

## ARTICLE

**Ab initio Study on Structures and Isomerization of Magnesium Fluorosilylenoid H<sub>2</sub>SiFMgF**Yi-jian Zhang<sup>a</sup>, Mei-jiang Li<sup>a</sup>, Guo-qiao Lai<sup>a</sup>, Da-cheng Feng<sup>b</sup>, Sheng-yu Feng<sup>a,b\*</sup>*a.* Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 310012, China*b.* School of Chemistry and Chemical Engineering, Shandong University, Ji'nan 250100, China

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The structures and isomerization of magnesium fluorosilylenoid H<sub>2</sub>SiFMgF were investigated by *ab initio* molecular orbital theory. Four equilibrium structures and three isomeric transition states were located and fully optimized at the B3LYP/6-31G(d,p) and G3MP2B3 levels, respectively. Based on the B3LYP/6-31G(d,p) optimized geometries, harmonic frequencies of various structures were obtained and <sup>29</sup>Si chemical shifts were calculated. The solvent effects were investigated by means of the polarizable continuum model using THF as a solvent at B3LYP/6-31G(d,p) level. Isomerization paths for isomers were confirmed by intrinsic reaction coordinate calculations. The calculated results show that tetrahedral structure has the lowest energy and is the most stable; tetrahedral, three-membered ring, and p-complex structures are suggested to be the experimentally detectable ones; and  $\sigma$ -complex structure has the highest energy and will not exist.

**Key words:** Magnesium fluorosilylenoid, *Ab initio* calculation, B3LYP/6-31G(d,p) theory, Isomerization**I. INTRODUCTION**

Molecules with the general formula R<sub>2</sub>SiMX (R, substituents such as H, CH<sub>3</sub>, Ph; M, usually alkali metals; X, usually halogens) are called silylenoid because their chemical behavior is similar to that of silylene R<sub>2</sub>Si. Recently, these have been more and more studied both experimentally and theoretically [1]. In 1980, Clark *et al.* first calculated the model silylenoid H<sub>2</sub>SiLiF using *ab initio* molecular orbital theory for the comparison with carbenoid H<sub>2</sub>CLiF [2], analyzed its four possible equilibrium structures, and lay the foundation for the studies on the silylenoid. Then, since the 1990s, our research group has investigated the silylenoids theoretically in detail [3-20]. We confirmed the existence, structures, stability and ambiphilic reactivity of silylenoid; discussed the factors and regularity of influencing their existence and stability; studied its addition reaction, substitution reaction and insertion reaction; and provided abundant theoretical foundation for related experimental research. In 1992, Tamao *et al.* prepared functionalized (aminosilyl)-lithiums, (Et<sub>2</sub>N)Ph<sub>2</sub>SiLi (Et=CH<sub>3</sub>CH<sub>2</sub>), (Et<sub>2</sub>N)PhMeSiLi, and (Et<sub>2</sub>N)<sub>2</sub>PhSiLi stable in tetrahydrofuran (THF) at 0 °C by the direct reaction of the corresponding aminosilyl chlorides with metal lithium in THF at 0 °C in quantitative yields [21]. Subsequently, some experimental aspects of silylenoid chemistry were reported [22-24], and the results show that silylenoids also have ambiphilic reactivity, which accords well with the theo-

retical reports. Recently, Lee *et al.* synthesized stable silylenoids (TSi)X<sub>2</sub>SiLi (TSi=C(SiMe<sub>3</sub>)<sub>3</sub>; X=Br, Cl) at room temperature and studied their reactivity [25]. The ambiphilicity of silylenoids was further confirmed.

