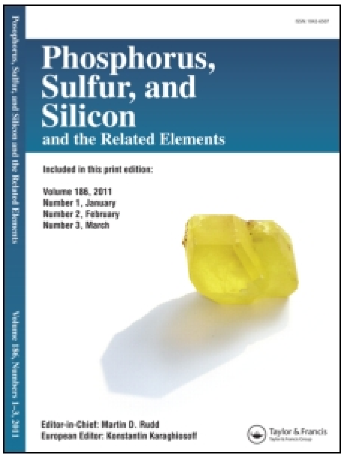

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Ab Initio Study of Structures, Metallotropic 1,2-Shifts and Prototropic 1,2-Shifts of Cyclopentadienyl(trimethyl)silane, -germane and -stannane

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AB INITIO STUDY OF STRUCTURES, METALLOTROPIC 1,2-SHIFTS AND PROTOTROPIC 1,2-SHIFTS OF CYCLOPENTADIENYL(TRIMETHYL)-SILANE, -GERMANE AND -STANNANE

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*Molecular structures, metallotropic and prototropic shifts of cyclopentadienyl(trimethyl)silane (**1**), cyclopentadienyl(trimethyl)germane (**2**), and cyclopentadienyl(trimethyl)stannane (**3**) were investigated using ab initio molecular orbital and the Becke, Lee, Yang, and Parr density functional (B3LYP) methods. The results show that the most stable structure of compounds **1–3** has the $(CH_3)_3M$ fragment in the allylic position. The energy barrier of metallotropic shifts in compound **1** is higher than in **2**, and in compound **2** higher than in **3**, in good agreement with experimental data. The cyclopentadienyl rings in compounds **1–3** are found to be planar but this result contradicts the reported experimental data.*

Keywords: Ab initio study; cyclopentadienyl(trimethyl)silane; metallotropic and prototropic 1,2-shifts

INTRODUCTION

Fluxional σ-cyclopentadienyl compounds such as $(\eta^1\text{-}C_5H_5)_2Hg$ and $(\eta^5\text{-}C_5H_5)$ $(\eta^1\text{-}C_5H_5)Fe(CO)_2$ were first discovered by Piper and Wilkinson in 1965.[1] The authors discussed in an undetailed but essentially correct manner why fast intramolecular 1,2-migrations of the metal moiety around the cyclopentadienyl ring occur. The 1,2-migration of carbon-group elements in cyclopentadienyl compounds was first discussed by Fritz and Kreiter for silicon-, germanium-, tin-substituted cyclopentadienes.[2,3] The fluxionality of these compounds with σ-bonded (η^1) cyclopentadienyl rings follows from a concerted sigmatropic

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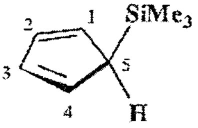
rearrangment. ^{1}H-NMR, ^{13}C-NMR, mass spectrometer and IR studies of the structures of cyclopentadienyl(trimethyl)silane, -germane and -stannane indicated that the 5-$Me_3MC_5H_5$ isomer is the more stable form, in which the Me_3M fragment is bound to a on allylic carbon atom. In solution, the compounds **1–3** have been found to undergo rapid metallotropic 1,2-shifts and much slower prototropic 1,2-shifts to give vinylic isomers, which are nonfluxional.[4–11] The composition of this mixture has been determined by analyzing the Diels-Alder adducts.[12–14]

The structure of compounds **1** and **2** have been investigated using electron diffraction method in the vapor phase and the results showed that the cyclopentadienyl ring is folded by about 22° and 24° from the planar conformation respectively.[15,16] In contrast to the reported sructural data for compounds **1** and **2**, the electron diffraction studies of compounds $H_3SiC_5H_5$ and $H_3GeC_5H_5$ indicate a planar conformation for cyclopentadienyl rings.[17,18]

In this work, we report the results of a theoretical investigation of the structural properties of compounds **1–3** which was performed by ab initio molecular orbital (MO) and density functional methods (DFT), using the GAUSSIAN 98 package programs.[19–23] Successful applications of density functional theory (DFT) based methods have broadened the applicability of the computational methods and now represent an interesting approach for determining activation barrier and moleculars energies.[19,20,22] The B3LYP functional method combines Beck's three-parameter exchange function with the correlation function of Lee et al.[19,20]



