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Arrhenius Parameters for the Head-to-Tail Dimerizations of 1,1-Diphenylsilene and 1,1-Diphenylgermene in Solution

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Arrhenius parameters for the head-to-tail dimerization of 1,1-diphenylsilene and 1,1-diphenylgermene have been determined in hexane solution by nanosecond laser flash photolysis. Both compounds exhibit near-zero activation barriers over the range 0−60 °C and preexponential factors of ca. 10^9 and 10^{10} M^{-1} s^{-1}, respectively. While the results do not allow one to distinguish conclusively between concerted and stepwise mechanisms for the reaction, they provide an indication of what the kinetic behavior of the putative reaction intermediates must be if dimerization proceeds nonconcertedly.

Introduction

The chemistry of silicon−carbon and germanium−carbon double bonds has been the subject of considerable interest over the past ~30 years.[1−6] As might be expected, the chemistry of silenes and germenes share many common features; for example, they both exhibit potent reactivity as electrophiles, as dienophiles, and toward dimerization, and most of their reactions are highly regioselective. Much of the recent mechanistic work on their rich reactivity has been devoted to the study of nucleophilic additions, and the mechanisms of these reactions are now reasonably well understood, at least for silenes.[7−13] Relatively little experimental work has been done on the kinetics and mechanism of the dimerization of silenes and germenes, despite the considerable interest that theoreticians have shown in these reactions.[14−22]

Silenes are known to dimerize in three ways: head-to-tail [2+2]-cycloaddition, head-to-head [2+2]-cycloaddition, or head-to-head ene-dimerization.[1−5] Theoretical calculations suggest that the regiochemistry of the reaction is dictated by the electronic nature of the substituents at carbon and silicon and their effect on the polarity of the $^{\delta+}Si{=}C^{\delta-}$ bond.[16,17] Similar factors appear to control the regiochemistry of dimerization of germenes.[22,23]

Head-to-tail dimerization is most common, as this is the preferred regiochemistry for relatively polar, electrophilic silenes such as 1,1-dimethylsilene (**2a**). The kinetics of dimerization of **2a** have been studied in the gas phase by two groups, using the gas-phase thermolysis or photolysis of 1,1-dimethylsilacyclobutane (**1a**) to generate the silene (eq 1).[24,25] Gusel'nikov and co-workers determined a value of $k_{\mathrm{dim}} = 5.9 \times 10^{-15}$ cm^3 s^{-1} (corresponding to a solution-phase value of only 3.55×10^6 M^{-1} s^{-1}) and found the rate constant to be temperature independent over the 25−300 °C range ($E_a = 0 \pm 1$ kcal/mol; $\log(A/\mathrm{cm}^3\ \mathrm{s}^{-1}) = -14.2$).[26] Potzinger and co-workers later reexamined the dimerization of **2a** using laser flash photolysis techniques and reported a value of $k_{\mathrm{dim}} = (3.3 \pm 0.8) \times 10^{-11}$ cm^3 s^{-1} at ~298 K.[25] This corresponds to a solution phase rate constant of 2×10^{10} M^{-1} s^{-1} and is more reasonable

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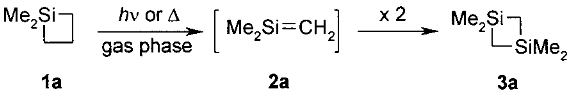
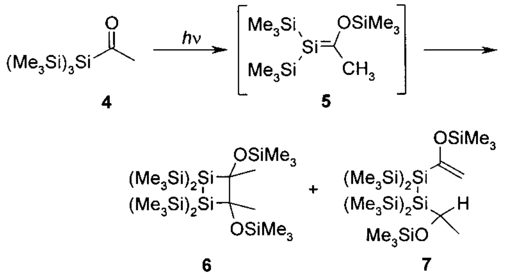
considering the very high reactivity that **2a** exhibits toward nucleophiles.[10,27] It is also consistent with a more recent determination of the rate constant for head-to-tail dimerization of 1-methylsilene ($k_{\mathrm{dim}} = (2.4 \pm 0.5) \times 10^{-11}$ cm^3 s^{-1} at 300 K).[28] While there is indirect support from other studies for the original conclusion that the rate of dimerization of **2a** is temperature independent,[29] the problem has never been reexamined by direct methods.



