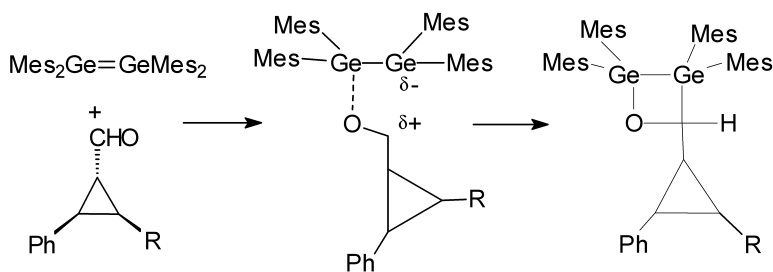


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## Mechanistic Studies of the Addition of Carbonyl Compounds to Tetramesityldigermene

Mini S. Samuel and Kim M. Baines\*

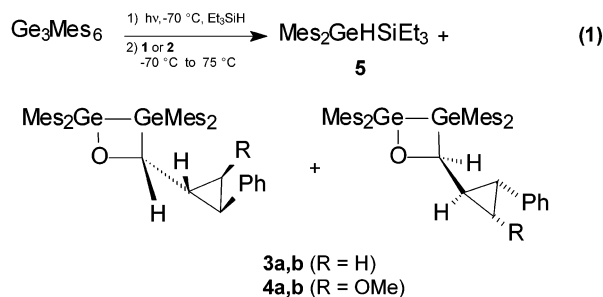
Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

Received June 23, 2003; E-mail: kbaines2@uwo.ca

Mechanistic studies are essential for the understanding and development of chemical reactions. Surprisingly, although the addition of carbonyl compounds to digermenes<sup>1</sup> to give 2,3-digermoxetanes was one of the first reported reactions<sup>2</sup> of this class of compounds, there is only one theoretical<sup>3</sup> and no experimental studies of the mechanism of this addition.<sup>4</sup> In fact, with a few notable exceptions,<sup>5,6</sup> the mechanism of the addition of carbonyl compounds to any doubly bonded Ge derivative remains unexplored. In addition to the fundamental importance of such mechanistic studies in molecular digermene chemistry, the results of such investigations are also relevant in the study of the chemical modification of germanium surfaces, particularly the Ge(100)-2 × 1 surface which is believed to be composed of germanium dimers.<sup>7</sup>

We have used molecular probes to investigate the mechanism of the addition of carbonyl compounds to both disilenes and germasilenes.<sup>8,9</sup> The probes, *trans*-2-phenylcyclopropane carbaldehyde (**1**) and *trans,trans*-2-methoxy-3-phenylcyclopropane carbaldehyde (**2**), contain the same (alkoxy)phenylcyclopropylcarbonyl framework found in the hypersensitive probes developed by Newcomb.<sup>10,11</sup> The cyclopropane carbaldehydes are able to discriminate between the development of a radical or a cationic center at the aldehydic carbon by following different, subsequent reaction pathways.<sup>8,9</sup> The oxy-substituted phenylcyclopropylcarbonyl radical has been shown to undergo rapid ring-opening toward the phenyl substituent, whereas the analogous oxonium ion does not rearrange. However, in the event that the cation does undergo ring-opening, it has been shown that cleavage toward the methoxy group in the (alkoxy)phenyl-substituted cyclopropane ring will occur. Thus, a reliable means of determining the nature of a putative intermediate in an addition reaction to the carbonyl moiety has been demonstrated. The addition of either carbaldehyde **1** or **2** to tetramesityldisilene and tetramesitylgermasilene produced ring-opened products, an oxadimetallacycloheptene and/or an oxapentadienyldimetallane.<sup>8,9</sup> The structures of these products were only consistent with the intermediate formation of an oxy-substituted radical which had subsequently undergone ring-opening toward the phenyl substituent followed by ring-closure or disproportionation. In this way, we were able to establish, for the first time, that a biradical intermediate is involved in the addition of carbonyl compounds to disilenes and germasilenes. Given the paucity of information regarding the mechanism of the addition of carbonyl compounds to digermenes, we have now examined the addition of the mechanistic probes to Mes<sub>2</sub>Ge=GeMes<sub>2</sub> and report our results herein.

