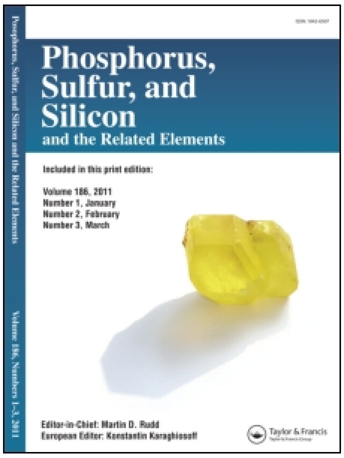

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Mechanistic Investigations of the Addition Reactions of Aldehydes to Disilenes and Germasilenes

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Evidence for the formation of a biradical intermediate in the addition reactions of aldehydes to tetramesitylgermasilene and tetramesityl-disilene is presented.

Keywords: Group 14 dimetallenes; germasilene; disilene; addition reactions; aldehydes

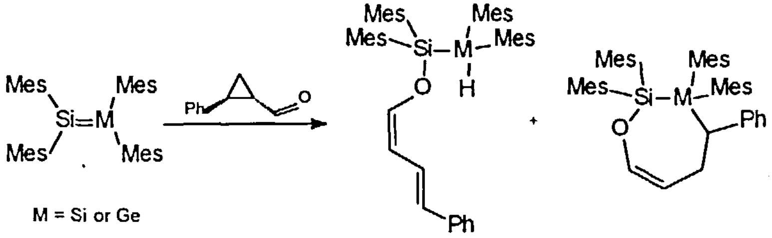
INTRODUCTION

The discovery of stable (or relatively stable) disilenes,[1], [2] digermenes,[3] and germasilenes[3] was significant because these compounds, not surprisingly, parallel alkenes in their usefulness as synthetic precursors. One reaction that has been extensively explored is the addition of carbonyl compounds where products derived from a formal [2 + 2] cycloaddition between the carbonyl group and the M-M double bond are typically observed.[4] However, little is known about the mechanism of the addition of carbonyl compounds to Group 14 dimetallenes.

The use of mechanistic probes to establish the intermediacy of radicals in chemical reactions is well established.[5] We designed a probe to explore the mechanism of the addition of aldehydes to Group 14 dimetallenes based on the well known class of probes developed by Newcomb and co-workers which take advantage of the rapid ring opening reaction of phenyl-substituted cyclopropylcarbinyl radicals.[6] Thus, the addition of *trans*-(2-phenyl)cyclopropane carbaldehyde to tetramesityldisilene and -germasilene was investigated and the results are presented here.

RESULTS AND DISCUSSION

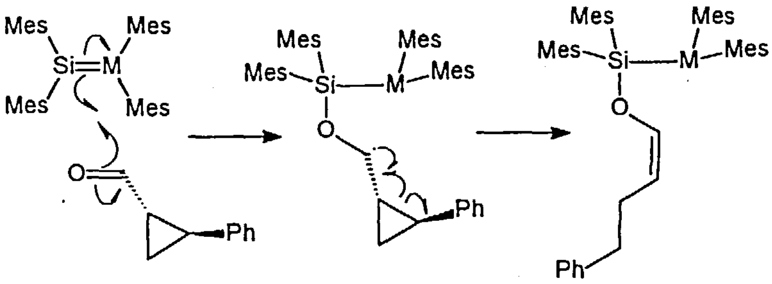
When *trans*-(2-phenyl)cyclopropane carbaldehyde was allowed to react with tetramesityldisilene at -60 °C in hexanes, two adducts, **1** and **2**, were produced in approximately a 1:1 mixture as determined by ^{1}H NMR spectroscopy. Likewise, addition of *trans*-(2-phenyl)cyclopropane carbaldehyde to a solution of tetramesitylgermasilene, produced by photolysis of hexamesitylsiladigermirane at -70 °C in the presence of Et_3SiH, yielded three products, $(Et_3Si)GeMes_2H$ (**3**),[7] **4** and **5**, in a ratio of 2:1:1, respectively, as determined by ^{1}H NMR spectroscopy.