(1)

Head-to-head regiochemistry is favored for silenes of relatively low Si=C bond polarity and electrophilicity. For example, the 1,1-bis(trimethylsilyl)silene **5**, formed in the photolysis of acylpolysilane **4**, dimerizes to give two products: the 1,2-disilacyclobutane **6** and the ene-dimer **7** (eq 2).[30] The two products were proposed to result either from concerted [2+2]-cycloaddition and ene-reaction, respectively, or via a stepwise pathway involving the common 1,4-biradical intermediate **8** (eq 3). The kinetics of dimerization of **5** in cyclohexane solution have been studied by Conlin and co-workers, who reported a rate constant of $k_{\mathrm{dim}} = 1.3 \times 10^{7}$ M^{-1} s^{-1} at 293 K and the Arrhenius parameters $E_a = 0.2 \pm 0.1$ kcal/mol and $\log(A/\mathrm{M}^{-1}\,\mathrm{s}^{-1}) = 7 \pm 1$.[31] These values are consistent with either concerted or stepwise dimerization mechanisms, provided that the formation of the biradical intermediate (**8**) by the latter pathway is reversible.



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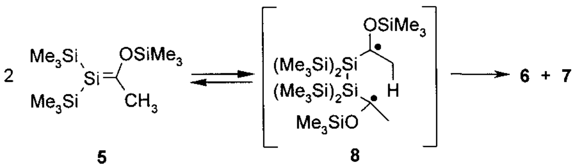
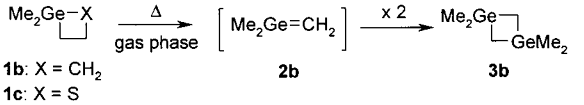


(3)

As might be expected, the same bond polarity factors appear to govern the regiochemistry of germene dimerization. For example, 1,1-dimethylgermene (**2b**) dimerizes with head-to-tail regiochemistry to yield 1,1,3,3-tetramethyl-1,3-digermacyclobutane **3b** (eq 4),[32,33] while the stabilized germene **9b** dimerizes in head-to-head fashion, the same as its silicon counterpart **9a** (eq 5).[34,35] Except for one example from our group (vide infra),[36] no kinetic studies of germene dimerization have yet been reported.



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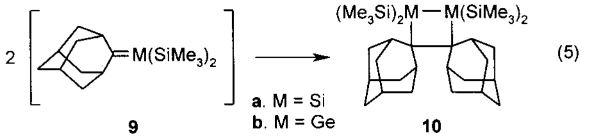

(5)

High-level theoretical studies of the mechanism of the head-to-tail dimerization of the parent silene ($H_2Si{=}CH_2$, **11**) have led to conflicting conclusions. Schaefer and co-workers proposed a concerted ($\pi2s+\pi2s$) mechanism on the basis of calculations carried out at the CCSD (DZ+d) level of theory, in which reaction proceeds via a C_{2h}-symmetric transition state that is 3.8 kcal/mol higher in energy than the reactants.[18] Two later studies by Bernardi and co-workers concluded in favor of stepwise mechanisms for the reaction.[19,21] In the first study, CAS-SCF calculations, with geometries optimized at the DZ+d or 3-21G* levels of theory, predicted the reaction to proceed via the initial, effectively irreversible formation of the *trans*-1,3-disilabutane-1,4-diyl biradical **12** (eq 6). The biradical then undergoes bond rotation and coupling to yield the head-to-tail dimer (**13**) through an activation barrier of 2.7 kcal/mol.[19] In the second, carried out at the CASPT2/6-311G*//CAS−SCF/6-31G* level of theory, the reaction was predicted to proceed via the initial formation of the *trans*-2,3-disilabutane-1,4-diyl biradical **14**, of energy ~5.3 kcal/mol lower than the reactants. Collapse of the biradical to **13** by 1,2-sigmatropic shift (eq 10) then proceeds through an activation barrier of ca. 4.2 kcal/mol,[21] via a transition state similar to that originally proposed by Schaefer and co-workers for the concerted dimerization pathway.[18] Only one theoretical study of germene dimerization has been reported,[22] in which a concerted mechanism analogous to that of Seidl et al.[18] was proposed.

In this paper, we report the first determination of the Arrhenius parameters for the head-to-tail dimerization of a transient silene and its germanium homologue in solution. 1,1-Diphenylsilene (**16a**) and 1,1-diphenylgermene (**16b**), generated by photolysis of the corresponding 1,1-diphenylmetallacyclobutanes **15a**,**b**, are both known to dimerize to give the head-to-tail cycloadducts **17a**,**b** (eq 8).[36–38] We have previously shown that the dimerizations of these two compounds proceed with absolute rate constants on the order of 10^{10} M^{-1} s^{-1} in hexane solution at room temperature, the fastest of any