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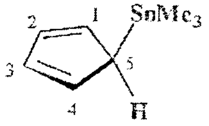

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CALCULATIONS

Ab initio calculations were carried out using HF/3-21G, B3LYP/3-21G//HF/3-21G levels of theory with the GAUSSIAN 98 package program,[23] implemented on a Pentium-PC computer with 300 MHz processor. Initial structural geometries of the compounds **1–3** were obtained by a molecular mechanics program PCMODEL (88.0)[24] and for reoptimizing of geometries, we used the AM1 method of a MOPAC 6.0 computer program.[25] Energy minimum geometries were located by minimizing the energy with respect to all geometrical coordinates and without imposing any symmetry constraints.

The GAUSSIAN 98 program was finally used to perform ab initio calculations at the HF/3-21G level in order to obtain the energy-minimum structures, and B3LYP/3-21G//HF/3-21G method for the single point energy calculations.

The nature of the stationary points for compounds **1–3** has been determined by virtue of the number of imaginary frequencies. For minimum state structures, only real frequency values, and in the transition state only single imaginary frequency values (with negative sign) are accepted.

The structure of the transition state geometries was located using the optimized geometries of the equilibrium structure according to the procedure of Dewar et al. (keyword: SADDLE).[26]

These structures were then reoptimized by the QST2 option at the HF/3-21G level. The vibrational frequencies of ground states and transition states were calculated by the keyword FREQ.

RESULTS AND DISCUSSION

Structural parameters, corrected zero point (ZPE), and total electronic (E_{el}) energies for compounds **1–3**, as calculated on the ab initio HF/3-21G level are given in Tables I–III. For single-point energy calculations, the DFT method (B3LYP/3-21G//HF/3-21G) was used.

Veniaminov et al.[15] found for 5-$Me_3SiC_5H_5$ (**1**) a structure by electron diffraction in the vapor phase containing a non planar C_5H_5 ring, in which the dihedral angle between the planes C(2)-C(3)-C(4) and C(1)-C(5)-C(4) is 158°. This ring folding also is reported for the germyl analogue. In 5-$Me_3GeC_5H_5$ (**2**), the folding angle has been reported to be 156.[16] However, contrary to these exprimental reported data, electron diffraction studies of the compounds $H_3SiC_5H_5$ and $H_3GeC_5H_5$ have shown that the C_5H_5 rings are essentially planar.[17,18]

Studies on the HF/3-21G level of theory indicate a planar C_5H_5 ring in the ground state structure of compounds **1–3**. The results show that the required energy for folding the ring from the planar conformation is about 7 kcal mol^{-1}. In view of this findings, it must concluded that the reported structures of compounds **1** and **2** are incorrect concerning the ring folding. From a structural point of view, there is also no reason which could justify such a ring folding.

TABLE I HF/3-21G Calculated Structural Parameters and Energies of the Ground States and Transition States of Cyclopentadienyl(trimethyl)silane **1**. Bond Lengths are in Ångström Units (Å) and Angles in Degrees (°)