It is known that the silylenoid R<sub>2</sub>SiMX (M=Li, Na, K; X=halogen) has been reported theoretically and R<sub>2</sub>SiLiX (X=halogen) has been studied experimentally. Recently, we studied H<sub>2</sub>SiClMgCl using *ab initio* methods [26], and found that, like H<sub>2</sub>SiMX (M=Li, Na, K; X=halogen, OH, NH<sub>2</sub>, OR'), H<sub>2</sub>SiClMgCl has the character of silylenoids. It is called chloromagnesium silylenoid. Compared with H<sub>2</sub>SiMX (M=Li, Na, K; X=halogens), chloromagnesium silylenoid has a different stability sequence of four equilibrium structures. Later, Lee *et al.* obtained the first magnesium silylenoid Mes (TSi)SiBrMgBr in the laboratory, which encouraged us to continue to study magnesium silylenoid [27]. Considering the different effects of halogen atoms on the structures and stability of magnesium silylenoid, and based on our research results, we compare H<sub>2</sub>SiFMgF with H<sub>2</sub>SiClMgCl in this work.

**II. COMPUTATIONAL METHODS**

Calculations on the optimized geometries and energies for the stationary points were carried out at the B3LYP/6-31G(d,p) [28-31] and G3MP2B3 [32] levels, respectively. Based on the B3LYP/6-31G(d,p) optimized geometries, harmonic frequencies of various equilibrium structures and transition states were obtained and <sup>29</sup>Si chemical shifts were calculated using the GIAO method [33] with a magnetic shielding  $\delta^{29}\text{Si}$  of tetramethylsilane (TMS) as the reference molecule. Isomerization paths among isomers were confirmed by the in-

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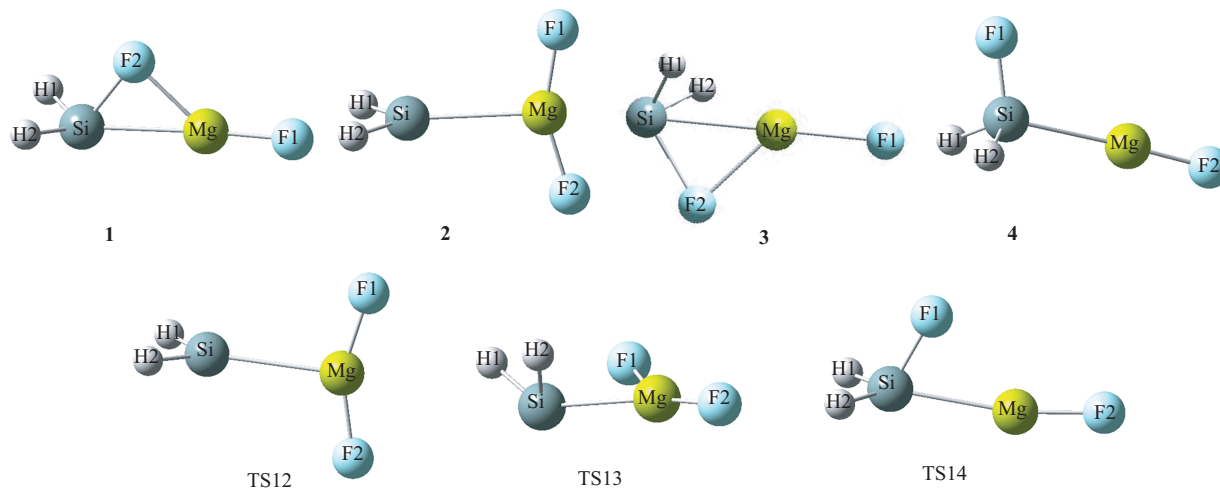


FIG. 1 The equilibrium structures and their isomerization transition states of  $\text{H}_2\text{SiFMgF}$ .

TABLE I The B3LYP/6-31G(d,p) optimized structural parameters (bond length in unit of Å; angles in unit of  $^\circ$ ); X, imaginary atom; SiX, bisector of angle HSiH) in the gas phase and solution (in parentheses)<sup>a</sup>.

