$O^-\cdot + CH_4 \rightarrow OH^- + CH_3 \tag{3}$$

When the ionizing reagent was $O^-\cdot$, it was produced from N_2O as shown in eq 1. We have previously suggested that the other processes involving N_2O in this system are those summarized in eq 4-9, where reaction 9

$$O^-\cdot + N_2O \rightarrow [N_2O_2^-\cdot]^* \tag{4}$$

$$[N_2O_2^-\cdot]^* \rightarrow O_2^-\cdot + N_2 \tag{5}$$

$$[N_2O_2^-\cdot]^* \rightarrow NO^- + NO \tag{6}$$

$$[N_2O_2^-\cdot]^* + N_2O \rightarrow NO_2^- + NO + N_2 \tag{7}$$

$$[N_2O_2^-\cdot]^* + N_2O \text{ (or M)} \rightarrow N_2O_2^-\cdot + N_2O \text{ (or M)} \tag{8}$$

$$X^- \rightarrow X + e \tag{9}$$

is any electron-loss process that may take place.[6] We have discussed our reasons for preferring this scheme to that discussed earlier by Caledonia.[7] Also, we have noted[6] that we have no way of ascertaining whether spectra determined in N_2O alone result specifically from reaction of $O^-\cdot$ with the substrate molecule or alternatively arise through transfer of $O^-\cdot$ to the molecule from some other species, presumably NO_2^-, that is formed in reactions 4-9. For convenience and simplicity, however, we discuss these

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