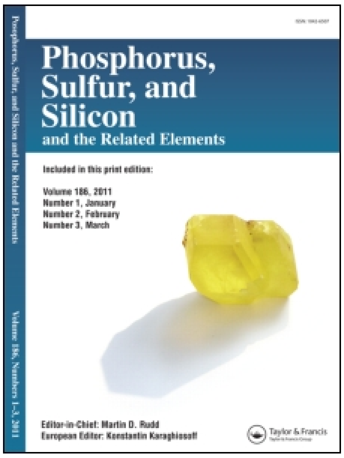

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Disilagermirene and Silagermasilirene: from a Stable Disilene to a Stable Germasilene

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The reaction of 2,2,2-tribromo-1-methyl-1,1-di(*tert*-butyl)disilane and bis[di-*tert*-butyl(methyl)silyl](dichloro)germane with sodium in toluene at room temperature has produced tetrakis[di-*tert*-butyl(methyl)-silyl]disilagermirene. X-ray crystallography of this compound showed a *trans*-bent configuration of Si=Si double bond with a bond length of 2.146 Å. Disilagermirene easily undergoes photochemical and thermal isomerization to a silagermasilirene – first example of a stable germasilene. Reactivity of disilagermirene and silagermasilirene as well as *ab initio* calculations of geometries and stabilities of both compounds have been studied.

Keywords: disilagermirene; silagermasilirene; germasilene

I. INTRODUCTION

The chemistry of three-membered ring systems consisting of heavier Group 14 elements has been in the focus of the intensive study during last two decades, due to the unique stuctures and reactivity of such compounds [1]. Although the first examples of cyclotrimetallanes of Group 14 elements have been prepared almost twenty years ago [2], their unsaturated analogues, that is cyclotrimetallenes, were synthesized quite recently: cyclotrigermenes in 1995 [3], cyclotrisilenes in 1999 [4] and cyclotristannene in1999 [5]. Cyclotrimetallenes consisting of different Group 14 elements were unknown to date, and here we report

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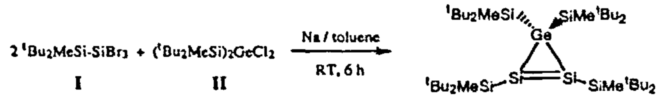
the synthesis, characterization and structure of the first "mixed" cyclotrimetallenes - disilagermirene and its photochemical and thermal isomerization to a silagermasilirene. The reactivity of both compounds as well as the results of theoretical calculations of their geometries and stabilities will be also discussed.

II. RESULTS AND DISCUSSION

The reaction of 2,2,2-tribromo-1-methyl-1,1-di(*tert*-butyl)-disilane **I** and bis[di-*tert*-butyl(methyl)silyl](dichloro)germane **II** with excess sodium in toluene at room temperature has produced dark-red mixture, containing tetrakis[di-*tert*-butyl(methyl)silyl]disilagermirene **III** as a major product.



III

Compound **III** was isolated from hexane as very air- and moisture sensitive ruby hexagonal crystals.

The structure of **III** was established by NMR and mass spectra data, and finally confirmed by X-ray crystallography (Figure 1). The three-membered ring represents an almost isosceles triangle with a Si=Si double bond lenth of 2.146 (1) Å, which is rather short in comparison with other examples of Si=Si distances reported to date (2.138-2.261 Å) [1b]. The geometry of Si=Si double bond is *trans*-bent with a torsion angle Si3-Si1-Si2-Si4 of 37.0 (2) °.

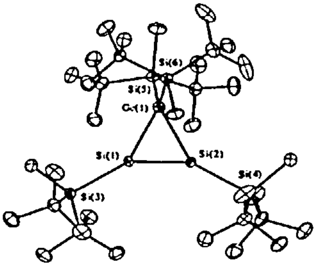
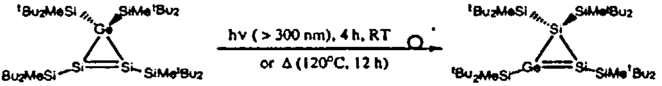


Figure 1. Crystal structure of III

Photolysis of the disilagermirene **III** in deuterobenzene solution ($\lambda >$ 300 nm) or thermolysis at 120 °C in a mesitylene solution caused a migration of silyl-substituent to form tetrakis[di-*tert*-butyl(methyl)-silyl]silagermasilirene **IV** in almost quantitave yield represented the first example of a stable germasilene [6].



III IV

Silagermasilirene **IV** was isolated as air- and moisture sensitive scarlet plate crystals and appeared to be extremely thermally stable with a melting point 194-196 °C. The stucture of **IV** was determined by NMR and mass spectra data, and confirmed by X-ray crystallography, which showed the triangle structure, composed of one saturated Si atom, one unsaturated Si and one unsaturated Ge atoms. Exact determination of bond lengths and angles was impossible because of significant disorder in the positions of double-bonded Si and Ge atoms. Geometry around Ge=Si double bond is also *trans*-bent with torsion angle of 40.3 (5) °.

The *ab initio* calculations on the model H_3Si-substituted three-membered ring compounds at MP2/DZd and B3LYP/DZd levels has predicted the Ge=Si double bond length of about 2.18 Å. It was also found that silagermasilirene is more stable than disilagermirene by 3.9 (MP2) or 2.1 (B3LYP) kcal/mol.

Both **III** and **IV** easily reacted with CCl_4 to produce in high yields the corresponding *trans*-1,2-dichloro-derivatives, whose structures were established by spectral data, and X-ray analysis (for the adduct of **III** with CCl_4).

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