

A Theoretical Study of Mechanisms of 1,3-Silyl Migration in Formylmethylsilane and Related Migrations. Comparison with Allylsilane

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Abstract: Two concerted pathways leading to retention and inversion of stereochemistry at the migrating silicon center were found for the isomerization of formylmethylsilane to siloxyethene by ab initio molecular orbital calculations. The activation energy for the retention pathway has been calculated at the MP2/6-311++G(3df, 2p)/MP2/6-311++G** level to be 32 kcal/mol, which is ca. 30 kcal/mol smaller than that for the inversion pathway. The predicted exclusive retention stereochemistry and the calculated activation energy are in good agreement with the experimental results for a silylmethyl ketone with an optical active silyl group. Remarkable differences in the retention transition structures between the 1,3-silyl migrations in formylmethylsilane and the 1,3-silyl migrations in allylsilane are revealed by detailed analysis of geometries, natural bond orbitals, and the Laplacian ($\nabla^2\rho$) of the wave function. The retention 1,3-silyl migration in formylmethylsilane is best described as an intramolecular nucleophilic substitution at silicon, while the corresponding 1,3-silyl migration in allylsilane is as an electrocyclic sigmatropic rearrangement controlled by subjacent orbital interactions. For related 1,3-migrations in $\text{HC(=O)CH}_2\text{MH}_3$ ($\text{M} = \text{C, Si, Ge, Sn}$), the E_a values for the retention pathway are much lower than the inversion pathway and they decrease in the following order: $\text{M} = \text{C} \gg \text{Si} > \text{Ge} > \text{Sn}$ (as expected from the relative stability of the pentacoordinate structure among the metals). A facile 1,3-migration from carbon to nitrogen in iminomethylsilane is predicted to occur with retention stereochemistry via an intramolecular nucleophilic substitution, which is similar to that in formylmethylsilane.

Introduction

Although a large number of concerted thermal 1,3-migrations of a group-14 element group have been known, their mechanistic aspects are rather complicated. Following the Woodward–Hoffmann rules,¹ suprafacial 1,3-migration with retention at the migrating center (suprafacial-retention) is symmetry-forbidden; antarafacial-retention and suprafacial-inversion processes are allowed, though they are usually sterically disfavored. However, the suprafacial-retention process, which includes carbon as the migrating center, has been observed in several sophisticated systems.^{2–4} This exception of the Woodward–Hoffmann rules is rationalized by invoking the so-called subjacent orbital control,^{3b,c} where the transition state is stabilized by the interaction between the next HOMO of allyl π system and the pertinent orbital at the migration center.

On the other hand, compared to carbon groups or hydrogen,⁵ 1,3-silyl migrations are quite common because of their high migratory aptitudes. Intramolecular thermal 1,3-migrations have been well established to occur concertedly in allylic silanes⁶ and in silylmethyl ketones.⁷ These migrations have been considered until quite recently to be distinguished mechanistically by the striking difference in the stereochemical outcome investigated using an optical active silyl group; 1,3-silyl migrations in allylic silanes⁶ and silylmethyl ketones⁷ were found to occur with inversion and retention stereochemistry, respectively.

Recent theoretical studies by us⁸ and Yamabe et al.⁹ have revealed, however, that for thermal 1,3-silyl migration in $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$, the two concerted pathways which lead to retention and inversion at the silicon are both allowed with the retention pathway being lower in energy.⁸ In our previous paper,⁸ the following points were noted: (1) The activation energy for the retention pathway is lower than that for the

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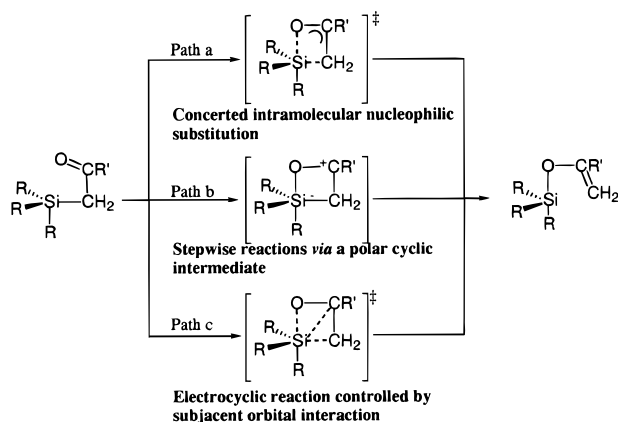
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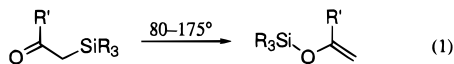
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Scheme 1



inversion pathway by ~ 9 kcal/mol, (2) the energy of the retention transition structure is lowered by significant adjacent orbital interaction, that is, orbital interaction between 3p orbital on the migrating silicon and the occupied allylic π orbital.^{3b,c} In good accordance with the theoretical results, we have recently obtained the first experimental evidence for the retention stereochemistry in the thermal 1,3-silyl migration in allylic silanes and have demonstrated the significant dependence of the stereochemical outcome on the substituents at silicon.¹⁰ These recent advancements in the mechanistic view of the 1,3-silyl migration caused us to further investigate the mechanisms of the related 1,3-silyl migration in silylmethyl ketones theoretically.