Compounds	**1**	**2**	**3**	**1** → **2**	**2** → **3**	**3** → **3′**	**1** → **1′**
Bond lengths							
Si—C_5	1.948	1.896	1.900	1.886	1.893	1.902	2.254
C_5—C_1	1.506	1.532	1.336	1.485	1.409	1.402	1.476
C_1—C_2	1.337	1.518	1.519	1.397	1.491	1.399	1.404
C_2—C_3	1.471	1.329	1.517	1.391	1.401	1.496	1.396
C_3—C_4	1.337	1.482	1.328	1.387	1.391	1.199	1.396
C_4—C_5	1.506	1.338	1.496	1.412	1.404	1.402	1.404
C—H	1.086	1.086	1.087	1.301	1.332	1.330	1.070
Bond angles							
Si—C_5—C_1	109.1	124.6	127.2	126.6	125.0	125.8	70.0
Si—C_5—C_4	109.1	127.5	125.2	127.6	127.1	125.8	70.0
C_5—C_1—C_2	109.6	102.9	110.9	107.0	107.3	109.6	106.8
C_1—C_2—C_3	109.1	109.6	101.8	107.0	106.3	106.2	108.6
C_2—C_3—C_4	109.1	109.1	109.6	109.8	108.4	106.2	109.3
C_3—C_4—C_5	109.6	110.5	110.1	109.6	110.0	109.6	108.6
C_4—C_5—C_1	102.3	107.9	107.6	104.6	106.0	108.4	106.8
Torsion angles							
Si—C_5—C_1—C_2	111.0	180.0	180.0	−167.5	−178.9	−177.7	102.3
C_5—C_1—C_2—C_3	2.9	0.0	0.0	−0.3	0.0	0.0	0.0
C_1—C_2—C_3—C_4	0.0	0.0	0.0	−0.3	−0.3	0.0	0.0
C_4—C_5—C_1—C_2	−3.0	0.0	0.0	0.8	0.4	0.0	0.0
ZPE^a	0.19664	0.19662	0.19653	0.19277	0.19286	0.19274	0.19651
E_{el}	−596.79635	−596.79537	−596.79436	−596.72985	−596.72822	−596.72613	−596.75929
$E_\alpha = E_{el} + ZPE$	−596.59971	−596.59875	−596.59783	−596.53708	−596.53536	−596.53339	−596.56278
ΔE_α^b (Hartree)	0.00000	0.00096	0.00188	0.06263	0.06435	0.06632	0.03693
ΔE_α (kcal mol^{-1})	0.00	0.60	1.18	39.30	40.38	41.62	23.17
E_α^c (kcal mol^{-1})	—	—	—	—	—	—	13.0 ± 1.0
$\Delta G^{\#c}$ (kcal mol^{-1})	—	—	—	—	—	—	15.2 ± 0.2

[a] Corrected by multiplying by a scaling factor (0.9409).

[b] Relative to the most stable structure.

[c] Ref. 10.

TABLE II HF/3-21G Calculated Structural Parameters and Energies of the Ground States and Transition States of Cyclopentadienyl(trimethyl)germane **2**. Bond Lengths are in Ångström Units (Å) and Angles in Degrees (°)

Compounds	**1**	**2**	**3**	**1 → 2**	**2 → 3**	**3 → 3′**	**1 → 1′**
Bond lengths							
Ge—C_5	1.996	1.943	1.945	1.948	1.939	1.946	2.266
C_5—C_1	1.501	1.528	1.334	1.504	1.406	1.399	1.465
C_1—C_2	1.338	1.517	1.518	1.398	1.491	1.399	1.404
C_2—C_3	1.469	1.329	1.517	1.394	1.401	1.496	1.396
C_3—C_4	1.338	1.481	1.328	1.391	1.390	1.399	1.396
C_4—C_5	1.501	1.335	1.492	1.407	1.401	1.399	1.404
C—H	1.085	1.087	1.087	1.329	1.332	1.331	1.070
Bond angles							
Ge—C_5—C_1	108.8	124.4	127.4	126.3	126.1	125.8	71.1
Ge—C_5—C_4	108.8	127.7	125.1	127.5	126.9	125.8	71.1
C_5—C_1—C_2	109.6	103.0	110.9	107.3	107.4	109.7	106.8
C_1—C_2—C_3	109.0	109.5	101.8	108.5	106.2	106.1	108.6
C_2—C_3—C_4	109.0	108.0	109.5	109.7	108.3	106.0	109.2
C_3—C_4—C_5	109.6	110.6	110.3	109.9	111.1	109.8	108.6
C_4—C_5—C_1	102.5	107.9	107.5	104.6	106.0	108.4	106.8
Torsion angles							
Ge—C_5—C_1—C_2	−110.5	180.0	180.0	−165.8	−179.1	−177.9	102.7
C_5—C_1—C_2—C_3	−3.0	0.0	0.0	−0.3	0.0	0.0	0.0
C_1—C_2—C_3—C_4	0.0	0.0	0.0	−0.3	−0.3	0.0	0.3
C_4—C_5—C_1—C_2	3.0	0.0	0.0	0.9	0.3	0.0	0.0
ZPE^a	0.19501	0.19510	0.19507	0.19130	0.19142	0.19131	0.19500
E_{el}	−2374.76078	−2374.76069	−2374.76020	−2374.69546	−2374.69421	−2374.69231	−2374.72834
$E_\alpha = E_{\mathrm{el}} + ZPE$	−2374.56577	−2374.56559	−2374.56513	−2374.50416	−2374.50279	−2374.50100	−2374.53334
ΔE_α^b (Hartree)	0.00000	0.00018	0.00064	0.06161	0.06298	0.06477	0.03243
ΔE_c (kcal mol^{-1})	0.00	0.11	0.40	38.66	39.52	40.64	20.35
E_a^c (kcal mol^{-1})	—	—	—	—	—	—	9.2 ± 1.0
$\Delta G^{\#c}$ (kcal mol^{-1})	—	—	—	—	—	—	13.3 ± 1.0

[a] Corrected by multiplying by a scaling factor (0.9409).

