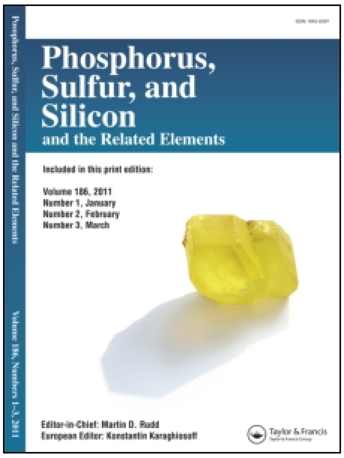

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CYCLOADDITION REACTIONS OF GROUP 14 DIMETALLENES: EVIDENCE FOR A RADICAL PATHWAY

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Evidence for a radical pathway in the cycloaddition reactions of alkenes to tetramesitylgermasilene and tetramesityldisilene is presented.

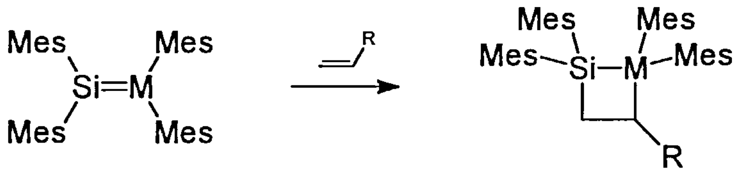
Keywords: Group 14 dimetallenes; germasilene; disilene, cycloaddition reactions

INTRODUCTION

Transient disilenes react readily with conjugated dienes. In fact, the isolation of a Diels-Alder adduct between a disilene and a diene from a reaction believed to involve a transient disilene is taken as good evidence in support of the transient doubly-bonded species[1]. In contrast, tetramesityldisilene[2], -germasilene[3], and -digermene[3], relatively stable dimetallenes, do not react readily with 2,3-dimethylbutadiene. Thus, the report of an adduct between tetra-*tert*-butyldisilene and the simple conjugated alkene, *o*-methylstyrene was surprising[4]. We have since investigated a number of reactions between tetramesitylgermasilene and various alkenes[5],[6],[7]. It has been found that the addition of the alkene to the germasilene occurs in only a limited number of cases. In those instances where addition of the alkene to the germasilene was observed, the analogous reactivity for tetramesityldisilene was also found[5],[6]. To understand the observed reactivity trend between tetramesitylgermasilene and -disilene with alkenes and conjugated dienes, the mechanism of alkene additions to the germasilene and disilene was probed.

RESULTS AND DISCUSSION

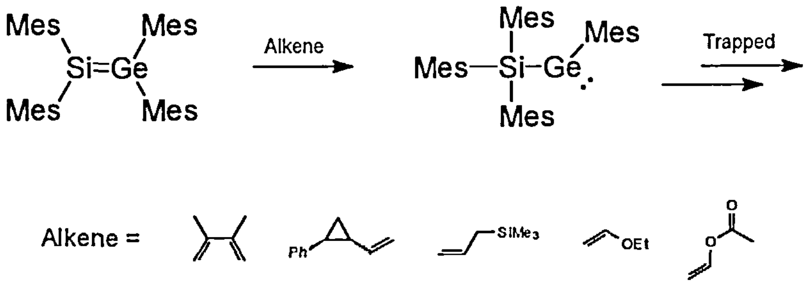
1-Methoxybutadiene,[5] styrene[5] and acrylonitrile[6] have each been shown to add to the germasilene to give the corresponding germasilacyclobutane, regioselectively. The analogous reaction between tetramesityldisilene and styrene[5] or acrylonitrile[6] also occurs. However, when 2,3-dimethylbutadiene[3], *trans*-1-phenyl-2-vinylcyclopropane,[7] allyltrimethylsilane,[7] ethyl vinyl ether[5] or vinylacetate[5] are allowed to react with tetramesitylgermasilene,