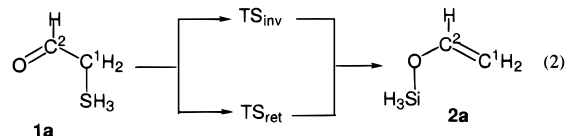
The first uncatalyzed thermal 1,3-silyl migration in silylmethyl ketones giving the corresponding siloxyalkenes was reported by Brook et al. in 1967.⁷



Although much attention has been focused on the mechanistic comparison of the 1,3-migration in silylmethyl ketones and in allylsilanes, the mechanism for 1,3-migration in silylmethyl ketones has been controversial.⁵ Three pathways in Scheme 1 have been taken into consideration. Brook et al. proposed a concerted four-center mechanism with synchronous Si–O bond-making and Si–C bond-breaking (pathway a in Scheme 1) on the basis of the exclusive retention of the configuration at silicon in the reaction products and relatively insensitive substituent and solvent polarity effects on the migration rates.^{5a} Although the possibility of a fully associative mechanism involving the formation and pseudorotation of polar pentacoordinate silicon intermediates was addressed (pathway b in Scheme 1),^{5a} it was ruled out.¹¹ On the other hand, Kwart and Barnette¹² claimed that since the kinetic data reported by Brook et al.^{11a} and others^{11b} were accumulated at temperatures close to the isokinetic temperature, the substituent effects might not have meaningful mechanistic information. They concluded that pathway b in Scheme 1 is operating, on the basis of the solvent effects on the rates, kinetic isotope effects,¹² and the different stereochemical outcome between the 1,3-silyl migrations in allylsilanes⁶ and in silylmethyl ketones.⁷ Our recent theoretical results on the 1,3-silyl migration in allylsilane suggest that the

migration in silylmethyl ketones may proceed via a concerted pathway controlled by a adjacent orbital interaction (pathway c in Scheme 1).

In this paper, we report the results of the detailed ab initio molecular orbital calculations for the mechanisms of the 1,3-migrations of group-14 element groups in $\text{HC}(\text{=O})\text{CH}_2\text{MH}_3$ ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{and Sn}$) and $\text{HC}(\text{=NH})\text{CH}_2\text{SiH}_3$; effective core potentials were used for Ge and Sn. We show that the retention 1,3-silyl migration in formylmethylsilane is best described as an intramolecular nucleophilic substitution at silicon, while the corresponding migration in allylsilane is as an electrocyclic sigmatropic rearrangement controlled by adjacent orbital interactions.



Computational Details

Ab initio molecular orbital calculations were performed using the Gaussian 94 program¹³ running on an IBM/RS6000. Optimized structures and the molecular orbitals were drawn by the MOLDEN software on an SGI O2 computer. The geometries of all stationary points were fully optimized at the MP2(full)/6-311++G** level of theory and in some cases at the MP2(full)/6-31G* and HF/6-31G* levels. The stationary points were characterized by frequency analysis (minimum with 0, transition state with 1 imaginary frequency). For transition structures, the intrinsic reaction coordinate (IRC) calculations were used to follow reaction pathways. The calculations for molecules containing germanium and tin were performed using LanL2DZ basis set with effective core potentials by Hay and Wadt¹⁴ for Ge and Sn. Bond critical points and ring critical points were obtained using Bader's topological one-electron density analysis with the MP2(fc)/6-311++G** wave functions at the HF/6-31G* optimized geometry.¹⁵

The displacements of the pentacoordinate transition structures from the ideal TBP (trigonal bipyramidal geometry) toward the ideal SP (square pyramidal geometry) were estimated (as a percentage), using the method of Holmes et al.^{8,16}

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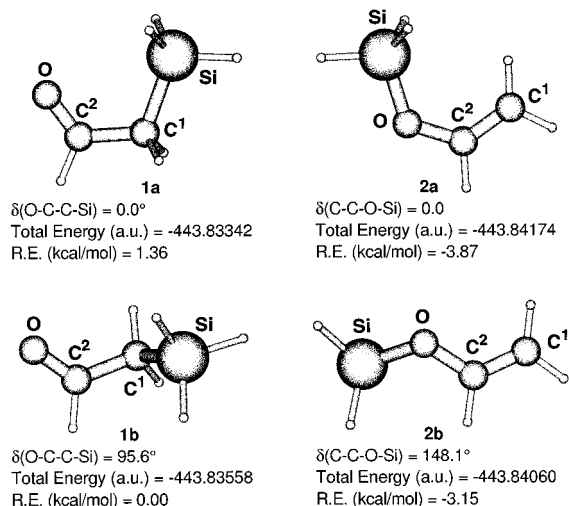


Figure 1. Optimized structures of formylmethylsilane (**1a** *synperiplanar*, **1b** *anticlinal*) and siloxyethene (**2a** *synperiplanar*, **2b** *anticlinal*). Total energy is shown in a.u. for each structure. The relative energy (R.E.) is given relative to the energy for **1b**. The structure and the energy are obtained at the MP2(full)/6-311++G** level. Selected bond lengths (\AA): **1a**: C²–O 1.217, C¹–C² 1.506, and C¹–Si 1.893; **1b**: C²–O 1.217, C¹–C² 1.506, and C¹–Si 1.893; **2a**: C²–O 1.361, C¹–C² 1.314, and O–Si 1.679; **2b**: C²–O 1.367, C¹–C² 1.337, and O–Si 1.674.