Parameter	1	2	3	4	TS12	TS13	TS14	$\text{H}_3\text{SiF}$	$\text{H}_3\text{SiMgF}$
Bond length									
Si-H1	1.497 (1.503)	1.507 (1.502)	1.591 (1.569)	1.496 (1.504)	1.507	1.500	1.494	1.484	1.493
Si-H2	1.497 (1.503)	1.507 (1.502)	1.591 (1.569)	1.496 (1.504)	1.507	1.566	1.494		
Si-F1	1.802 (1.804)		1.842 (1.838)	1.632 (1.655)		1.874	1.693	1.613	
Si-Mg	2.494 (2.548)	2.768 (2.750)	2.570 (2.624)	2.582 (2.590)	2.769	2.522	2.489		2.565
Mg-F1	1.986 (1.997)	1.757 (1.788)	1.921 (1.937)	3.515 (3.593)	1.756	1.893	2.512		
Mg-F2	1.743 (1.775)	1.757 (1.788)	1.740 (1.771)	1.745 (1.781)	1.756	1.737	1.744		1.746
Bond angle									
HSiH	102.4 (100.5)	97.5 (99.6)	86.6 (88.4)	105.2 (102.5)	97.5	93.8	104.6	109.7	106.5
XSiF1	110.7 (108.5)		84.3 (85.4)	119.1 (113.8)		95.8	119.2	109.2 <sup>b</sup>	
XSiMg	162.8 (160.0)	180.0 (180.0)		129.8 (132.4)	180.0	84.0			129.5
F1SiMg	52.1 (51.5)			111.1 (113.8)		149.0	70.9		
SiF1Mg			86.1 (88.0)						
FMgF		154.3 (142.0)	142.2 (143.3)		154.5				
F2MgSi	176.7 (174.3)	102.8 (109.0)		177.9 (173.1)	102.7		169.8		179.9
Dihedral angle									
F1SiXH1	90.0 (90.0)	90.0 (90.0)	90.0 (90.0)	90.0 (90.0)	90.0	99.7			
MgF1SiX						107.2			
F2MgF1Si	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)	180.0	-174.0			

<sup>a</sup>  $\text{H}_2\text{Si}$ : Si-H, 1.530 Å (1.527 Å); HSiH, 91.2 Å (92.2 Å);  $\text{MgF}_2$ : Mg-F, 1.737 Å (1.773 Å); FMgF, 180.0° (180.0°).

<sup>b</sup> HSiF.

trinsic reaction coordinate (IRC) calculations [34]. The solvent effects were investigated by means of the polarizable continuum model (PCM) [35-38] using THF as a solvent, which is usually used in synthetic work, at B3LYP/6-31G(d,p) level. All the calculations were carried out using the GAUSSIAN 03 series of programs [39].

### III. RESULTS AND DISCUSSION

Like magnesium chlorosilylenoid  $\text{H}_2\text{SiClMgCl}$ ,  $\text{H}_2\text{SiFMgF}$  has four equilibrium structures 1-4, as shown in Fig.1, where TS12, TS13, and TS14 are three isomeric transition states between equilibrium structures. The optimized structural parameters are listed in Table I, and their energies and  $^{29}\text{Si}$  chemical shifts are given in Table II. As the B3LYP/6-31G(d,p)

TABLE II Total energies in unit of a.u. (relative energies in unit of kJ/mol) and  $\delta^{29}\text{Si}$  chemical shifts<sup>a</sup> in ppm.

Geometry	B3LYP/6-31G(d,p)	G3MP2B3	B3LYP/PCM <sup>b</sup>	$\delta^{29}\text{Si}$	$\delta^{29}\text{Si}$ (PCM)
<b>1</b>	-690.57282 (0.0)	-689.56261 (0.0)	-690.60315 (0.0)	-115.8	-201.8
<b>2</b>	-690.52825 (117.0)	-689.52709 (93.3)	-690.56812 (92.0)	-631.7	-637.7
<b>3</b>	-690.57293 (-0.3)	-689.56601 (-8.9)	-690.60202 (3.0)	1.5	-5.6
<b>4</b>	-690.57634 (-9.2)	-689.57227 (-25.4)	-690.61377 (-27.9)	-17.9	-21.6
TS12	-690.52825 (117.0)	-689.52711 (93.2)			
TS13	-690.55223 (54.1)	-689.54495 (46.4)			
TS14	-690.56902 (10.0)	-689.56179 (2.2)			
H <sub>2</sub> Si( <sup>1</sup> A <sub>1</sub> )+MgF <sub>2</sub>	-690.50538 (177.1)	-689.50826 (142.7)	-690.55438 (128.0)		

<sup>a</sup> Both  $\delta^{29}\text{Si}$  and  $\delta^{29}\text{Si}$  (PCM) of TMS are 412.5 ppm.