Photolysis of hexamesitylcyclotrigermene at -70 °C in the presence of Et<sub>3</sub>SiH in toluene produces a solution of tetramesityldigermene.<sup>12</sup> Subsequent addition of carbaldehyde **1** or **2** to the solution of the digermene followed by warming of the solution to 75 °C produced two adducts (**3a,b** or **4a,b**, respectively) in addition to dimesityl(triethylsilyl)germane, **5**,<sup>13</sup> derived from the addition of triethylsilane to dimesitylgermylene (eq 1).



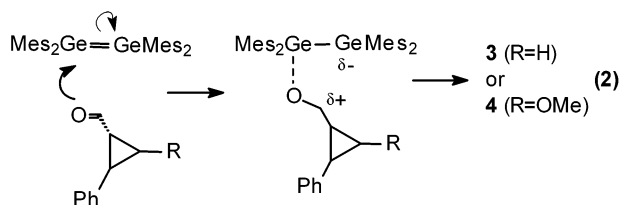
1-Hydroxy-1,1,2,2-tetramesityldigermene, **6**, was also formed during the addition of **1** to Mes<sub>2</sub>Ge=GeMes<sub>2</sub>. The hydroxydigermene was presumably produced either by the addition of adventitious water to the digermene or, more likely, by addition of atmospheric water to unreacted digermene upon quenching of the reaction mixture. The water adduct, **6**, was readily identified by comparison of its <sup>1</sup>H NMR spectral data with the known literature values.<sup>14</sup> The four products, **3a**, **3b**, **5**, and **6**, were formed in a ratio of 1.5:1.5:4:1, respectively, as determined by <sup>1</sup>H NMR spectroscopy. Compounds **3a,b** were unequivocally identified as the diastereomers of the formal [2+2] cycloaddition adduct between Mes<sub>2</sub>Ge=GeMes<sub>2</sub> and *trans*-2-phenylcyclopropane carbaldehyde. The <sup>1</sup>H, <sup>13</sup>C, <sup>1</sup>H-<sup>13</sup>C HSQC, and <sup>1</sup>H-<sup>1</sup>H COSY NMR spectra completely support the structural assignment.<sup>15</sup> Close examination of the <sup>1</sup>H-<sup>1</sup>H coupling constants in the three-membered ring of **3a,b** revealed that the relative stereochemistry of the three-membered ring was unaffected by the reaction.<sup>16</sup> Although every attempt was made to isolate **3a** from **3b**, only a mixture of **3a** and **3b** (1:4) and a mixture of **3a** and **6** (1.8:1) could be obtained.

Compounds **4a,b** were unambiguously identified as diastereomers of the formal [2+2] cycloaddition adduct between Mes<sub>2</sub>Ge=GeMes<sub>2</sub> and aldehyde **2**. The <sup>1</sup>H, <sup>13</sup>C, <sup>1</sup>H-<sup>13</sup>C HSQC, and <sup>1</sup>H-<sup>1</sup>H COSY NMR spectra all support the structural assignments of **4a,b**.<sup>15</sup> Again, close examination of the <sup>1</sup>H-<sup>1</sup>H coupling constants in the three-membered ring of **4a,b** revealed that the relative stereochemistry of the ring was unaffected by the reaction.<sup>16</sup>

There is a striking difference in the structures of the aldehyde adducts isolated from the addition of **1** and **2** to Mes<sub>2</sub>Ge=GeMes<sub>2</sub> and those isolated from addition to the analogous disilene and germasilene: the cyclopropyl ring remains intact in digermene adducts **3** and **4**. In the addition of aldehydes **1** and **2** to tetramesityldisilene and -germasilene, only ring-opened products were isolated.<sup>8,9</sup> The difference in the structure of the adducts signals a significant change in the mechanism of the addition of carbonyl compounds to digermenes in comparison to disilenes and germasilenes. The formation of 2,3-digermoxetanes **3** and **4** is consistent with two plausible mechanisms: the concerted addition of the carbonyl moiety to the Ge-Ge double bond or the formation of a zwitterionic intermediate. The absence of ring-opened products

indicates that an intermediate oxy-substituted cyclopropylcarbanyl radical did not form.

