

# Theoretical Investigation of Electrocyclic Reactions of Siloles

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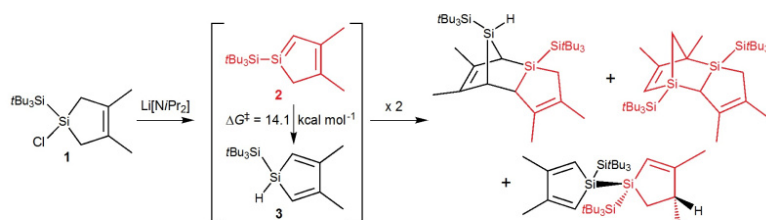
Project Term  
2015 - 2015

Project Areas  
Analytical Chemistry, Method  
Development (Chemistry)

Clusters  
LOEWE CSC Cluster Frankfurt

Institute  
Computational Chemistry

University  
Goethe Universität Frankfurt am  
Main



## Introduction

Siloles are five-membered heterocyclic dienes, in which a silicon atom replaces one of the carbon atoms of cyclopentadiene. Silole derivatives find application as building units for  $\sigma$ - and  $\pi$ -conjugated compounds for use in organic electroluminescent devices,[1] and their synthesis, reactions, and properties have been subject to intensive studies.[2]

## Results

In an earlier investigation, the 1-chlorosilacyclopentene **1** has been obtained starting from perchlorinated silanes,  $\text{Li}[\text{Si}t\text{Bu}_3]$ , and 2,3-dimethylbutadiene[3] and siloles can readily be obtained from this compound by deprotonation and  $\text{LiCl}$  elimination. In a recent combined experimental and theoretical study we have shown that the resulting siloles are very reactive and can isomerise, dimerise or be trapped by reagents like cyclohexene or 2,3-dimethylbutadiene, and the mechanisms underlying these reactions have been investigated in detail by means of double-hybrid density functional theory calculations.[4] Silole **2** can easily isomerise to the more stable silole **3** (Figure 1) via hydrogen shift. Alternatively, it can also dimerise to yield several products: two dimers are formed via Diels-Alder reactions (2+3 and 2+2) and the last one is an head-to-head dimer of **2** and its isomer **3**. This latter, more unusual product is accessible via both singlet and triplet intermediates (Figure 1). Further, compound **2** can be trapped prior to isomerisation or dimerisation by addition of excess cyclohexene yielding the racemate of the [4+2] cycloadduct. Under similar conditions, the reaction of **2** with 2,3-dimethylbutadiene yields the [2+4] and [4+2] cycloadducts and hence, **2** acts as silene (dienophile) as well as diene. Our results show that both reaction steps occur without activation barriers (Figure 2).

## Figures

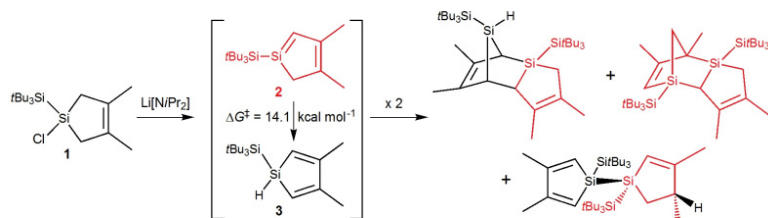


Fig. 1: Formation of silole 2 (and subsequent isomerisation to silole 3) which can dimerise to three different products.

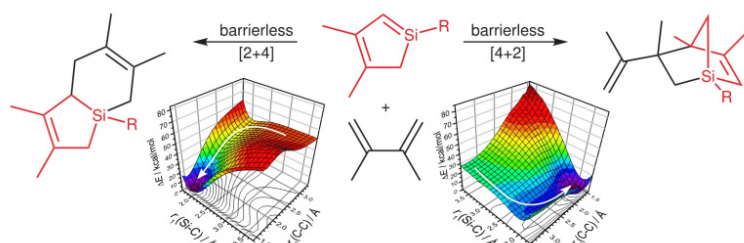


Fig. 2: Barrierless Diels-Alder reaction of the silole (red) with 2,3-dimethylbutadiene can lead to two different products.

## Reference

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- [4] F. Meyer-Wegner, J.H. Wender, K. Falahati, T. Porsch, T. Sinke, M. Bolte, M. Wagner, M.C. Holthausen, and H.-W. Lerner (2014): Electrocyclic Reactions of Siloles: A Combined Experimental and Theoretical Study. *Chem. Eur. J.*, 16 (20): 4681-4690. <https://doi.org/10.1002/chem.201302544>

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