Results and Discussion

Geometry. Geometrical parameters of all stationary points for the 1,3-silyl migration in formylmethylsilane at various theoretical levels are listed in Table S1 as Supporting Information. The MP2/6-311++G** level of calculations is used for structural discussion throughout the paper unless otherwise noted.¹⁷ Since the structures calculated at the 6-31G* levels are in agreement with those calculated at the 6-311++G** levels within errors of 0.01 \AA in bond lengths, 1° in bond angles, and 5° in dihedral angles, the results at the 6-31G* level were used to compare the geometrical characteristics of the transition states with those reported previously⁸ for the 1,3-silyl migration in allylsilane.

(a) Optimized Structures of Formylmethylsilane and Siloxyethene. Two conformers were found for formylmethylsilane (**1a** and **1b**) and siloxyethene (**2a** and **2b**), as shown in Figure 1. An *anticlinal* formylmethylsilane (**1b**) with an OCCSi dihedral angle of 95.6° is 1.36 kcal/mol more stable than a *synperiplanar* formylmethylsilane (**1a**) with an OCCSi angle of 0° . This is probably due to the effective hyperconjugation between the C=O π orbital and the C–Si σ orbital in **1b**. In the siloxyethene, the *synperiplanar* conformation **2a** ($\angle\text{C-C-O-Si} = 0^\circ$) is only 0.72 kcal/mol more stable than that of the *anticlinal* conformation **2b** ($\angle\text{CCOSi}$ angle = 148.1°). The energy difference between **1b** and **2a** is only 4 kcal/mol, which indicates that the reaction is nearly thermoneutral and that the mechanism is not driven by thermodynamics.

(b) Transition Structures. Two transition structures were obtained for the 1,3-silyl migration between formylmethylsilane and siloxyethene (at all levels of calculations used). Although the two transition structures (TS_{ret} and TS_{inv} in Figure 2) are both four-centered cyclic structures, TS_{ret} structures lead to retention, and TS_{inv} structures lead to inversion of the configuration at the migrating silicon atom. Since the two transition

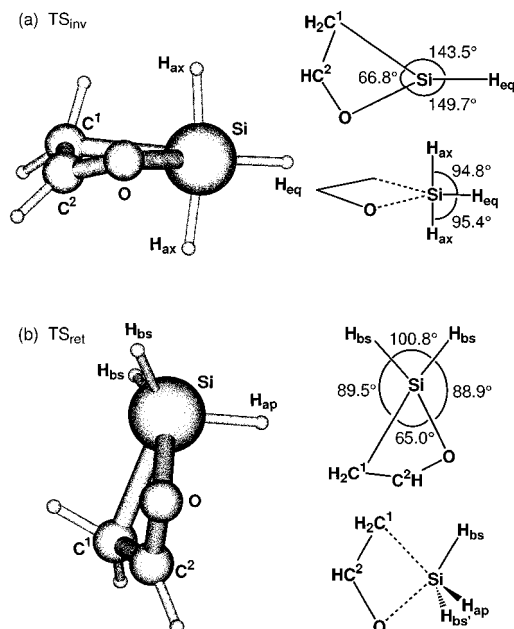


Figure 2. Optimized transition structures for the isomerization of formylmethylsilane with inversion (TS_{inv}, (a)) and retention (TS_{ret}, (b)) of configuration at the MP2(full)/6-311++G** level. An equatorial plane of TS_{inv} and a basal plane of TS_{ret} are shown on the right side of the figures schematically. Selected bond lengths (\AA) for TS_{inv}: C²–O 1.293, C¹–C² 1.402, C¹–Si 2.299, and O–Si 1.934; TS_{ret}: C²–O 1.286, C¹–C² 1.392, C¹–Si 2.238, and O–Si 1.935.

structures were obtained also at the HF/6-31G level, it is evident that *d*-functions are not essential for the formation of the transition structures, while previous semiempirical MO calculations suggested the indispensable participation of the *d*-orbitals.^{11a} Pentacoordinate silicon *intermediates*, as suggested by Kwart and Barnette,¹² were not found, which is indicative of the concerted nature of the migration; the IRC (intrinsic reaction coordinate) calculations confirm that both TS_{ret} and TS_{inv} connect **1a** and **2a** (vide infra).

The C¹–C² and C²–O bond lengths of the transition structures are intermediate between the corresponding bond lengths of reactant **1** and product **2**. While the average value of C¹–C² is 1.424 (C-C_{av}) and the average value of C²–O is 1.289 \AA (C-O_{av}), the C¹–C² bond of TS_{inv} (1.402 \AA) is shorter than C-C_{av} and the C²–O bond (1.302 \AA) is longer than C-O_{av} . The inversion pathway thus proceeds via a somewhat later transition state. On the other hand, the C²–O (1.286 \AA) and C¹–C² bonds (1.392 \AA) of TS_{ret} are shorter than C-O_{av} and C-C_{av} . Therefore, it cannot be determined whether TS_{ret} is early or late, but the results suggest that the major contribution to the Si–O bond formation at TS_{ret} comes from the oxygen lone-pair electrons and not from the C–O π electrons. The C¹–Si and O–Si bonds in TS_{inv} (TS_{ret}) are 21 (18) and 16% (17%) longer than C¹–Si bond of **1a** and the O–Si bond of **2a**, respectively.