1 M=Si
4 M=Ge

2 M=Si
5 M=Ge

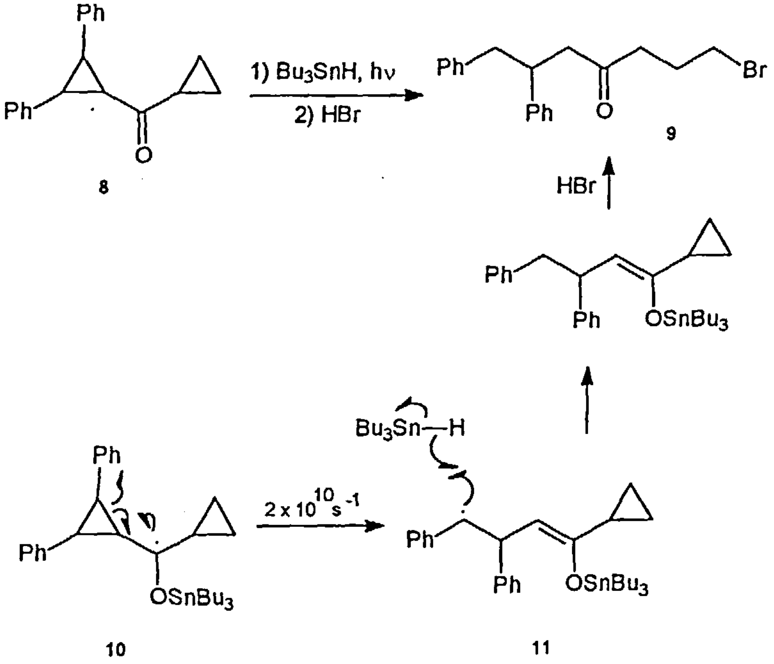
The structures of compounds **1**, **2**, **4**, and **5** indicate that the cyclopropyl ring found in the aldehyde opened during the course of the reaction. We believe the ring opening is the result of the rearrangement of an intermediate biradical. Initial addition of the carbonyl double bond to the Si-M double bond of germasilene or the disilene would lead to biradical **6**. We expect the cyclopropylcarbinyl radical moiety in **6** to undergo rapid rearrangement to the 2°-benzyl/homoallyl radical, 7, which can disproportionate to give **1** or **4** or can undergo ring closure to yield **2** or **5**.



M = Ge or Si **6** **7**

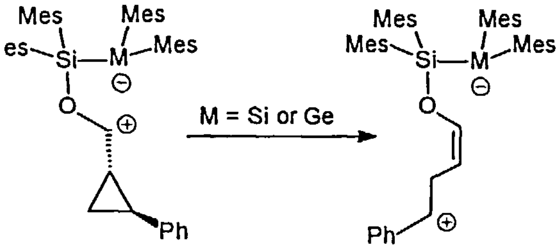
Biradical **6** contains an *oxy*-substituted cyclopropylcarbinyl radical. Although the rate constant for the ring opening of oxy-substituted cyclocarbinyl radicals is unknown, Newcomb and co-workers have shown that the cyclization rate constant of the 1-methoxy-6,6-diphenyl-5-hexenyl radical is nearly equal to the related radical without the methoxy group.[8] Thus, it is not unreasonable to assume that the oxy-substituted cyclopropylcarbinyl radical will open at a rate similar to the unsubstituted analog. The following two examples give additional precedents for the rapid ring opening of an oxy-substituted cyclopropylcarbinyl radical. Thermolysis of *trans*-(2-phenyl)cyclopropane carbaldehyde and tributyltin hydride in the presence of AIBN gave a 2.5:1 mixture of 4-phenylbutanal and (2-phenylcyclopropyl)carbinol.[9] The tributyltin radical is believed to add to the carbonyl oxygen of the aldehyde to give the oxy-substituted cyclopropylcarbinyl radical which either undergoes ring opening before hydrogen atom abstraction or abstracts a hydrogen atom directly. The observed products are obtained after solvolysis (ethanol) of the stannyl ethers.

Furthermore, Castellino and Bruice reported that the dicyclopropyl ketone **8** gave, among other products, compound **9**

