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Journal of Organometallic Chemistry 689 (2004) 1284–1287

Journal of Organometallic Chemistry

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Facile valence isomerization among bis(silacyclopropenyl), disila(Dewar benzene) and disilabenzvalene

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Received 20 November 2003; accepted 27 January 2004

Abstract

Hybrid density functional theory (B3LYP) and ab initio (CCSD(T)) calculations were performed to explore the reaction energy pathways of the valence isomerizations among the disilabenzene isomers, namely, bis(silacyclopropenyl) (**1**), disila(Dewar benzene) (**3**) and disilabenzvalene (**4**). The computational study predicts that the interconversion of **1** to **3** and **4** occurs spontaneously. However, the interconversion between Dewar benzene (**3**) and benzvalene (**4**) analogs is a multistep process involving a new intermediate structure **2a**, with energy barriers lying above 30 kcal/mol in energy compared to **3** and **4**.

Keywords: Disilabenzene valence isomers; Computational studies; Rearrangements; Isomerisation

1. Introduction

Recently, Ando et al. [1,2] have reported the crystal structures of bulky group substituted bis(silacyclopropene) (**1**), disila(Dewar benzene) (**3**) and disilabenzvalene (**4**) and inferred that valence isomerization reactions among them are probable (Scheme 1). In their elegant experimental study, they reported that **1** upon mild heating yields **3** and **4** in competitive proportions depending on the nature of substituent on Si and reaction conditions. Further, **3** upon irradiation rearranges to 1,4-disilabenzene (**5**). While the experimental study could not unequivocally establish the mechanism, they have proposed the possibility of a vinyl silylene intermediate (**2**). A study on the relative energies of the valence isomeric forms of sila- and disilabenzene were published recently from our group [3–5]. Yoshizawa and coworkers [6] have studied the rearrangement reaction of 1,4-disilabenzene (**5**) to the corresponding Dewar benzene isomer (**3**) and its Diels-Alder reactivity using density functional theory (DFT) and post-HF calculations. However, the proposal of Ando and co-workers regarding the valence isomerization could not be scrutinized from the above computational study. In the present study, we report a density functional theory (B3LYP) and ab initio (CCSD(T)) study on the reaction pathways of the conversion of **1** to **3** and **4** via the vinyl silylene intermediate (**2**). The experimentally reported valence isomers have trimethylsilyl substitution on the carbon atoms and methyl/ethyl on the silicon atoms. However, we have considered only the unsubstituted counterparts in the present analysis. The consideration of bulky group substituted isomers leads to an increase in 18 more non-hydrogen atoms and hence treating all the species considered and following the reaction pathways are computationally not viable with the available facilities.

2. Computational details

All the structures were optimized at the B3LYP level of theory using the 6-31G* basis set and the stationary points obtained were characterized using the frequency calculations. All the transition states for the rearrangement reactions were located and were found to possess one imaginary frequency. Intrinsic reaction coordinate (IRC) using mass-weighted Cartesian coordinates,

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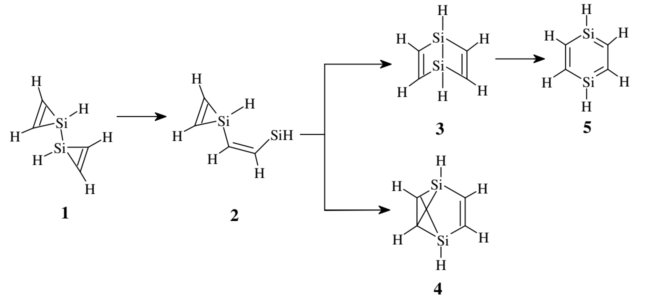
doi:10.1016/j.jorganchem.2004.01.024



Scheme 1.

