

Photochemistry of heavy cyclopropenes

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Derivates of cyclopropene play an important role in organic synthesis as highly reactive intermediates. This high reactivity is caused by ring strain which is even greater than the one in cyclopropane. Thus, it is not surprising that although heavy analogues of cyclopropane (containing Si, Ge or Sn atoms) were known for a long time,[1] first heavy cyclopropene analogues have not been synthesized until 1995.[2] Among these, cyclotrigermenes and cyclotrisilenes have been most thoroughly studied. In 2000, first example of stable disilagermirene was prepared. Interesting feature of this compound is its easy and fast isomerization to compound **2** (Figure 1) with Si=Ge double bond.[3] Interestingly, compound **2** is extraordinary thermally and photochemically stable. Both compounds **1** and **2** show similar high reactivity towards addition, cycloaddition and oxidation reactions and were already used as a precursors for other interesting molecules. [3]

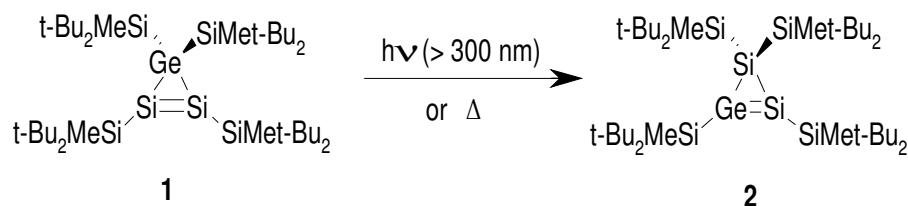


Figure 1: Isomeration of disilagermirene (adapted from [3])

In our work, we investigated the mechanism of the isomerization by means of theoretical chemistry. We performed multireference quantum chemical calculations on model systems **3** and **4** (Figure 2) and localized important points on PES for both ground and first excited state. Finally, *ab initio* quantum molecular dynamics (Full Multiple Spawning approach [4]) was performed on system **3** to account for entropic effects and also to get timescales.

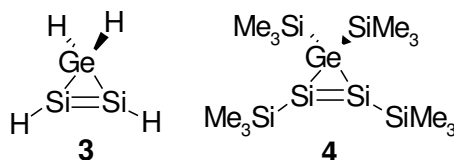


Figure 2: Our model systems for compound **1**

Our results imply that after excitation into the first excited state, system quickly regenerates the ground state via conical intersection in the vicinity of the initial geometry. Reaction of isomerization then proceeds through the vibrationally hot ground state.

Our results agree nicely with experimental data as the isomerization can be induced both photochemically and thermally.[3]

References

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