<sup>b</sup> The energies in solution.

optimized structural parameters are almost the same as the G3MP2B3 ones, only the B3LYP/6-31G (d,p) results are listed in Table I. For comparison, silylene H<sub>2</sub>Si, MgF<sub>2</sub>, H<sub>3</sub>SiF, and H<sub>3</sub>SiMgF were also calculated and the corresponding results are shown in Tables I and II, respectively. The B3LYP/6-31G(d,p) relative energies are in good agreement with the G3MP2B3 ones, so only the G3MP2B3 energies will be used in the following discussion.

### A. Equilibrium structures and their energies in the gas phase

It can be seen from the data in Table II that among the four isomers the tetrahedral structure of H<sub>2</sub>SiFMgF has the lowest energy, being the same as H<sub>2</sub>SiClMgCl [7]. However, the energies of the four isomers are in the order of **4**<**3**<**1**<**2**, which is different from H<sub>2</sub>SiClMgCl.

As is known, silylene H<sub>2</sub>Si: has a  $\sigma$  orbital with an electron lone pair in the plane HSiH and an unoccupied p orbital perpendicular to the plane HSiH. As a silylenoid, **1** can be regarded as a H<sub>2</sub>Si complex formed by the respective interaction of Mg atom and a F atom of MgF<sub>2</sub> molecule with the  $\sigma$  and p orbitals of H<sub>2</sub>Si (Fig.2(a)). Energy of **1** is 142.7 kJ/mol lower than the sum of energies of H<sub>2</sub>Si and MgF<sub>2</sub>. **1** has a lower energy in isomers of H<sub>2</sub>SiFMgF and is suggested to be an experimentally detectable structure of H<sub>2</sub>SiFMgF. There exists an Si-Mg-F three-membered ring in **1**, making **1** be stable. In the three-membered ring of **1**, the Si-F distance is 0.289 Å longer than that in H<sub>3</sub>SiF molecule; F-Mg distance is 0.249 Å longer than that in MgF<sub>2</sub> molecule, and Si-Mg bond is an active one. So **1** has the character of silylenoids and its three-membered ring is "loosely structured" and is an active region for **1** to react. In addition, the Si-Mg distance in **1** is 0.071 Å shorter than that in H<sub>3</sub>SiMgF, indicating that there is a stronger interaction between Si and Mg in **1**. Thus, **1** is also suggested to be the [H<sub>2</sub>SiMgF]<sup>+</sup>F<sup>-</sup> ion pair, and

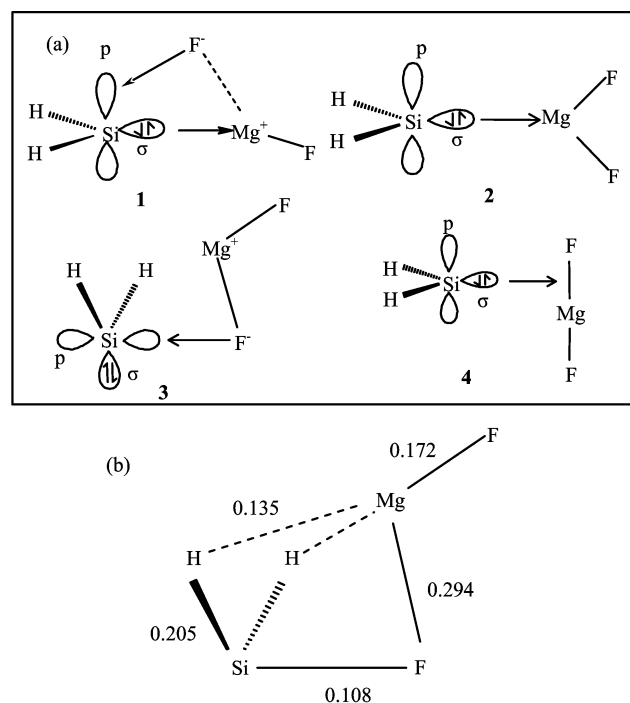


FIG. 2 (a) Scheme of **1**, **2**, **3**, **4**. (b) Mulliken populations between atoms in **3**.