The addition of formaldehyde to the parent digermene has been examined by density functional theory at the B3LYP/6-311++G(d,p) and CAS-MCQDPT2/6-31++G(d,p) levels of theory.<sup>3</sup> No evidence for a biradical intermediate was found on the potential energy surface. Furthermore, transition states along a concerted pathway were also not located. The only pathway identified was stepwise, involving the formation of a zwitterionic intermediate<sup>17</sup> which results from nucleophilic attack by the carbonyl oxygen on the Ge–Ge double bond. Our experimental results are completely consistent with the formation of a zwitterionic intermediate and have unequivocally ruled out the formation of a biradical in the addition of a carbonyl group to digermenes (eq 2), in excellent agreement with the theoretical report.



These results, together with our previous studies,<sup>8,9</sup> allow us to make a rare direct comparison of the reactivity of a disilene, a germsilene, and a digermene because each dimetallene has the same substituent (mesityl) and was allowed to react with the same probes under comparable conditions. There is a dramatic difference in the behavior of the disilene and the germsilene,<sup>8,9</sup> which follow a reaction pathway involving a biradical intermediate, and that of the digermene, which follows a reaction pathway involving a zwitterionic intermediate. The observed pathway selectivity can be understood in light of the results of the theoretical investigation of these reactions.<sup>3</sup> For disilenes, three reaction pathways were identified in the addition of formaldehyde: two involving the formation of zwitterionic intermediates and one, the energetically most favorable pathway, involving the formation of a biradical intermediate. The Si–O bond is completely formed in the biradical intermediate, whereas the interaction between the oxygen of the C=O group and the Si is weak<sup>18</sup> in the zwitterionic intermediates.<sup>3</sup> The strong Si–O bond (~117 kcal/mol)<sup>3</sup> is believed to play a major role in the stabilization of the biradical intermediate (where it is completely formed), resulting in the selection of the biradical over the zwitterionic pathway.<sup>3</sup> For digermenes, only one reaction pathway involving a zwitterionic intermediate with a weak O–Ge interaction<sup>17</sup> was identified on the potential energy surface of the addition. The biradical intermediate is believed to be inaccessible because the weaker Ge–O bond (~98 kcal/mol)<sup>3</sup> cannot stabilize the intermediate relative to the reactants.

Finally, a qualitative comparison of the rates of the addition of aldehydes **1** and **2** to the three dimetallenes was possible by monitoring the disappearance of the characteristic yellow color of the dimetallene. The disilene reacted instantly upon addition of the aldehyde in the cold (~–60 °C), the germsilene required warming to room temperature before the characteristic color of the germsilene had completely faded, and the digermene required heating for complete reaction. The observed rates agree qualitatively with

the calculated barriers for the addition of formaldehyde to the parent dimetallene.<sup>3</sup> Interestingly, the trend in the kinetic behavior of digermenes as compared to disilenes in the addition of aldehydes is mirrored in the rate of the addition of acetone to diphenylsilene and -germene.<sup>5c</sup> The silene reacts with acetone with a rate constant of  $\sim 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , whereas the germene was found to be unreactive under the same conditions. It is reasonable to conclude that the difference in the strength of the Si–O versus the Ge–O bond is again responsible for the difference in the observed reactivity.

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**Supporting Information Available:** Experimental preparations and spectral data for **3a,b** and **4a,b** and a comparison of selected <sup>1</sup>H NMR spectral data of aldehydes **1** and **2** and digermoxetanes **3** and **4** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (15) Complete experimental procedures and spectral data for digermoxetanes **3** and **4** are given in the Supporting Information.
- (16) A comparison of the chemical shifts and coupling constants present in aldehydes **1** and **2** and digermoxetanes **3** and **4** is presented in the Supporting Information.
- (17) The intermediate is characterized as a 1,4-zwitterionic complex with a Ge–O Wiberg bond order = 0.22 and a Ge–O bond length which is 1.24 times the Ge–O bond length in the parent digermoxetane.<sup>3</sup>
- (18) Si–O Wiberg bond order = 0.27; Si–O bond length in the intermediate is 1.24 times the Si–O bond length in the parent disiloxetane.<sup>3</sup>

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