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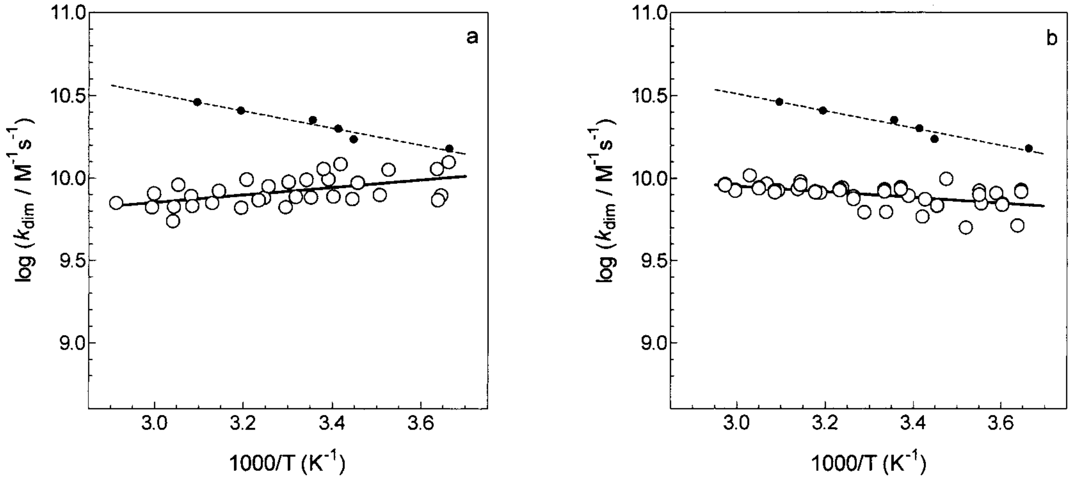
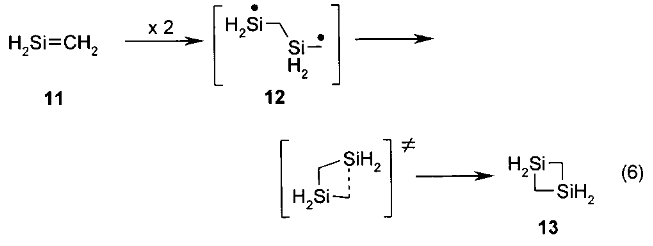
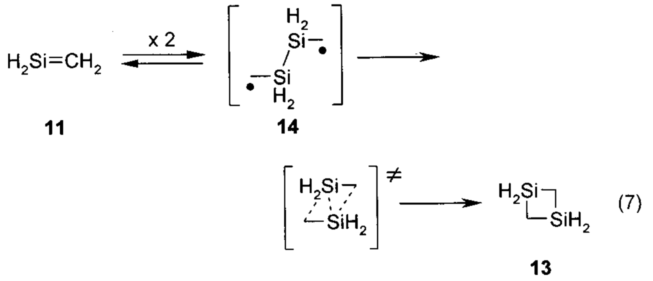
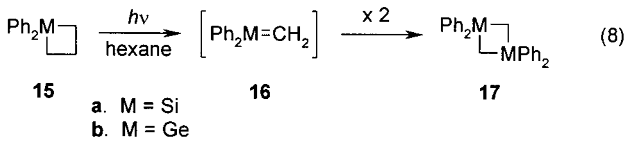


Figure 1. Arrhenius plots for dimerization of 1,1-diphenylsilene (**16a**) and 1,1-diphenylgermene (**16b**) in hexane. The dashed lines and associated solid points represent the temperature dependence of the diffusional rate constant in hexane, calculated using the modified Debye equation ($k_{diff} = 8RT/3000\eta$) and published temperature–viscosity data.





reaction that these two species undergo.[36] The present study, combined with other evidence from previously reported work, allows us to address the mechanism(s) of this characteristic reaction of Si=C and Ge=C double bonds.



Results and Discussion

Laser flash photolysis of continuously flowing, nitrogen-saturated solutions of **15a** and **15b** allows the corresponding 1,1-diphenylmetallaenes **16a**,**b** to be detected directly, as transient absorptions centered at $\lambda_{max} = 325$ nm.[9,36] In sodium-distilled hexane and using oven-dried glassware, the transients decay with kinetics ranging from mixed second-order and pseudo-first-order in the case of **16a** to pure second-order in the case of **16b**.

Although relatively insensitive to the presence of oxygen, silene **16a** is so reactive toward water and alcohols that under our experimental conditions we find it impossible to completely eliminate the pseudo-first-order component from the decays, even with the highest intensities we can achieve with our laser. Thus, the second-order decay rate constants (k_{dim}) were calculated by nonlinear least-squares fitting of absorbance vs time data to eq 9, where l is the path length of the cell (3 mm), ϵ is the extinction coefficient of **16a** at 325 nm ($\epsilon_{325\,nm} = 8900 \pm 1800$ M^{-1} cm^{-1}),[36] and k_1 is the pseudo-first-order component of the decay. The analyses generally afforded k_1-values on the order of 10^4 s^{-1}, while the second-order coefficients ($= 2k_{dim}\Delta OD_o/l\epsilon$) were on the order of (2–3) × 10^6 s^{-1}.