When the transition structures are classified as the pentacoordinate silicon structure,¹⁶ TS_{inv} is assigned to be TBP (trigonal bipyramidal) and TS_{ret} is assigned to be SP (square pyramidal). Using Holmes method¹⁶ the % SP values for TS_{inv} and TS_{ret} are estimated to be 36.6 and 66.7%, respectively (at HF/6-31G*). The correspondence is similar to that in allylsilane. However, the degree of distortion from the ideal TBP or SP is much larger in formylmethylsilane than in allylsilane (%SP value for TS_{inv} is 14.5 and for TS_{ret} is 88.8%).⁸ The equatorial plane of the TBP structure in TS_{inv} is formed by oxygen, an oxallyl carbon, and one silyl hydrogen (H_{eq}) (Figure 2a); the

(17) The MP2 results give slightly longer bond lengths than the HF calculations. See: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; pp 194–197.

sum of the three bond angles of C¹–Si–O, C¹–Si–H_{eq}, and O–Si–H_{eq} is 360°. The other two silyl hydrogens in TS_{inv} occupy the axial positions (H_{ax}) with an H_{ax}–Si–H_{ax} angle of 169.8°. Although electronegative atoms such as oxygen are known to favor the axial position in the TBP structure,¹⁸ the oxoallyl oxygen in TS_{inv} cannot occupy the axial position due to the steric reason. Two silyl hydrogens, the oxoallyl carbon, and oxygen make the basal plane of the distorted SP structure in TS_{ret} (Figure 2b); as expected, the Si–H_{ap} bond length of 1.488 Å is somewhat longer than the lengths of other two Si–H bonds (1.469 and 1.480 Å). The silyl group in TS_{ret} for formylmethylsilane is rotated around the formal C₃ axis by about 30° from that in TS_{ret} for allylsilane, suggesting that the structure around silicon in TS_{ret} for formylmethylsilane is regarded also as a distorted TBP, where one basal hydrogen (H_{bs} in Figure 2b) and oxygen atom occupy the axial positions.

While the C¹–Si–O angle in TS_{inv} (66.8°) is similar to that in TS_{ret} (65.0°), the angle strain in TS_{inv} is much larger than that in TS_{ret} because the ideal angle for TBP is 120° and the ideal angle for SP is 90°. The difference in the angle strain may be in part the reason for the lower activation energy of the retention pathway than that of the inversion pathway.

Significant differences between the transition structures of formylmethylsilane and those of allylsilane are observed in the puckering angles of the four-membered rings. At the HF/6-31G* geometry, the Si–O–C¹–C² dihedral angle of TS_{inv} and TS_{ret} are 139.3 and 147.1° for formylmethylsilane, while the corresponding Si–C³–C¹–C² angles for allylsilane are 103.4 and 94.2°, respectively. As previously⁸ pointed out, the retention transition structure in allylsilane is stabilized by subjacent orbital control. For TS_{ret} of formylmethylsilane, however, such subjacent orbital interaction cannot be expected since the ring structure is relatively flat.

IRC Calculations. The IRC calculations confirm that both TS_{ret} and TS_{inv} connect **1a** to **2a** in Figure 1.¹⁹ The structural changes along the IRC of the retention pathway suggest that oxygen attacks the axial site of the silicon center and that oxoallyl carbon leaves directly from an equatorial site without pseudorotation around the silicon center (retention path in Figure 3). On the other hand, in the inversion pathway, pseudorotation is involved during formation of TS_{inv} via the initial axial attack of the oxoallyl oxygen on silicon (inversion path in Figure 3), with the oxoallyl carbon leaving from an equatorial position. Although elimination of an axial ligand from a pentacoordinate silicon intermediate is usually favored over the elimination of an equatorial ligand,^{18,20} several reactions are known theoretically to proceed via the elimination of an equatorial ligand.²¹

Activation Energies. The activation energies (E_a) for TS_{ret} and TS_{inv} calculated at various levels are listed in Table 1. The

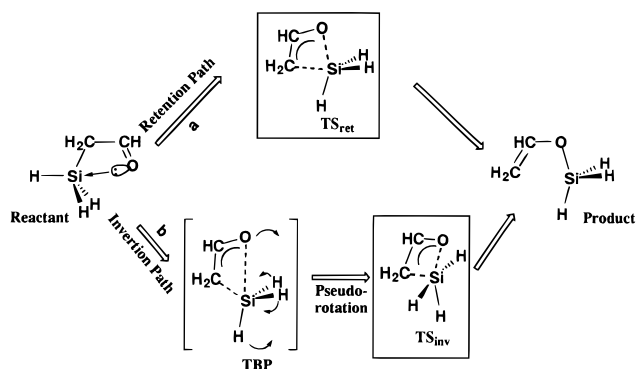


Figure 3. Schematic representation of the structural change along the intrinsic reaction coordinate.