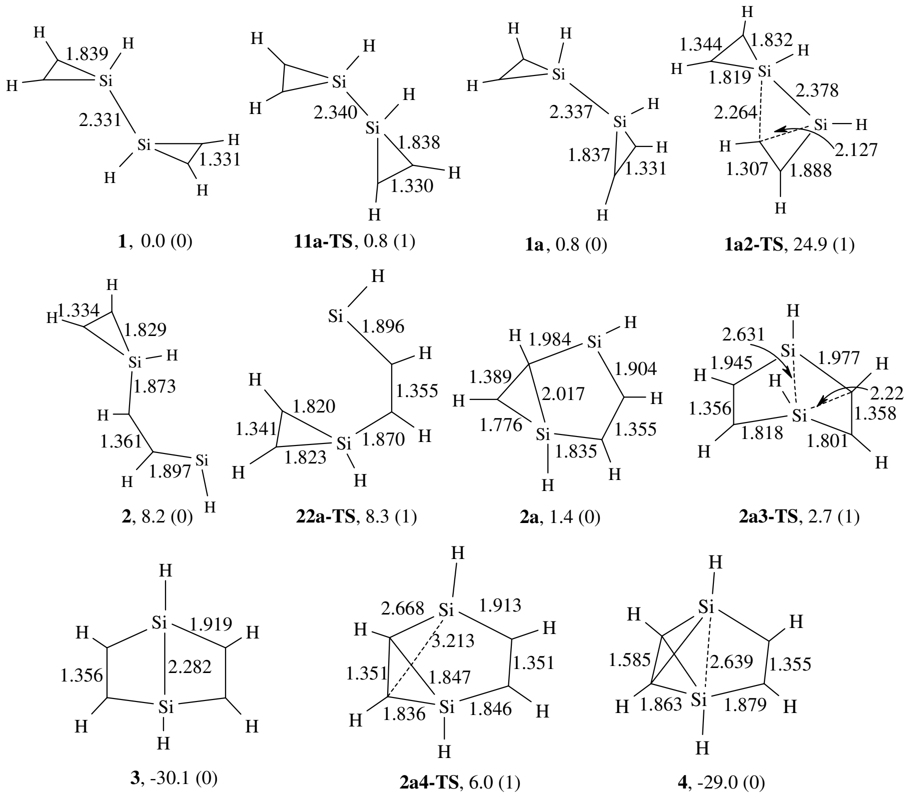
analyses were done to confirm the connectivity of all the transition states [7–10]. Single point energy calculations were performed at the B3LYP/6-311+G**, B3LYP/cc-pVTZ and CCSD(T)/6-31G* levels of theory. The following scheme (Eq. (1)) was used to obtain the best estimates of the relative energies. ΔH is the enthalpy corrections obtained at the B3LYP/6-31G* level. Our previous studies on similar class of compounds indicate that the relative energies obtained using these schemes are comparable to those obtained at the G2 level of theory [3–5,11–13]. All calculations were performed using the GAUSSIAN 98 suite of programs [14]. The bond orders were obtained using natural bond orbital (NBO) method [15] at B3LYP/6-31G* level.

Best estimate,

$$\Delta E = \Delta E_{\mathrm{CCSD(T)}} + \Delta E_{(\mathrm{B3LYP/cc\text{-}pVTZ\text{-}B3LYP/6\text{-}31G^{*}})} + \Delta H \tag{1}$$

3. Results and discussion

Fig. 1 depicts all the transition states and the minimum energy structures located along the reaction pathway of the valence isomerization considered in the study along with their principal geometries and their relative energies. Bond orders and the group charges of all the disilabenzene isomers and their corresponding transition states are given in Fig. 2 and the reaction path is depicted in Fig. 3. The qualitative results obtained are independent of the level of theory employed as is evident from Table 1; the discussion on energetics will be based on the best estimates of the relative energies. Bis(silacyclopropenyl), **1** connects the vinyl silylene intermediate (**2**) via its rotational isomer, **1a**. The rotation of the Si–Si bond in **1** yields **1a** via the transition state **11a-TS**. The closeness of **1**, **11a-TS** and **1a** in terms of energetics indicates that the rotation about the Si–Si single bond exhibits a very soft potential. The rotamer of **1**, **1a** rearranges to yield the vinyl silylene intermediate, **2** proposed by Ando and coworkers. The energy barrier for