M = Ge, R = Ph, CN or CH=CHOMe

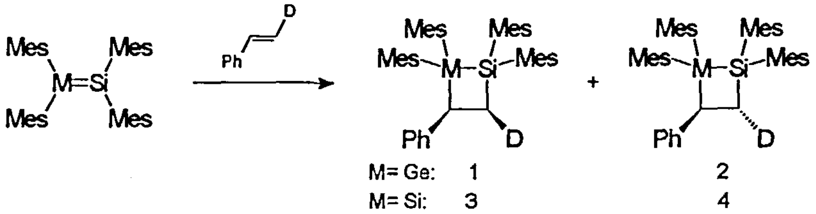
M = Si, R = Ph or CN

rearrangement of the germasilene to a silylgermylene occurs at a faster rate than addition of the alkene to the Si-Ge double bond[8]. The silylgermylene may then be trapped by triethylsilane (present in the reaction mixture).

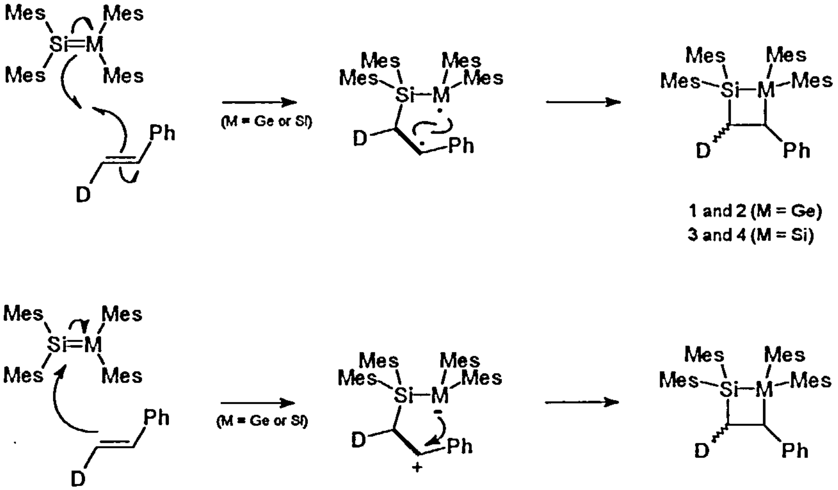


To rationalize these observations, a better understanding of the mechanism for addition reactions between tetramesitylgermasilene and alkenes or conjugated dienes was required. To begin, the concertedness of the alkene addition was examined using trans-*d*-styrene.

When trans-*d*-styrene was allowed to react with tetramesitylgermasilene, which was produced by low temperature photolysis of hexamesitylsiladigermirane in the presence of Et_3SiH, an 8:2 diastereomeric mixture of two cycloadducts, **1** and **2**, was produced. In the ^1H NMR spectrum of the undeuterated styrene-germasilene cycloadduct, the resonances for the hydrogen atoms on the germasilacyclobutane ring appear as an ABX pattern[5]. Replacement of one of the AB hydrogen atoms for a deuterium atom simplified the ABX system to an AX pattern for **1** and **2**. The *cis* and *trans* adduct mixture showed two sets of two doublets, which were well separated for each species. Integration of the appropriate signals (the doublets at 3.695 ppm, $^3J=15.6$ Hz and 3.694 ppm, $^3J=5.4$ Hz) gave the approximate composition of the diastereomeric mixture of **1** and **2** as 8 ($^3J=15.6$ Hz):2 ($^3J=5.4$ Hz). Which isomer is present in the greater amount is unknown.



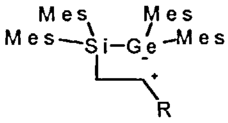
When the analogous experiment is conducted with tetramesityldisilene, a 7:3 diastereomeric mixture of two cycloadducts, **3** and **4**, is produced. Again, replacement of one of the AB hydrogen atoms of the disilacyclobutane ring with a deuterium atom likewise changed the ABX system observed in the undeuterated styrene-disilene adduct to an AX pattern for **3** and **4**. The *cis* and *trans* adduct mixture showed two sets of two doublets, which were well separated for each species and integration of the appropriate signals (the doublets at 3.441 ppm, $^3J=16$ Hz and 3.436 ppm, $^3J=6.9$ Hz) gave the approximate composition for the diastereomeric mixture of **3** and **4** as 7 ($^3J=16$ Hz):3 ($^3J=6.9$ Hz)[9]. When the same experiment was conducted with cis-*d*-styrene the relative intensity of the doublets changed accordingly. That is, the $^3J=16$ Hz doublet was now the minor component of the diastereomeric mixture.