Table 1. Relative Energies^a of TS_{ret} and TS_{inv} for 1,3-Silyl Migration in Formylmethylsilane

level	TS _{inv}	TS _{ret}
MP2/6-31G* ^b	65.79	35.44
MP2/6-311++G** ^b	66.31	37.15
MP2/6-31G* ^c	65.92	35.55
MP2/6-311++G(3df,2p) ^d	60.56	31.83
MP2/6-311++G(3df,2p) ^d +ZPE ^e	60.65	31.82

^a Relative to **1a**, in kcal/mol. ^b Full optimization. ^c Single point calculation at the HF/6-31G* geometry. ^d Single point calculation at the MP2(full)/6-311++G** geometry. ^e Zero point energy (ZPE) is the results at the MP2(full)/6-311++G** level.

activation energy for the retention pathway ($E_a(\text{ret}) = 30\text{--}40$ kcal/mol) is much lower than that for the inversion pathway ($E_a(\text{inv}) = 60\text{--}70$ kcal/mol); this clearly shows that the inversion pathway cannot compete with the retention pathway. This is in agreement with the experimental results for a silylmethyl ketone with an optical active silyl group. The experimental activation energies of ~ 30 kcal/mol¹¹ are reproduced well by the calculations at the MP2/6-311++G(3df,2p) level. It is interesting to note that $E_a(\text{ret})$ for formylmethylsilane (36 kcal/mol) is much lower than that for allylsilane (54 kcal/mol), while $E_a(\text{inv})$ values for both allylsilane and formylmethylsilane are similar (63 and 66 kcal/mol, respectively, at MP2/6-31G*/HF/6-31G* level). These results suggest that the transition structures and the mechanisms for 1,3-migrations in allylsilane and formylmethylsilane for the retention pathways are very different, while those for the inversion pathways are similar.

HOMOs of the Transition Structures. The HOMOs of TS_{inv} and TS_{ret} for formylmethylsilane are compared with those for allylsilane in Figure 4. The HOMO and the next HOMO of TS_{inv} for allylsilane are close in energy; HOMO is constructed by the bonding interaction between allylic antisymmetric π orbital and 3p orbital at silicon while next HOMO is constructed by the antibonding interaction between the lowest symmetric allyl π orbital and an orbital of T-shaped SiH₃ moiety (see also Figure 3 in our previous paper⁸). The HOMOs of TS_{inv} for formylmethylsilane are significantly modified due to the effects of the electronegative oxygen, but the essential feature is understood by the interaction between oxoallyl π orbitals and pertinent orbitals of SiH₃ moiety; flattening of the cyclobutane ring of TS_{inv} and the lowering of the second lowest allyl π orbital due to the electron-withdrawing effects of oxygen make the contribution of the 3p orbital at silicon to the HOMOs less important. On the other hand, the HOMO of TS_{ret} for formylmethylsilane is very different from that for allylsilane,^{8,9} which is composed of the allylic antisymmetric π orbital and a pseudo π orbital of two Si–H orbitals. In the HOMO of TS_{ret} for

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(19) Although IRC calculations using simple internal coordinates and mass-weighted internal coordinates, (dynamically defined as a minimum energy trajectory that goes infinitely and slowly from a transition state to either the reactant or the product), generally provide the same products and reactants, the two calculations sometimes give different results because of branching of the reaction pathway. The mass-weighted internal coordinates give reactant **1a** (*synperiplanar*) and product **2a** (*synperiplanar*) from both TS_{inv} and TS_{ret} for formylmethylsilane, while simple internal coordinates give reactant **1b** (*anticlinal*) from TS_{inv}. This discrepancy indicates that there is a divergence point between **1a** and **1b** in the inversion pathway. A similar divergence has been pointed out in the case of 1,3-silyl migration in allylsilane.⁹ See also: Ayala, P. Y.; Schlegel, H. B. *J. Chem. Phys.* **1997**, *107*, 375.

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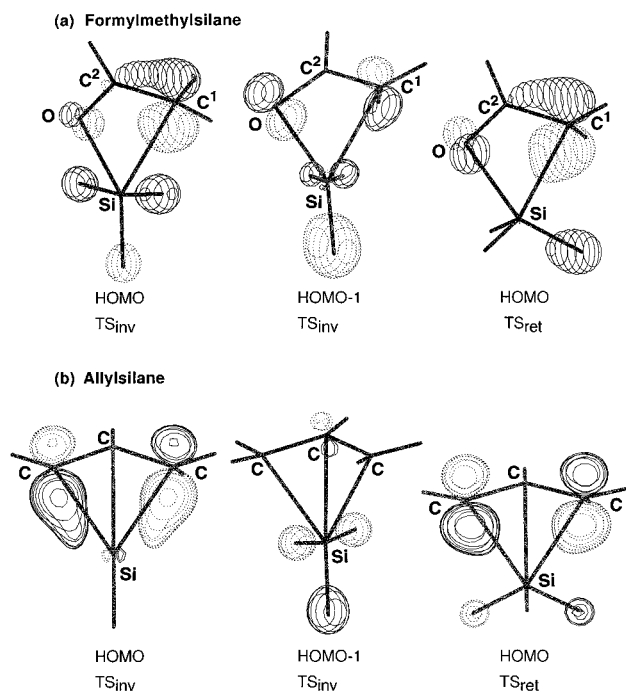


Figure 4. Schematic representation of the HOMO and HOMO-1 of TS_{inv} (left) and HOMO-1 of TS_{ret} (right) for 1,3-silyl migration in formylmethylsilane (a) and in allylsilane (b). Orbital energies in a.u. at HF/6-31G*: (a) -0.35064 (HOMO), -0.40188 (HOMO-1) for TS_{inv}, -0.35307 (HOMO) for TS_{ret}. (b) -0.33860 (HOMO), -0.34405 (HOMO-1) for TS_{inv}, -0.27301 (HOMO) for TS_{ret}.