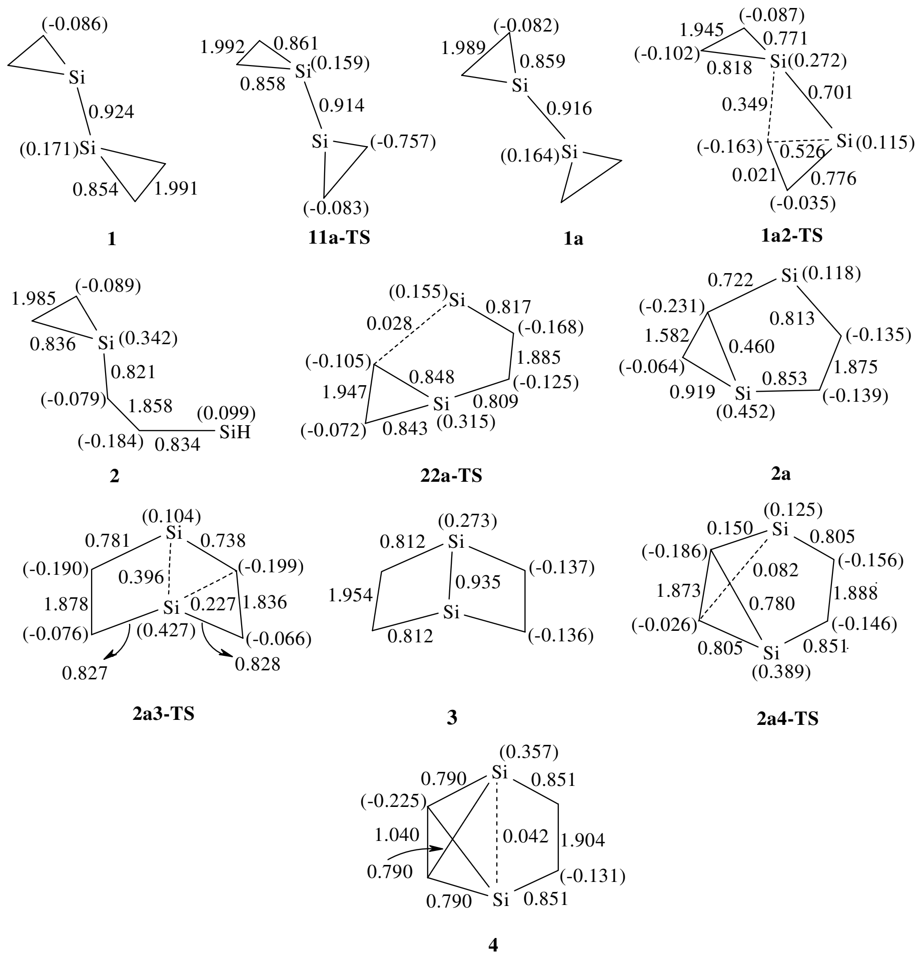


1, 0.0 (0) **11a-TS**, 0.8 (1) **1a**, 0.8 (0) **1a2-TS**, 24.9 (1)

2, 8.2 (0) **22a-TS**, 8.3 (1) **2a**, 1.4 (0) **2a3-TS**, 2.7 (1)

3, -30.1 (0) **2a4-TS**, 6.0 (1) **4**, -29.0 (0)

Fig. 1. The B3LYP/6-31G* optimized important bond length (in Å) of all the disilabenzene isomers and their corresponding transition states and intermediates.



1 **11a-TS** **1a** **1a2-TS**

2 **22a-TS** **2a**

2a3-TS **3** **2a4-TS**

4

Fig. 2. Bond orders and the group charges (in the parenthesis) of all the disilabenzene isomers and their corresponding transition states obtained by B3LYP/6-31G* level.

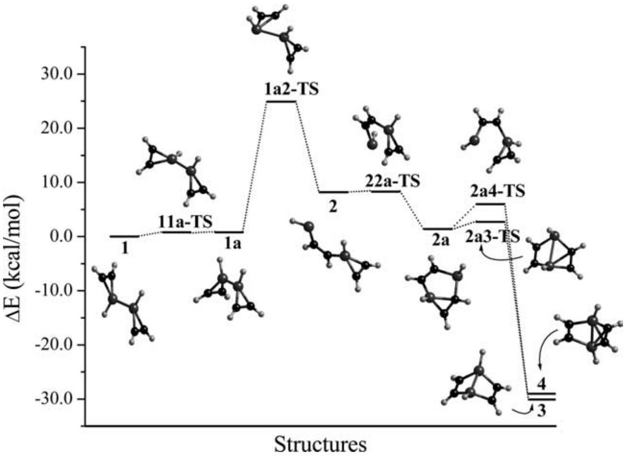


Fig. 3. The reaction energy pathway of the conversion of bis(silacyclopropenyl), **1** to disila(Dewar benzene), **3** and disilabenzvalene, **4**.

