

Theoretical Investigation of Electrocyclic Reactions of Siloles

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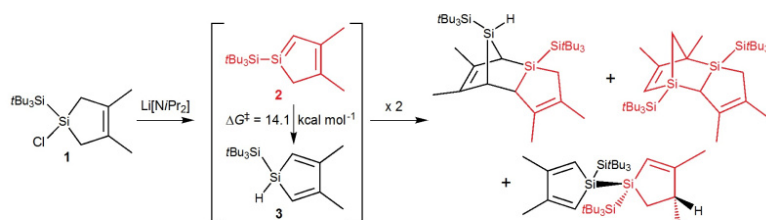
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Clusters
LOEWE CSC Cluster Frankfurt

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 σ - and π -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, Li[Si(tBu)₃], and 2,3-dimethylbutadiene[3] and siloles can readily be obtained from this compound by deprotonation and 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

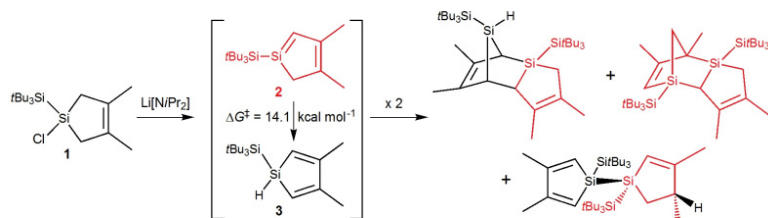


Fig. 1: Formation of silole 2 (and subsequent isomerisation to silole 3) which can dimerise to three different products.

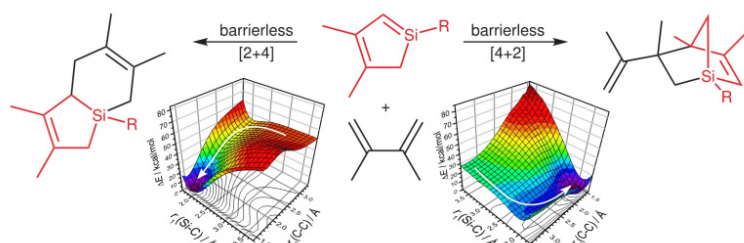


Fig. 2: Barrierless Diels-Alder reaction of the silole (red) with 2,3-dimethylbutadiene can lead to two different products.

Reference

- [1] S. Yamaguchi and K. Tamao (1998): Silole-containing σ - and π -conjugated compounds. *J. Chem. Soc. Dalton Trans.* 22: 3693-3702. <https://doi.org/10.1039/A804491K>
- [2] J. Dubac, A. Laporterie, and G. Manuel (1990): Group 14 metalloles. 1. Synthesis, organic chemistry, and physicochemical data. *Chem. Rev.*, 1 (90): 215-263. <https://doi.org/10.1021/cr00099a008>
- [3] F. Meyer-Wegner, A. Nadj, M. Bolte, N. Auner, M. Wagner, M.C. Holthausen, and H.-W. Lerner (2011): The Perchlorinated Silanes Si_2Cl_6 and Si_3Cl_8 as Sources of SiCl_2 . *Chem. Eur. J.*, 17 (17): 4715-4719. <https://doi.org/10.1002/chem.201003654>
- [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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