Table 2. Calculated Properties of Stationary Points for 1,3-Silyl Migration in Formylmethylsilane Calculated at the MP2(full)/6-311++G** Level

	1a	2a	TS _{inv}	TS _{ret}
dipole moment (Debye)	3.25	0.73	2.04	2.68
qSi ^a	1.08	1.38	1.32	1.21
qSiH ₃ ^b	0.44	0.65	0.51	0.49

^a Partial charges at the migrating atom Si obtained by natural population analysis. ^b Sum of partial charges in the migrating group obtained by natural population analysis.

formylmethylsilane, the oxygen's lone-pair orbital (which is a π -type but perpendicular to the π_{CO} orbital) is incorporated significantly. As shown in a previous section, the structure of TS_{ret} for formylmethylsilane is mainly SP but has a significant TBP character as analyzed by the Holmes' method.¹⁶ From this view, the HOMO of TS_{ret} looks very similar to the HOMO (nonbonding orbital) of a TBP silicate having oxygen and silyl hydrogen at the axial positions.

Natural Bond Orbital Analysis of the Total Density in Transition Structures. The IRC calculations confirm the concerted nature of the 1,3-silyl migration in formylmethylsilane and rule out the polar mechanism via a zwitterionic intermediate proposed by Kwart et al.¹² However, since Kwart et al. observed significant lowering of the activation energy in the 1,3-silyl migration of a silylmethyl ketone in polar solvents, it is of interest to study the polarity of the transition states. The dipole moments and charge distribution of all the stationary points in the 1,3-silyl migration in formylmethylsilane are listed in Table 2. The dipole moments of TS_{ret} and TS_{inv} are intermediate between 1a and 2a in Figure 1, and the polarity during the migration from 1a (3.25 D) to the transition states (2.04 and 2.68 D) is reduced. NPA (natural population analysis) charges of the migrating center (qSi) and group (qSiH₃) increase along the reaction pathways from 1a to the transition structures but

Table 3. Hybridization at O and C¹ in TS_{inv} and TS_{ret} for the 1,3-Migration in Formylmethylsilane^a

atom	bonding	TS _{inv}	TS _{ret}
O	O–C ² (σ)	sp ^{1.8}	sp ^{2.0}
	O–C ² (π)		p _{π} (99.55%)
	O–Si	p _{σ} (89.91%)	sp ^{3.0}
	lone pair (s type)	sp ^{1.3}	sp ^{1.4}
	lone pair (p type)	p (88.29%)	
C ¹	C ¹ –C ² (σ)	sp ^{2.1}	sp ^{2.2}
	C ¹ –C ² (π)	p _{π} (93.69%)	
	C ¹ –H	sp ^{2.1}	sp ^{2.3}
	C ¹ –H	sp ^{2.4}	sp ^{2.6}
	lone pair (p type)		p (89.81%)

^a The results of natural bond orbital calculation at the MP2(full)/6-311++G** level of calculation.

the extent is very small. Although the reason remains open, these results may not be compatible with the observed solvent effects in the 1,3-migration in the silylmethyl ketone.

The above analysis shows that the retention migration in formylmethylsilane is not compatible with the electrocyclic sigmatropic rearrangement controlled by subjacent orbital interactions found for the retention migration in allylsilane.^{8,9} The lone-pair electrons of the oxygen are suggested to play a significant role in the transition state. To elucidate the characteristics of the retention transition structure for 1,3-silyl migration of formylmethylsilane, a natural bond orbital analysis (NBO)²² of TS_{ret} was performed where the occupancy threshold for the NBO search was taken to be 1.90 for TS_{ret}, but was lowered to 1.70 in TS_{inv}; four heavy atoms (C, C, O, Si) were located close to the x - y plane. There are eight doubly occupied (more than 1.999) core orbitals, 10 bonding orbitals, and two lone pairs for both TS_{inv} and TS_{ret}.²³ In TS_{inv}, one lone-pair orbital is an sp-type (occupancy of 1.971; 43% s character and 57% p character) and the other is a p-type oxygen (occupancy of 1.841; 88% p-character). While in TS_{ret}, one lone-pair orbital is an sp-type (occupancy of 1.973; 42% s character and 58% p character) and the other is a p-type carbon (occupancy of 1.402; 90% p-character). The p-type carbon lone pair is in the direction pointing to the silicon center. As shown in Table 3, the hybridization on O and C¹ indicates that the sp² hybrids (double bonds) exists on C¹–C² in TS_{inv} and on O–C² in TS_{ret}. These results are compatible with the characteristics of the transition states drawn from their geometries and from the IRC analysis (Figure 3).

Topological Comparison of TS_{ret} between Formylmethylsilane and Allylsilane. Theoretical calculations of the 1,3-silyl migrations in allylsilane and in formylmethylsilane indicate that both migrations proceed concertedly via a four-membered cyclic transition structures, preferably with retention of configuration at the migrating silicon atom. However, the above theoretical results suggest also that the electronic and geometric properties of the retention transition structures in the two reactions are quite different in character. To gain further insight into the electronic differences between the two retention transition states, Bader's topological analysis¹⁵ was carried out. As shown in Table 4, one ring critical point was surrounded by

(22) (a) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1988**, 169, 41. (b) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, 102, 7211. (c) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, 83, 1736. (d) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, 78, 4066 (e) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, 83, 735. (f) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899.