[b] Relative to the most stable structure.

[c] Ref. 4.

TABLE III HF/3-21G Calculated Structural Parameters and Energies of the Ground States and Transition States of Cyclopentadienyl(trimethyl)stannane **3**. Bond Lengths are in Ångström Units (Å) and Angles in Degrees (°)

Compounds	**1**	**2**	**3**	**1** → **2**	**2** → **3**	**3** → **3′**	**1** → **1′**
Bond lengths							
Sn—C_5	2.215	2.147	2.149	2.151	2.139	2.148	2.443
C_5—C_1	1.491	1.533	1.338	1.508	1.410	1.403	1.467
C_1—C_2	1.346	1.518	1.520	1.398	1.492	1.399	1.406
C_2—C_3	1.459	1.329	1.516	1.393	1.401	1.495	1.397
C_3—C_4	1.345	1.482	1.329	1.391	1.391	1.399	1.397
C_4—C_5	1.492	1.339	1.497	1.411	1.405	1.403	1.406
C—H	1.081	1.087	1.087	1.330	1.332	1.330	1.071
Bond angles							
Sn—C_5—C_1	105.0	125.8	126.1	127.3	126.1	125.9	72.5
Sn—C_5—C_4	104.7	126.7	126.7	126.8	127.2	125.9	72.5
C_5—C_1—C_2	109.3	103.1	111.1	107.4	107.5	109.8	106.7
C_1—C_2—C_3	109.0	109.5	101.8	108.5	106.2	106.1	108.7
C_2—C_3—C_4	109.0	109.0	109.6	109.7	108.4	106.1	109.2
C_3—C_4—C_5	109.3	110.7	110.3	109.0	111.2	109.8	108.7
C_4—C_5—C_1	103.1	107.6	107.2	104.3	106.7	108.2	106.7
Torsion angles							
Sn—C_5—C_1—C_2	−104.2	180.0	180.0	−165.6	180.0	−178.6	101.2
C_5—C_1—C_2—C_3	−3.4	0.0	0.0	−0.5	0.0	0.0	0.0
C_1—C_2—C_3—C_4	0.0	0.0	0.0	−0.3	−0.3	0.0	0.0
C_4—C_5—C_1—C_2	4.0	0.0	0.0	1.2	0.4	0.0	0.0
ZPE^a	0.19194	0.19262	0.19256	0.18881	0.18894	0.1883	0.19244
E_{el}	−6306.05911	−6306.05312	−6306.05215	−6305.98898	−6305.98646	−6305.98439	−6306.04151
$E_\alpha = E_{\mathrm{el}} + ZPE$	−6305.86717	−6305.86050	−6305.85959	−6305.80017	−6305.79752	−6305.79856	−6305.84907
ΔE_α^b (Hartree)	0.00000	0.00667	0.00758	0.06700	0.06965	0.06861	0.01810
ΔE_α (kcal mol^{-1})	0.00	4.19	4.76	42.04	43.71	43.05	11.36
E_α^c (kcal mol^{-1})	—	—	—	—	—	—	7.8 ± 1.0
$\Delta G^{\#c}$ (kcal mol^{-1})	—	—	—	—	—	—	6.6 ± 1.0

[a] Corrected by multiplying by a scaling factor (0.9409).

[b] Relative to the most stable structure.

[c] Ref. 4.