to easily cause nucleophilic substitution with the departure of F<sup>-</sup>. Table III gives atomic natural charges of various species. It can be found by respective comparison of natural charges of Si, Mg, and F atoms in **1** with those of H<sub>2</sub>Si and MgF<sub>2</sub> that an electron transfer of Si→Mg→F→Si occurs in the three-membered ring, and more negative charge on the F atom transfers to the Si atom. The  $\delta^{29}\text{Si}$  value of **1** shifts downfield and is -115.8 ppm.

**2** is a  $\sigma$ -complex of H<sub>2</sub>Si and MgF<sub>2</sub> and is formed by the donating of the  $\sigma$ -electron of silylene moiety to Mg atom with positive charge in the MgCl<sub>2</sub> molecule (Fig.2(a)). In **2**, planes HSiH and FMgF are perpendicular to each other and **2** has C<sub>2v</sub> symmetry. Positive

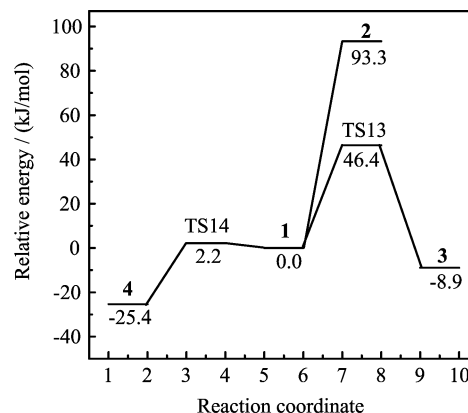
TABLE III Atomic natural charges.

Atom	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	TS12	TS13	TS14	H <sub>2</sub> Si	MgF <sub>2</sub>	H <sub>3</sub> SiF	H <sub>3</sub> SiMgF
Si	0.359	0.507	0.650	0.544	0.506	0.321	0.442	0.575		1.287	-0.177
H1	-0.195	-0.229	-0.382	-0.206	-0.228	-0.167	-0.198	-0.288		-0.225	-0.128
H2	-0.195	-0.229	-0.382	-0.206	-0.228	-0.294	-0.198	-0.288		-0.225	-0.128
Mg	1.552	1.615	1.667	1.311	1.615	-1.683	1.437		1.664		1.382
F1	-0.694	-0.832	-0.727	-0.622	-0.832	-0.740	-0.661		-0.832	-0.613	-0.819
F2	-0.827	-0.832	-0.827	-0.820	-0.832	-0.829	-0.822		-0.832	-0.225 (H3)	-0.128 (H3)

charge on the Mg atom in **2** is slightly decreased by 0.049 (see Table III), relative to the MgF<sub>2</sub> molecule. The Si–Mg distance is 2.768 and 0.112 Å longer than that in H<sub>3</sub>SiMgF while the Mg–F distance is only 0.02 Å longer than the Mg–F bond in the MgF<sub>2</sub> molecule. So there exists a weaker complex interaction between H<sub>2</sub>Si and MgF<sub>2</sub>, and the energy of **2** is only 49.4 kJ/mol lower than the sum of energies of H<sub>2</sub>Si and MgCl<sub>2</sub> and 93.3 kJ/mol higher than that of **1**. In addition, the structure and energy of **2** are almost the same as that of transition TS12, so conversion of **2** to **1** proceeds with no barrier. **2** is practically not a real local minimum on the potential energy surface of H<sub>2</sub>SiFMgF. Just like H<sub>2</sub>SiClMgCl [7], **2** is suggested to be nonexistent.