the vinyl silylene formation from **1a** is relatively high and is around 25 kcal/mol and the transition state (**1a2-TS**) corresponds to a single step Si–C bond breaking in one of the three membered rings, Si–Si bond breaking and the bond formation of the carbon to the Si of the other ring in **1a**. The vinyl silylene intermediate undergoes virtually barrierless rearrangement to a bicylo[3.1.0] analog, **2a**, before the formation of **3** and **4**. The new intermediate structure, **2a**, is found to be more stable than **2** by about 6 kcal/mol. Thus, in addition to the vinyl silylene intermediate (**2**), one more key intermediate structure (**2a**) was identified along the reaction pathway. The intermediate structure **2a** is a bicyclic structure and minima on the potential energy surface. The C–C bond (1.389 Å) in the three-membered ring is a double bond with bond order 1.582 Å and the bond order of the Si–C bond (1.776 Å) is 0.919 Å. The new intermediate structure (**2a**) undergoes skeletal reorganization to yield **3** and **4**, which are more stable than **2a** by 31.5 and 30.4 kcal/mol, respectively. The barrier of these two interconversions from **2a** are computed to be only 1.5 and 4.8 kcal/mol, respectively. The conversion of either **3** or **4** to **1** is not favored thermodynamically. **3** further rearranges to **5** and the barrier corresponding to the interconversion is 34.6 kcal/mol obtained at the B3LYP/6-31G** level [6]. Thus, the low barrier in the

Table 1
The relative energies of the stationary points located along the reaction pathway corresponding to the conversion of **1** to **3** and **4** obtained at various levels of theory and the best estimates of the relative energies

Structure	B3LYP			CCSD(T)/6-31G*[a]	Best estimate[b]
	6-31G*	6-311+G**[a]	cc-pVTZ[a]		
1	0.0	0.0	0.0	0.0	0.0
11a-TS	1.7	1.7	2.0	1.1	0.8
1a	0.8	0.9	0.8	0.7	0.8
1a2-TS	26.7	27.1	26.2	26.7	24.9
2	7.4	7.6	8.3	7.2	8.2
22a-TS	9.6	9.7	10.2	8.6	8.3
2a	−0.2	0.7	0.4	0.6	1.4
2a3-TS	2.4	3.9	3.0	2.6	2.7
3	−28.9	−27.8	−28.1	−31.9	−30.1
2a4-TS	7.2	7.6	7.8	6.3	6.0
4	−25.9	−25.2	−25.9	−29.5	−29.0

[a] Single point calculations on B3LYP/6-31G* geometries.
[b] Calculated using Eq. (1).

series of rearrangements starting from **1** to yield **3** and **4** indicates that the skeletal rearrangement reactions are spontaneous and explains the high reactivity of this class of compounds.

4. Conclusions

The present study reports a computational study, which explores the reaction pathways of the rearrangement of bis(silacyclopropenyl) (**1**) to Dewar disilabenzene (**3**) and disilabenzvalene (**4**). Our study proves that the reaction proceeds through a vinyl silylene intermediate (**2**) as proposed by Ando and coworkers. However, a new intermediate structure (**2a**) also has been identified which is formed during the course of the reaction, which further isomerised to **3** and **4**. While the barrier corresponding to the rearrangement of **1** to **3** or **4** is about 25 kcal/mol, the rearrangement of **3** to **4** is just above 30 kcal/mol. The low reaction energy barriers point to high reactivity and facile interconversions among this class of compounds.

Acknowledgements

U.D.P. thanks UGC, New Delhi for a research fellowship. We thank Dr. J.S. Yadav, Director, IICT, for his support and encouragement.

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