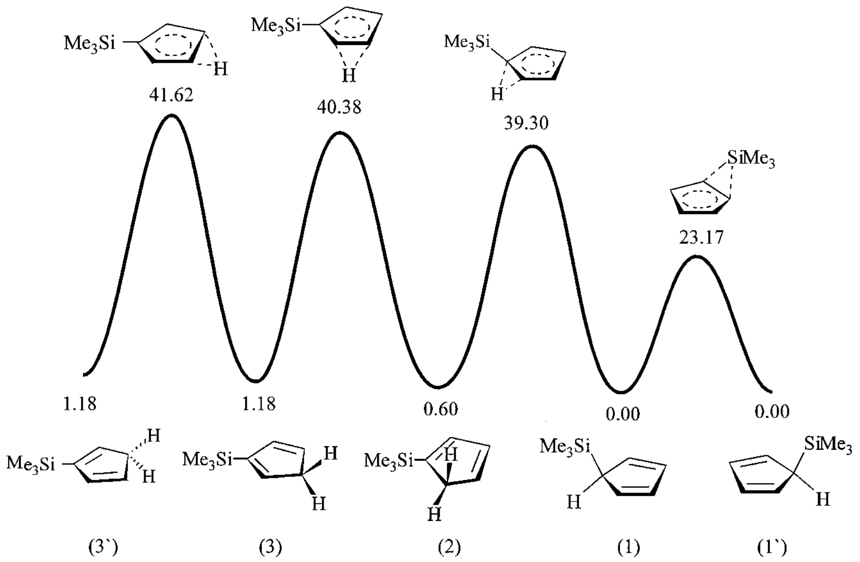

FIGURE 1 Calculated HF/3-21G profile for metallotropic and prototropic 1,2-shifts in cyclopentadienyl(trimethyl)silane.

The 1,2-shift mechanisms for the Me_3M and hydrogen migrations were also investigated and reaction pathways are shown in Figures 1–6. In metallotropic 1,2-shifts, the reaction pathways are symmetrical and in the transition state structure, the Si, Ge, and Sn atoms are equidistant from two carbon atoms of the C_5H_5 ring (see Tables I–III). The HF/3-21G//HF/3-21G and B3LYP/3-21G//HF/3-21G calculated energies are given in Tables I–III. The metallotropic shifts energy barriers in compounds **1–3**, as calculated by B3LYP/3-21G//HF/3-21G method are in good agreement with the reported dynamic ^{1}H-NMR data.[4,10] These results show that the energy barrier of the metallotropic shifts decreases in the following order: $E(3) < E(2) < E(1)$. As the C—M bond lenghts increase, the dissociation of a C—Sn bond is easier than that of a C—Si bond and consequently, the migration of the metal around the cyclopentadienyl ring occurs with a lower energy barrier. This result is in good agreement with the experimental data.

As it can be seen from the Figures 1–6 the prototropic 1,2-shifts require higher energy barrier than metallotropic 1,2-shifts, consequently, the rate of this process is much slower than metal migration. It can be concluded that the prototropic 1,2-shifts occur only at higher temperatures.

The prototropic 1,2-shifts convert 5-$Me_3MC_5H_5$ into 1-$Me_3MC_5H_5$ and 2-$Me_3MC_5H_5$. The hydrogen migrates stepwise from C(5) to C(1),

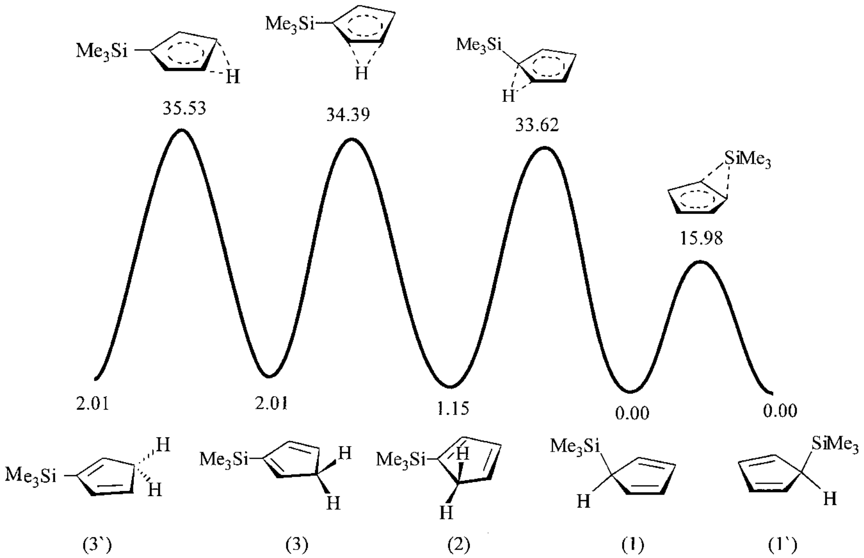

FIGURE 2 Calculated B3LYP/3-21G//HF/3-21G profile for metallotropic and prototropic 1,2-shifts in cyclopentadienyl(trimethyl)silane.