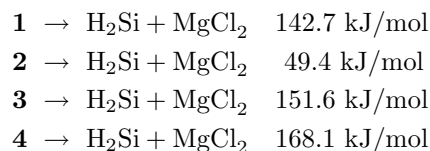
**3** is a p-complex formed by donating of electron of a F atom in MgF<sub>2</sub> molecule toward unoccupied p orbital of Si atom in H<sub>2</sub>Si (Fig.2(a)). There also exists a stronger interaction among Mg atom with positive charge and two H atoms with negative charge (see Fig.2(b)), that is, there exist two four-membered rings in **3**. An electron transfer of F→Si→H (H)→Mg→F occurs in the four-membered ring of **3**. Energy of **3** is 151.6 kJ/mol lower than the sum of energies of H<sub>2</sub>Si and MgF<sub>2</sub>, and 8.9 kJ/mol lower than that of **1**. So **3** should be also an experimentally detectable structure. The interaction among Mg and H atoms makes the angle HSiH 4.6° smaller and the Si–H distance 0.061 Å longer than H<sub>2</sub>Si. In **3**, the Mg–F1 distance is longer by 0.184 Å than that in the MgF<sub>2</sub> molecule, and the Si–F1 distance is 0.229 Å longer than the typical Si–F bond in H<sub>3</sub>SiF, showing that **3** has obvious character of silylenoids. In addition, **3** is also regarded as a [H<sub>2</sub>SiF]<sup>−</sup>[MgF]<sup>+</sup> ion pair. In **3**, the occupied σ orbital of the silylene moiety is exposed, so **3** easily causes electrophilic substitution with the departure of [MgF]<sup>+</sup>. The δ<sup>29</sup>Si value of **3** shifts upfield and is 1.5 ppm.

**4** is the “classical” tetrahedral structure, which may be thought to be formed by insertion of H<sub>2</sub>Si: into a Mg–F bond in the MgF<sub>2</sub> molecule (Fig.2(a)). Si, Mg, and F<sub>2</sub> atoms are almost in a straight line. Its energy is 168.1 kJ/mol lower than the sum of energies of H<sub>2</sub>Si and MgF<sub>2</sub>, and even 25.4 kJ/mol lower than that of **1**. **4** has the lowest energy among all the equilibrium structures of H<sub>2</sub>SiFMgF, and is suggested to be an experimentally detectable structure. The Si–F distance in **4** is 0.17 Å shorter than that in **1**, indicating that there is a stronger

FIG. 3 Potential energy surface profile along the isomeric reaction pathways of various isomers of silylenoid H<sub>2</sub>SiFMgF.

interaction between Si and F atoms in **4** than in **1**, but still 0.019 Å longer than the Si–F bond in H<sub>3</sub>SiF. So it can be said that **4** has character of silylenoids. The strong Si–F bond may be a main reason for **4** to be the most stable among all isomers. The δ<sup>29</sup>Si value of **4** shifts downfield and is -17.9 ppm.

Defining associative energy of H<sub>2</sub>SiFMgF as the difference between the sum of energies of H<sub>2</sub>Si and MgF<sub>2</sub> and energy of H<sub>2</sub>SiFMgF, associative energies of **1**, **2**, **3**, and **4** are 142.7, 49.4, 151.6, and 168.1 kJ/mol, respectively. So,



Thus when H<sub>2</sub>Si coexists with MgF<sub>2</sub>, it should exist in silylenoid R<sub>2</sub>SiFMgF, and not in a dissociative state. **1**, **3** and **4** will be three experimentally detectable structures of silylenoid H<sub>2</sub>SiFMgF.

## B. Isomerization of equilibrium structures in the gas phase

Figure 3 is a sketch map of isomerization paths between equilibrium structures. The isomerization paths were confirmed by our intrinsic reaction coordinate

(IRC) calculations. As mentioned above, the conversion of **2** to **1** is a non-barrier path. TS13 and TS14 are two transition states of interisomerization between structures **1** and **3**, and **1** and **4**, respectively. Vibrational analyses show that each of them has only one imaginary harmonic vibrational frequency ( $-358.4\text{ cm}^{-1}$  for TS13 and  $-142.0\text{ cm}^{-1}$  for TS14).

