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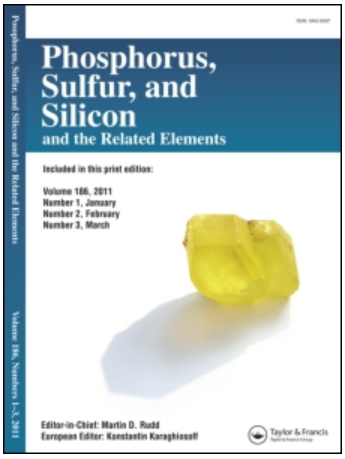

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ISOMERIZATION OF 2-PHOSPHA-4-SILA-BICYCLO[1.1.0]BUTANE

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*In analogy with the valence isomerism of the hydrocarbons bicyclobutane, 1,3-butadiene and cyclobutene, the rearrangements for 2-phospha-4-sila-bicyclo[1.1.0]butane were studied at the B3LYP / 6-311+G** level of theory. The monocyclic 1,2-dihydro-1,2-phosphasilete is shown to be the thermodynamically preferred product, in contrast to the isomerism of the hydrocarbons that favors the 1,3-butadiene structure.*

Keywords: DFT calculations; isomerism; phosphasilabicyclobutane

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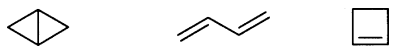
It is well established that bicyclo[1.1.0]butane (**1**) opens to the more stable valence isomer *s*-trans-1,3-butadiene (**2**). In this pericyclic rearrangement, which is characterized by a concerted, asynchronous conrotatory ring opening, the central bond remains intact.[1] According to the Woodward-Hoffmann orbital symmetry rules it concerns an allowed [σ2s + σ2a] conrotatory process.[2] The calculated activation barrier of 41.5 kcal·mol^{-1} [1] agrees closely with the experimental value of 40.6 kcal·mol^{-1}.[3] *s*-Trans-1,3-butadiene (**2**) also is more stable than the other valence isomer, cyclobutene **3**. Rearrangement of **3** to **2**[4] via an electrocyclic ring opening is a pericyclic reaction too, which follows a W–H allowed[2] concerted, conrotatory pathway. The calculated activation barrier of 29.6 kcal·mol^{-1} [5] for this process is in agreement with the experimental value of 32.9 kcal·mol^{-1}.[4]



1 **2** **3**

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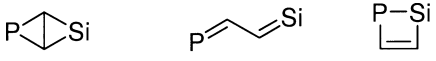
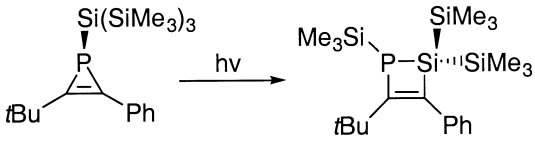
Bicyclo[1.1.0]butanes with main group hetero elements in the ring have also received considerable attention.[6] However, little is known about the phosphorus containing analogs.[7] In our ongoing research on small strained organophosphorus ring systems we became interested in the yet unknown 2-phospha-4-sila-bicyclo[1.1.0]butanes **4**.[8] Here we report on the isomerization of **4** to its valence isomers 1-phospha-4-sila-1,3-butadiene (**5**) and 1,2-dihydro-1,2-phosphasilete (**6**) using DFT calculations at the B3LYP/6-311+G** level of theory.[9]*



4 **5** **6**

Of the three valence isomers, only a derivative of **6** is known experimentally from the photochemical ring expansion of the corresponding 1-silyl-1*H*-phosphirenes (Eq. 1).[10]



(1)

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RESULTS

We found that 2-phospha-4-sila-bicyclo[1.1.C]butane (**4**) opens with a modest exothermicity (3.9 kcal·mol^{-1}) to its valence isomer *s*-trans-1-phospha-4-sila-1,3-butadiene (**5**) via a concerted, asynchronous conrotatory ring opening. In this process the P—C2 bond becomes elongated well before that of the Si—C1 bond (Figure 1).

The activation barrier of 40.7 kcal·mol^{-1} is very similar to the calculated activation barrier of 41.5 kcal·mol^{-1} for the [σ2s+σ2a] process in bicyclo[1.1.0]butane (**1**).[1] *s*-Trans-butadiene **5** can isomerize to the slightly less stable *gauche*-butadiene **7** (ΔE = 3.9 kcal·mol^{-1}) with an energy barrier of only 11.3 kcal·mol^{-1}. Surprisingly, isomer **7** is subject to a conrotatory electrocyclic ring closure to the much more stable

*The 6-311+G** basis set was employed throughout for the geometry optimizations. First and second order energy derivatives were computed to confirm the nature of the minima and transition structures. Intrinsic reaction coordinate calculations (IRC) were performed to establish connections between transition structures and minima.