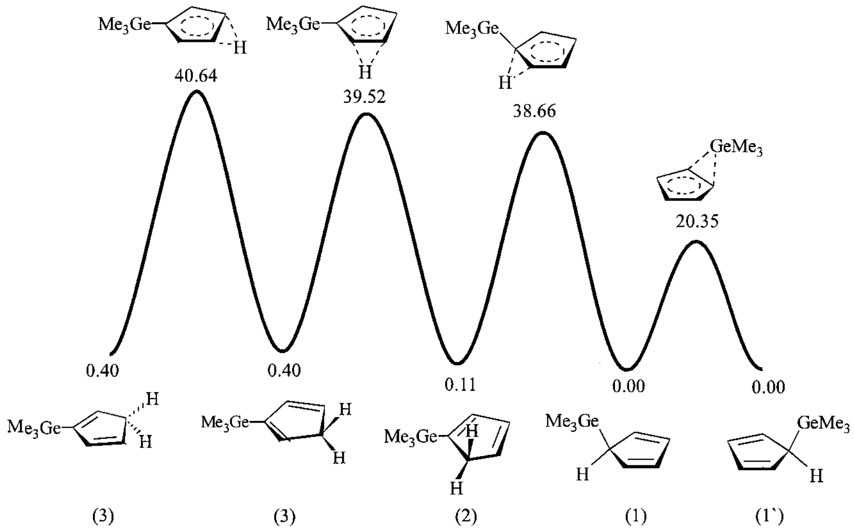

FIGURE 3 Calculated HF/3-21G profile for metallotropic and prototropic 1,2-shiftin cyclopentadienyl(trimethyl)germane.

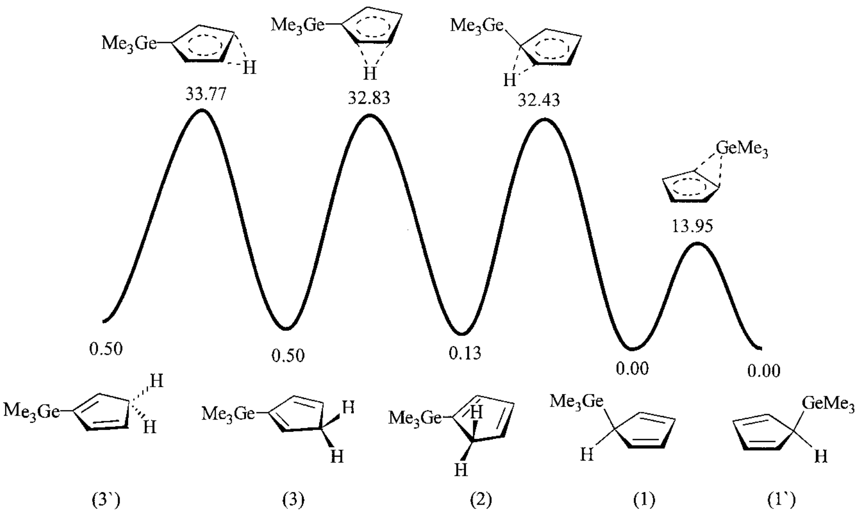

FIGURE 4 Calculated B3LYP/3-21G//HF/3-21G profile for metallotropic and prototropic 1,2-shifts in cyclopentadienyl(trimethyl)germane.