TS13 is a transition state of interisomerization between **1** and **3** with rotating of the H<sub>2</sub>Si moiety around the Si-F bond axis, which has only one imaginary harmonic vibrational frequency of  $-358.4\text{ cm}^{-1}$ . Isomerization of **3** to **1** happens with a barrier of 55.3 kJ/mol and the H<sub>2</sub>Si moiety rotating around the Si-F bond axis by about 107°. F2MgF1Si is almost kept in the same plane during the isomerization. The Si-Mg distance shortens gradually. The barrier may be mainly attributed to overcoming the interaction between Mg and H atoms. **1** isomerizes to **3** with cleavage of the Si-Mg bond and the H<sub>2</sub>Si moiety rotates around the Si-F bond axis by about 73° via TS13 with a barrier of 46.4 kJ/mol, being slightly easier than isomerization of **3** to **1**. This may mainly result from breaking the Si-Mg bond in **1**.

The interisomerization between **1** and **4** takes place via TS14 with main rotation of the Mg-Si bond up or down around the Si atom in the plane F1SiMg. TS14 has only one imaginary harmonic vibrational frequency of  $-142.0\text{ cm}^{-1}$ . **4** isomerizes to **1** only with a very low barrier of 2.2 kJ/mol when the Mg atom approaches the F1 atom and the Mg-Si bond rotates toward F1 by 67.4° (the Si-Cl1 bond simultaneously rotates apart from the Mg atom by 8.4°) while **1** isomerizes to **4** with a slightly higher barrier of 27.6 kJ/mol. It should be said that the interisomerization between **1** and **4** takes place easily.

### C. The solvent effects

In order to simulate the true reaction system, and probe the effects of solvent on the structures, THF was chosen as the solvent. It can be seen from Table I that the geometries of the four equilibrium structures in solvent do not differ much from those in the gas phase. The bond lengths, which are related to the magnesium atom, change to be slightly larger, indicating the solvation center of THF is the magnesium atom. By comparing the energies at the level of B3LYP/6-31G(d,p) and B3LYP/PCM in Table II, it can be concluded that **4** and **2** become more stable in solution, but the relative energy of **3** becomes a little higher. The energies of the four equilibrium structures are in the order of  $4 < 1 < 3 < 2$ . The solvent effects decrease the stability of **1-4** relative to H<sub>2</sub>Si+MgF<sub>2</sub> (see Table II), but the dissociation energy is still very high. In the other words, when H<sub>2</sub>Si and MgF<sub>2</sub> coexist in the THF solution, they are in the form of silylenoid, and not in the form of separation. Compared with gas phase, the  $\delta^{29}\text{Si}$  of equilibrium structures all shift downfield in the THF solution.

The changes of  $\delta^{29}\text{Si}$  of **2**, **3**, and **4** are not obvious, but the change of  $\delta^{29}\text{Si}$  of **1** is obvious, and  $\delta^{29}\text{Si}$  of **1** shifts 86 ppm downfield.

### IV. CONCLUSION

The calculations show that H<sub>2</sub>SiFMgF has four equilibrium structures and has the character of silylenoids. The tetrahedral structure of H<sub>2</sub>SiFMgF has the lowest energy. Different from silylenoid H<sub>2</sub>SiClMgCl, the stability of the four equilibrium structures of H<sub>2</sub>SiFMgF is in the order of tetrahedron > p-complex > three-membered ring >  $\sigma$ -complex. Tetrahedral and three-membered ring structures may interisomerize easily to each other with relatively low barriers. Three-membered ring and p-complex structures may also interisomerize to each other, with slightly higher barriers. Tetrahedral, three-membered ring, and p-complex structures are suggested to be the experimentally detectable ones.  $\sigma$ -complex structure has the highest energy and its conversion to three-membered ring structure proceeds with no barrier. Practically,  $\sigma$ -complex is not a real local minimum on the potential energy surface of H<sub>2</sub>SiFMgF and does not exist. The solvent effect has little effect on the structures of isomers, and only has effect on the relative stability of isomers. When H<sub>2</sub>Si and MgF<sub>2</sub> coexist in gas phase or THF solution, they are in the form of silylenoid, not in the form of monomers. It can be also concluded that silylenoids R<sub>2</sub>SiFMgF would be an intermediate in some organosilicon reactions.

### V. ACKNOWLEDGMENTS

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