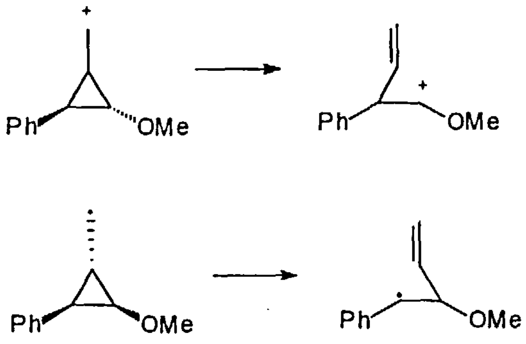


when irradiated in the presence of Bu_3SnH, followed by addition of HBr to the reaction mixture.[10] The oxy-substituted cyclopropylcarbinyl radical, **10**, rearranges selectively to the 2°-benzyl/ homoallyl radical, **11**, which then abstracts a hydrogen atom to give the stannyl enol ether. The rate of this rearrangement was estimated to be at least 2×10^{10} sec^{-1}. Treatment of the stannyl enol ether with HBr gives **9**. Given these precedents, as well as the investigations by Newcomb on the rapid ring opening reactions of phenyl-substituted cyclopropylcarbinyl radicals,[6] it is reasonable to propose the formation of biradical **6** during the addition of *trans*-(2-phenyl)cyclopropane carbaldehyde to tetramesitylgermasilene and -disilene which undergoes rapid ring opening to biradical **7**.

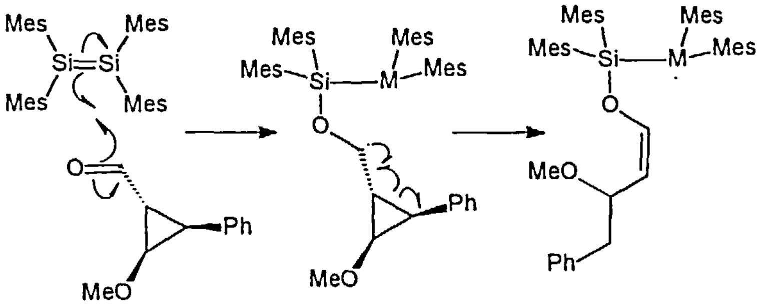
However, despite the precedents that favour the formation of a biradical intermediate en route to compounds **1**, **2**, **4** and **5**, the observation of these compounds may also be explained by rearrangement of a zwitterionic cyclopropylmethyloxonium ion to a 2° benzyl carbocation.[11],[12]



Newcomb and co-workers have developed a probe to distinguish between radical and carbocationic intermediates. The design takes advantage of the fact that a phenyl group stabilizes a radical center more strongly than an alkoxy group, whereas, an alkoxy group provides greater stabilization to a carbocation. Accordingly, they have shown that a cyclopropylcarbinyl cation will ring open preferentially towards an alkoxy substituent whereas a cyclopropylcarbinyl radical will open preferentially towards a phenyl group.[13]



To unequivocally distinguish between a mechanism involving a zwitterionic or a biradical intermediate, we examined the addition of *trans-trans*-2-methoxy-3-phenylcyclopropane carbaldehyde to tetramesityldisilene. *Trans-trans*-2-methoxy-3-phenylcyclopropane carbaldehyde was allowed to react with tetramesityldisilene at -60 °C in hexanes. After removal of the solvent, the product mixture was dissolved in a benzene/acetone mixture. Compound **12** crystallized in 41% yield from this solution. We believe that compound **12** results from the regioselective ring opening of *biradical* **13** towards the phenyl group to give biradical **14** which upon ring closure gives compound **12**.



13

14

SUMMARY

In summary, the addition of *trans*-(2-phenyl)cyclopropane carbaldehyde to tetramesitylgermasilene or-disilene and the addition of *trans-trans*-2-methoxy-3-phenylcyclopropane carbaldehyde to tetramesityldisilene yielded products which are completely consistent with the rapid ring opening of a cyclopropylcarbinyl radical. The formation of compounds **1**, **2**, **4**, and **5** demonstrates that the addition of aldehydes to tetramesitylgermasilene and -disilene most likely proceeds via a biradical intermediate. The results detailed here are interesting in light of a report by Leigh on the mechanism of the ene-addition of acetone to several 1,1-diphenylsilene derivatives.[14] The results of their study are consistent with a mechanism involving initial, reversible formation of a zwitterionic silene-ketone complex which collapses to product by rate-controlling proton transfer. Furthermore, it is suggested that the formal [2 + 2] addition of non-enolizable carbonyl compounds to reactive silenes might also proceed through the intermediacy of silene-carbonyl complexes.[14],[15] Our results, however, indicate that it is unlikely there is an initial dimetallene-carbonyl zwitterionic complex formed in the addition of aldehydes to dimetallenes, but rather, the cycloaddition most likely proceeds through a stepwise, biradical pathway without the involvement of the oxygen lone pair.

Acknowledgments

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