1 and 2 (M = Ge)
3 and 4 (M = Si)

The formation of two diastereomeric adducts is evidence for a stepwise mechanism for the addition of trans-*d*-styrene to tetramesitylgermasilene and tetramesityldisilene. The simplest process that could lead to this result would involve addition of trans-*d*-styrene to the dimetallene, giving either a biradical or zwitterionic intermediate. The resulting species could then close, without bond rotation (highlighted bond in the above scheme), to give the *trans* isomer, or the intermediate could close following bond rotation giving the *cis* isomer. Unfortunately, we have not been able to chemically distinguish between these two possible mechanisms to date. However, if the ability of the substituent on the alkene to stabilize the general intermediate (biradical or ionic) produced by reaction of the alkene with tetramesitylgermasilene is examined and then compared to the observed reactivity of the alkenes, some conclusions may be drawn about the possible nature of the intermediates.

It is reasonable to assume that as the ability of R (as shown in the general intermediates 5 and 6 below) to stabilize the adjacent centre (either radical or cationic) changes, the overall stability of the proposed intermediate will change accordingly. Therefore, as the ability of R to stabilize the adjacent centre increases, the overall stability of the proposed intermediate should also improve. Accordingly, the formation of the intermediate becomes favoured and the addition of the alkene to the germasilene is observed, rather than rearrangement of the germasilene to the silylgermylene.



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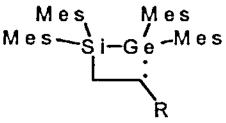


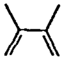
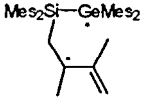
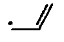
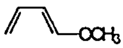
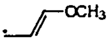
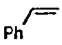
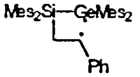
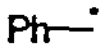
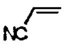
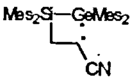
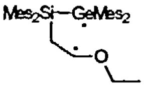
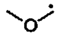
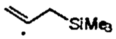
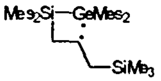
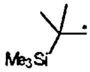
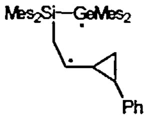
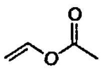
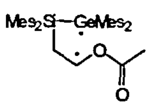
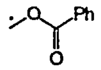
6

At this time, we feel that the observed reactivity of tetramesitylgermasilene toward alkenes is best rationalized by proposing a biradical intermediate, such as 6. An approximation for the relative stabilities of each of the possible intermediates derived from reaction between tetramesitylgermasilene and the alkenes can be achieved by examining the relative ability of R, as shown in the general structure 6, to stabilize an adjacent radical centre. By selecting radicals to represent the radical centre plus the substituent R, as seen in 6, and examining their relative bond dissociation energies, the various possible intermediates may be ranked in terms of their expected stabilities. Table 1 indicates that the trend in radical stability, as afforded by R, correlates well with the observed reactivity of tetramesitylgermasilene and the various alkenes or conjugated dienes.

This suggests that it is the ability of the substituent R to stabilize the adjacent radical centre in the biradical intermediate that determines whether cycloaddition is observed between a given alkene and tetramesitylgermasilene. As the ability of the R group to stabilize the radical increases, the activation energy for the formation of the corresponding intermediate should decrease. Thus, the rate of addition of the alkene to tetramesitylgermasilene increases relative to the rate of the 1,2-mesityl shift. Likewise, the alkenes where the R groups had the least ability to stabilize an adjacent radical centre did not add to tetramesitylgermasilene at a rate greater than the 1,2-mesityl shift. The exception to this observation is 2,3-dimethyl-butadiene, where the 1,2-mesityl shift occurred at a greater rate than addition of the diene to tetramesitylgermasilene. A possible explanation may the relative steric bulk of 2,3-dimethylbutadiene. It has been found that the reactivity of dimetallenes is quite sensitive to changes in the size of the reagent. For example, tetramesityldisilene was found to be unreactive toward *trans*-methylstyrene[7], where previously the disilene was found to give a cycloadduct with styrene[5]. So, despite the relatively stable intermediate possible from reaction between tetramesitylgermasilene and 2,3-dimethylbutadiene, the diene may be too bulky to permit reaction with the sterically crowded germasilene.