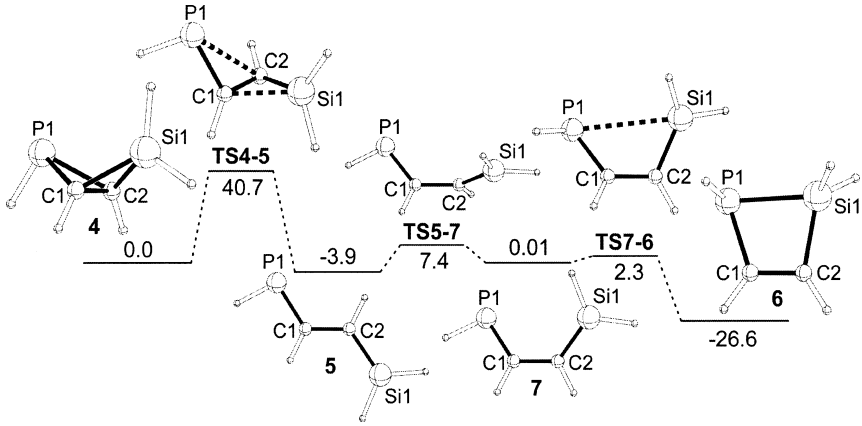

FIGURE 1 Relative B3YLP/6-311+G** energies (in kcal·mol^{-1}) for the rearrangement of **4** into **6**. Selected bond lengths [Å], angles and torsion angles [°] of **4**: P1—C1 1.852, Si1—C1 1.833, C1—C2 1.554, C1—P1—C2 49.6, C1—Si1—C2 50.1; **TS4-5**: P1—C1 1.765, P1—C2 2.590, Si1—C1 2.004, Si1—C2 1.763; **5**: P1—C1 1.705, Si1—C1 1.733, C1—C2 1.423; **TS5-7**: P1—C1—C2—Si1 99.5; **7**: P1—C1—C2—Si1 33.0; **TS7-6**: P1—C1 1.723, P1—Si1 3.073, Si1—C2 1.758, C1—C2 1.406, P1—C1—C2—Si1 34.6; **6**: P1—C1 1.868, P1—Si1 2.302, Si1—C2 1.865, C1—C2 1.343, Si1—P1—C1 71.6, P1—Si1—C2 78.2.

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1,2-dihydro-1,2-phosphasilete (**6**) (ΔE = 26.6 kcal·mol^{-1}) with a rearrangement barrier of only 2.3 kcal·mol^{-1}. Clearly, if a 1-phospha-4-sila-butadiene is to be formed from **4** it will rearrange to the four-membered ring structure **6**. We conclude that much in contrast to the hydrocarbons, where **2** is the favored product, the P,Si-derivatives **5** and **7** are not likely candidates to be observed on rearranging bicyclic compound **4**.

As the formation of **6** is thermodynamically driven, we also explored whether it could be formed directly from bicyclic **4**. Indeed, forcing an asynchronous conrotatory ring opening with an initial SiH_2 group rotation resulted in transition structure **TS4-6** for the direct rearrangement of **4** into **6** (Figure 2). The barrier of 34.7 kcal·mol^{-1} for this process is even less than the conversion via the P,Si-butadienes (Figure 1). The rearrangement via **TS4-6** obeys the orbital symmetry rules and can be described as a [σ2s+σ2a] process.[2] Such a pathway is unprecedented for the isomerization of the carbon analog bicyclo[1.1.0]butane (**1**).[2]

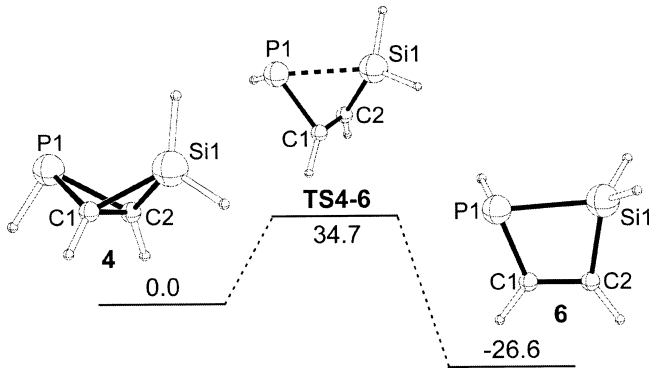

FIGURE 2 Relative B3YLP/6-311+G** energies (in kcal·mol^{-1}) for the direct rearrangement of **4** into **6**. Selected bond lengths [Å] and torsion angles [°] of **TS4-6**: P1—C1 1.828, P1—Si1 2.428, Si1—C2 1.795, C1—C2 1.417, P1—C1—C2—Si1 76.5.

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CONCLUSIONS

Hetero substitution changes the stability of the valence isomers of bicyclo[1.1.0]butane (**1**). 2-Phospha-4-sila-bicyclo[1.1.0]butane (**4**) is the least stable isomer and 1,2-dihydro-1,2-phosphasilete (**6**) the most stable one at the B3LYP/6-311+G** level of theory.[11] Two reaction pathways for the thermal isomerization of 2-phospha-4-sila-bicyclo[1.1.0]butane (**4**) have been found: (a) a higher energy three step process starting with a barrier of 40.7 kcal·mol^{-1} for the concerted, asynchronous conrotatory ring opening of **4** to *s*-trans-1-phospha-4-sila-1,3-butadiene (**5**), followed by a conformational change to the *gauche* isomer **7** and a subsequent conrotatory electrocyclic ring closure to **6**, and (b) a lower-energy transformation of **4** directly into **6** via a [σ2s+σ2a] process with a barrier of 34.7 kcal·mol^{-1}. This latter path is unprecedented in the analogous isomerization of bicyclo[1.1.0]butane.

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