(23) No bonding interaction was found between C¹ and Si in TS_{inv} for formylmethylsilane. Although TS_{inv} is assigned to be a strongly distorted TBP structure, it may be regarded as a tetracoordinate structure around the silicon center.

Table 4. Electron Density (ρ), Laplacian ($\nabla^2\rho$) and Ellipticity (ϵ) at Bond and Ring Critical Points around Pentacoordinated Silicon of TS_{ret} in Formylmethylsilane and in Allylsilane^a

critical point	TS_{ret} (formylmethylsilane)			TS_{ret} (allylsilane)				
		ρ	$\nabla^2\rho$	ϵ	ρ	$\nabla^2\rho$	ϵ	
(3,-1) ^b	apical	H _{ap} -Si	0.122	0.289	0.023	0.122	0.288	0.033
	basal	H _{bs} -Si	0.120	0.276	0.019	0.118	0.258	0.013
		C ¹ -Si ^b	0.118	0.266	0.017			
	other ^c	O-Si ^b	0.056	3.97×10^{-4}	0.509			
		C ² -Si ^b	0.074	0.28	0.046			
(3,+1) ^b		Si-O-C ² -C ¹ ^c	0.049			0.061	0.067	7.113

^a Units of $\rho = e/\text{au}^3$ and $\nabla^2\rho = e/\text{au}^5$. MP2(fc)/6-311++G** wave functions were used at the HF/6-31G* geometry. ^b According to the topological analysis of the density, a chemical bond is characterized by a (3,-1) "bond" critical point of the Laplacian ($\nabla^2\rho$) between the bonding nuclei; a site of nucleophilic attack or a characteristic structure of a ring is often characterized by a (3,+1) "ring" critical point.¹⁵ The terminal and central carbons in formylmethylsilane and allylsilane are denoted as C¹ and C², respectively.

Table 5. Relative Energies^a for the 1,3-MH₃ Migration in $\text{HC(=O)CH}_2\text{MH}_3$ (M = C, Si, Ge, and Sn) and in Iminomethylsilane

compd	level ^b	TS_{inv}	TS_{ret}
1	HF/6-31G*	74.24	42.99
3	HF/6-31G*	125.21	119.64
1	LanL2DZ ^c	84.60	52.09
4	LanL2DZ ^c	75.97	46.58
5	LanL2DZ ^c	56.33	29.76
6	HF/6-31G*		39.09

^a Relative to the *anticlinal* isomer of the reactant, in kcal/mol. ^b Full geometry optimization. ^c Dunning/Fuzinaga full double- ζ on first row, Los Alamos effective core potential plus double- ζ on Ge and Sn.

a four-membered ring (Si-O-C²-C¹) but there was no bond critical point between Si and C² in TS_{ret} of formylmethylsilane.²⁴ The ring critical point Si-O-C²-C¹ is almost in the plane of O-Si-C¹ but slightly displaced from the Si-O-C¹ plane toward C². Two bond critical points are found between C¹ and Si and between O and Si of the TS_{ret} in formylmethylsilane.

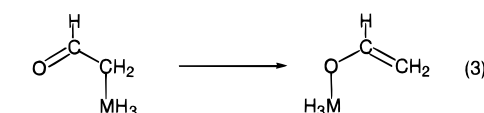
In the TS_{ret} of allylsilane, there is a bond critical point between Si and C². The high ellipticity at the bond critical point (C²-Si), which indicates a rather unsymmetric distribution of the electron density around the C²-Si bond at this point, can be related to the significant orbital interaction between the subjacent bonding π -orbital of the allyl moiety and the Si 3p orbital. Although only four bond critical points are found around silicon in the TS_{ret} of allylsilane, the bond critical point of C²-Si may represent the bonding between the silicon and three allylic carbons.

When the Laplacian ($\nabla^2\rho$) at a bond critical point is positive, the bonding is characterized as a closed-shell interaction (ionic and hydrogen bonds). When the $\nabla^2\rho$ value is negative, the bonding is characterized as a shared interaction (covalent bond).^{15a} By using this criterion, all the bonding interactions listed in Table 4 are dominated by a closed-shell interaction.

The clear difference in the Laplacians between the retention transition structures for allylsilane and formylmethylsilane can be interpreted as the mechanistic difference between the two migrations; the retention 1,3-silyl migration in formylmethylsilane is best described as an intramolecular nucleophilic substitution at silicon, while the corresponding migration in

allylsilane is assigned to an electrocyclic sigmatropic rearrangement controlled by subjacent orbital interactions.

Related 1,3-Metal Migrations. Similar theoretical calculations are extended to related 1,3-migrations of other group-14 element groups in $\text{HC(=O)CH}_2\text{MH}_3$ (M = C (**3**), Ge (**4**), and Sn (**5**)) (eq 3), and the results are compared with those for formylmethylsilanes. For this purpose, calculations for **1**, **4**, and **5** were performed using the LanL2DZ level¹⁴ and a comparison between **3** and **1** was performed at the HF/6-31G* level.