If the ionic intermediate is considered, then intermediate **7**, which should result from reaction between tetramesitylgermasilene and ethyl vinyl ether, would be expected to be more stable than intermediate **8**, which would result from reaction between the germa-

TABLE 1 Bond Dissociation Energies for Selected Radicals

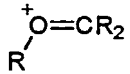
Alkene	**Intermediate**	**Model Radical**	**BDE (kcal/mol)**[a]
			86.3
			87.9[b]
			88.0
			93[c]
			93[c]
			96.8
			97.4
			100.2

(a) McMillen, D.F.; Golden, D.M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493 as reported in the Handbook of Chemistry and Physics, 71st Edition, 1990-1991.

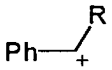
(b) Value estimated using "Structures and Properties" Software Version 2.01, Stephen E. Stein, Standards Reference Program, NIST, MD, 1994.

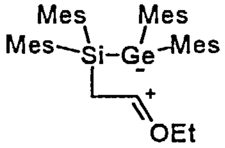
(c) Although the BDE for the primary -CN and -OMe substituted alkanes are within experimental error of one another, the values for the corresponding secondary radicals show the expected trend: $NC\dot{C}HCH_3$, 89.2 kcal/mol; $EtO\dot{C}HCH_3$, 91.7 kcal/mol.

silene and styrene[10]. This is expected since it is well known that alkoxonium ions are more stable than benzyl carbocations. Thus, the activation energy for the reaction between tetramesitylgermasilene and ethyl vinyl ether, leading to **7**, should be lower than the activation energy for reaction between tetramesitylgermasilene and styrene, leading to **8**. Therefore, cycloadduct formation would be expected to be observed between tetramesitylgermasilene and ethyl vinyl ether.



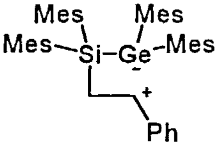
more stable than





7

more stable than



8

However, this is not the case. The rearrangement of tetramesitylgermasilene to the silylgermylene occurs at a greater rate than addition of ethyl vinyl ether to the Si-Ge bond. It may be inferred from this result that the activation energy leading to the formation of any intermediate resulting from reaction between ethyl vinyl ether and tetramesitylgermasilene must be greater than the activation energy associated with the 1,2-mesityl shift. By this argument, intermediate **7** may be excluded because it is expected to be more stable than **8** and accordingly, have a lower energy of activation relative to the 1,2-mesityl shift. Consequently, the formation of **7** should be favoured over the 1,2-mesityl rearrangement of tetramesitylgermasilene. This implies that the stepwise mechanism for alkene additions to tetramesitylgermasilene does indeed involve a biradical species.

Clearly, mechanistic studies of the addition reactions of Group 14 dimetallenes are in their infancy. This field promises to provide a fruitful area of research in the future and one in which we are continuing to work with enthusiasm!

Acknowledgments

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[8.] K.M. Baines and J.A. Cooke, *Organometallics*, 11, 3487 (1992).

[9.] The original solution of the ABX spin system for the adduct between styrene and $Mes_2Si{=}SiMes_2$[5] is not consistent with the J values found through the addition of *trans*-deuterostyrene. The ABX portion of the ^1H nmr spectrum of the adduct was successfully simulated using $J_{AX/BX}=16$ Hz/7 Hz.

[10.] A zwitterionic *intermediate* with a positive charge on germanium and a negative charge on carbon was not considered likely given the lack of experimental evidence for heavy Group 14 cations in solutions (see *Science*, 263, 983-985 (1994). A *transition state* with this charge distribution probably would not have led to scrambling of the stereochemistry in the addition of *trans*-deuterostyrene.