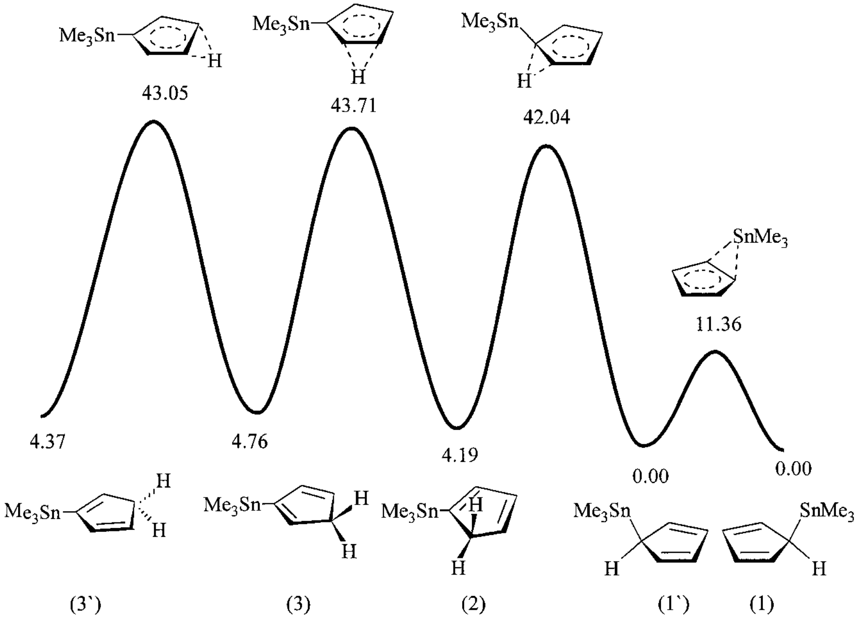

FIGURE 5 Calculated HF/3-21G profile for metallotropic and prototropic 1,2-shifts in cyclopentadienyl(trimethyl)stannane.

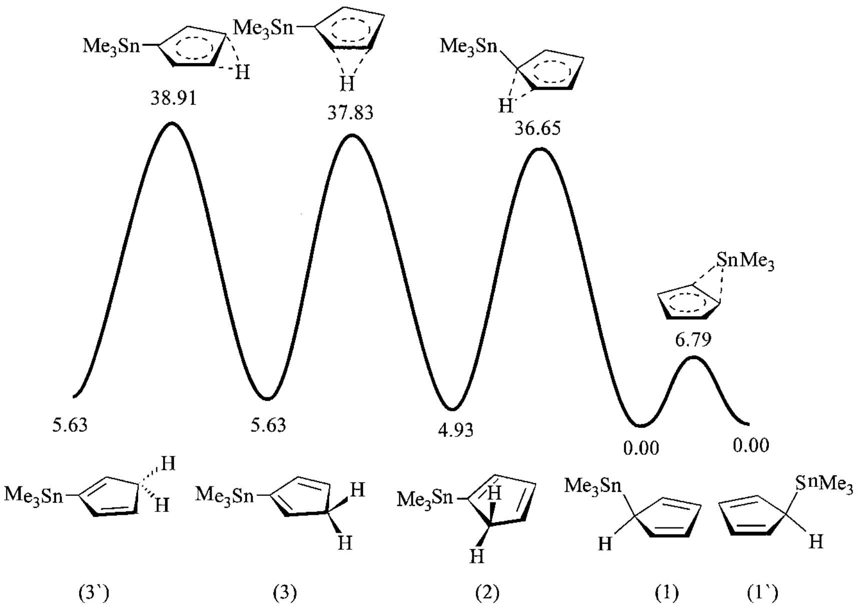

FIGURE 6 Calculated B3LYP/3-21G//HF/3-21G profile for metallotropic and prototropic 1,2-shifts in cyclopentadienyl(trimethyl)stannane.

C(1) to C(2), and then from C(2) to C(3). Unlike the Me_3M fragment migration, the rearrangements involving hydrogen migration C(5) to C(1) and C(1) to C(2) are nondegenerate and the reaction pathways are nonsymmetrical (see Figures 1–6). The prototropic shift from C(2) to C(3) has a symmetrical transition state. Ab initio and DFT calculations show that the energy barrier of the prototropic shift from C(2) to C(3) is higher than the prototropic shift from C(1) to C(2), and in a similar way the energy of the prototropic shift from C(1) to C(2) is higher than from C(5) to C(1).

CONCLUSION

Ab initio and density functional theory calculations provide a picture from both structural and dynamic points of view for compounds **1–3**. The results calculated by HF/3-21G and B3LYP/3-21G//HF/3-21G show that the most stable isomers of compounds **1–3** are the allylic isomers (the Me_3M fragment in an allylic position). These results are in good agreement with experimental data. The data show that the C_5H_5 rings in compounds **1–3** are planar, that is, about 7 kcal mol^{-1} more stable than the folded conformation. Consequently, it can be concluded that the reported experimental data[15,16] indicating a ring folding may be incorrect. For the hydrogenated compounds $H_3MC_5H_5$, planar structures also have been reported.[17,18]

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