M = C (**3**), Si (**1**),
Ge (**4**), Sn (**5**)

Activation energies for these 1,3-migrations are shown in Table 5. We found in our previous study of the 1,3-methyl migration in 1-butene⁸ that E_a for the inversion pathway was lower than that for the retention pathway, which is in line with the prediction of the Woodward-Hoffmann symmetry rules.¹ In contrast, for **3**, the E_a value for TS_{inv} is higher than that for TS_{ret} . The concerted 1,3-methyl migration in propanal is predicted to proceed via an intramolecular nucleophilic displacement with retention of stereochemistry. This pathway is not realistic because E_a for the C-C bond dissociation is much lower.²⁵

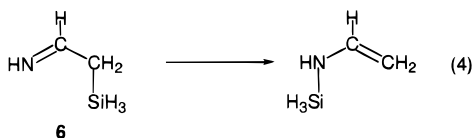
For both the inversion and the retention pathways of the 1,3-metal migrations, the E_a values decrease in the following order: **1** (M = Si) > **4** (M = Ge) > **5** (M = Sn), as expected from the relative stability of the pentacoordinate structure among the metals. In contrast to the 1,3-migrations in allylgermane and allylstannane, the activation energies of the retention pathways for **4** and **5** are much lower than the dissociation energies of the Ge-C and the Sn-C bonds, respectively.²⁵ Therefore, the concerted migration is expected to predominate over the competitive C-metal bond dissociation.

As shown in Table 5, theoretical calculations predict that a facile 1,3-migration from carbon to nitrogen in iminomethylsilane **6** occurs with retention stereochemistry via an intramolecular nucleophilic substitution, which is similar to that in formylmethylsilane. The calculated activation energy for the retention migration in **6** is similar to that for the corresponding migration in formylmethylsilane **1**. The transition structure for

(24) A (3,-1) critical point means that two curvatures of the Laplacian of ρ are negative (ρ is a maximum at this point) along two axes in the corresponding plane and a curvature is positive (ρ is a minimum at this point) along the third axis which is perpendicular to the plane. A (3,+1) critical point means that two curvatures of the Laplacian of ρ are positive (ρ is a minimum at this point) along two axes in the corresponding plane and a curvature is negative (ρ is a maximum at this point) along the third axis which is perpendicular to the plane.

(25) The BDE values of M-C in MMe_4 are reported to be 85.6, 74.4, 59.5, 51.9 kcal/mol for M = C, Si, Ge, and Sn, respectively: *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, p 5.

the inversion pathway was not found for the migration in **6**; a search starting from the structure with inversion of configuration leads to the transition state with retention of configuration.



Concluding Remarks

In this theoretical study, we have found that the concerted 1,3-silyl migration in formylmethylsilane occurs exclusively with retention of configuration at the silicon atom. The calculated activation energy as well as the retention stereochemistry is in good agreement with the experimental results for silylmethyl ketones. Although the 1,3-silyl migrations in both allylsilane and formylmethylsilane proceed concertedly (without formation of intermediates) via the four-membered cyclic transition structures with retention stereochemistry around silicon, there are essential differences between the transition structures (as indicated by the detailed analysis of the geometries, NBO, and the Laplacian of the electron density, shown in Table 6). The retention transition state of 1,3-silyl migration in formylmethylsilane is characterized by significant distortion from an ideal square pyramidal structure around silicon, a relatively flat four-membered ring, a HOMO which approximates to the nonbonding MO of a pentacoordinate silicate, and a ring critical point. On the other hand, the corresponding transition state for allylsilane has a near square pyramidal structure, a seriously bent four-membered ring, a bond critical point between C² and Si, and a HOMO which resembles the nonbonding MO of allyl π system. The activation energy for formylmethylsilane is much lower than that for allylsilane. The 1,3-silyl migration with retention in formylmethylsilane is best described as an *intramolecular nucleophilic substitution at silicon*, while the corresponding migration in allylsilane is assigned to be an *electrocyclic sigmatropic rearrangement controlled by subjacent orbital interactions* (as reported in the previous paper).⁸

Table 6. Comparison of TS_{ret} Structures for 1,3-Si Migrations in Allylsilane and Formylmethylsilane^a

	allylsilane	formylmethylsilane
geometry around Si (%SP) ^b	SP (88.8)	SP (66.7)
cyclobutane ring (puckering angle) ^c	bent (94.2 °)	flat (147 °)
orbital interaction	subjacent orbital control	3-center-4- electron bond
HOMO	allyl NBMO	TBP NBMO
E _a /(kcal/mol)	~50	~30
critical point	bond	ring
mechanism	electrocyclic reaction	intramolecular nucleophilic substitution

^a At the HF/6-31G* level. ^b %SP is in parentheses. ^c Dihedral angle Si-C³(or O)-C¹-C² is shown in parentheses.

For related 1,3-migrations in CH(O)CH₂MH₃ (M = C, Si, Ge, Sn), the E_a values for the retention pathway are much lower than the inversion pathway and they decrease in the following order: M = C ≫ Si > Ge > Sn (as expected from the relative stability of the pentacoordinate structure among the metals). In contrast to the 1,3-migrations in allylgermane and allylstannane, the retention 1,3-migrations in formylmethylgermane and the tin analogue are expected to predominate over the competitive C-metal bond dissociation.

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Supporting Information Available: Optimized geometries and some other properties of stationary points, and the activation energies for retention and inversion pathways during 1,3-silyl migration in formylmethylsilane are calculated at various theoretical levels (PDF). This material is available free of charge via the Internet at <http://www.pub.acs.org>.

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