Table 1. Rate Constants and Arrhenius Parameters for Dimerization of 1,1-Diphenylsilene (16a) and 1,1-Diphenylgermene (16b) in Deoxygenated Hexane Solution[a]

	metallaene	
	$Ph_2Si{=}CH_2$ (**16a**)	$Ph_2Ge{=}CH_2$ (**16b**)
$k_{dim}{}^{25°C}$/M^{-1} s^{-1} [b]	(9 ± 6) × 10^9	(8 ± 3) × 10^9
E_a/kcal mol^{-1}	−1.0 ± 0.6	+0.8 ± 0.4
log(A/M^{-1} s^{-1})	9.2 ± 0.4	10.4 ± 0.4

[a] Errors are reported as $\pm 2\sigma$, corresponding to confidence intervals of 94–95%. [b] Interpolated from the Arrhenius parameters.

$$\frac{\Delta OD_t}{\Delta OD_o} = \frac{k_1 \exp(-k_1 t)}{k_1 + 2k_{dim}(\Delta OD_o/l\varepsilon)(1-\exp(-k_1 t))} \qquad (9)$$

The decay traces for germene **16b** were more predominantly second-order, but plots of $1/(\Delta OD)_t$ vs time deviated significantly from linearity because of the presence of a residual absorption that we assume is due to the formation of a relatively long-lived, minor photoproduct. Therefore, the decays were fit to eq 10 ($\epsilon_{325\,nm} = 11400 \pm 2700$ M^{-1} cm^{-1}),[36] to correct for the residual absorption (ΔOD_∞), which did not exceed 10% of the initial signal intensity in any case.

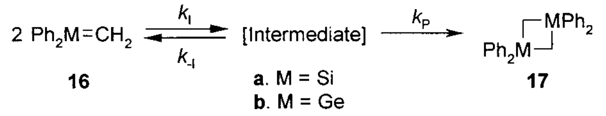
$$\frac{\Delta OD_t}{\Delta OD_o} = \frac{\Delta OD_\infty}{\Delta OD_o} + \frac{1}{1+2k_{dim}(\Delta OD_o/l\varepsilon)t} \qquad (10)$$

Second-order decay rate constants for **16a** and **16b** were determined at several temperatures over the

0–60 °C range and are shown in the form of Arrhenius plots in Figure 1. For comparison, the temperature dependence of the diffusional rate constant (calculated using the modified Debye equation ($k_{\mathrm{diff}} = 8RT/3000\eta$) and published temperature–viscosity data[39] (E_a = 2.4 ± 0.5; $\log(A/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = 12.1 \pm 0.4$) is also plotted in Figure 1. Table 1 lists the Arrhenius parameters obtained from linear least-squares analysis of the two sets of data, along with "best fit" values of k_{dim} at 25 °C, calculated from the Arrhenius parameters. We note that the errors in the Arrhenius parameters are reported as $\pm 2\sigma$, which represents confidence intervals close to 95% in both cases.

The similar absolute reactivities and Arrhenius parameters for dimerization of **16a** and **16b** are quite interesting, considering the substantial differences in their reactivity toward nucleophiles.[13,40] For example, **16a** reacts at close to the diffusion-controlled rate with methanol in solution, via a stepwise mechanism that is overall first-order in alcohol. In contrast, germene **16b** reacts by a mechanism that is strictly *second*-order in methanol, with the first-order pathway being too slow to be detected. The similarities in the rates of dimerization and methanol addition to **16a** are not surprising, considering what is known of the thermochemistries of the two reactions in simpler derivatives. For example, the heats of dimerization and hydration of 1,1-dimethylsilene (**2a**), calculated from experimental heats of formation for **2a** (ΔH_f° = 9 kcal/mol[41]), **3a** (ΔH_f° = −51.6 kcal/mol[42]), trimethylsilanol (ΔH_f° = −119 kcal/mol[43]), and water (ΔH_f° = −56 kcal/mol[39]), are ΔH_{dim} = −69.6 and ΔH_{hyd} = −70.0 kcal/mol, respectively. These compare reasonably well with high-level theoretical estimates of the corresponding parameters for the parent silene, $H_2Si{=}CH_2$: ΔH_{dim} = −77 to −83 kcal/mol[14,18–21] and ΔH_{hyd} = −77 kcal/mol.[44] A self-consistent set of data for germene dimerization and hydration are unfortunately not available. However, values of ΔH_{dim} = −75.3 kcal/mol[22] and ΔH_{hyd} = −61.7 kcal/mol[45] have been reported for head-to-tail dimerization and hydration of the parent molecule ($H_2Ge{=}CH_2$) on the basis of RHF/6-311G(d,p) and MP3/DZ ab initio calculations, respectively. These data indicate that the dimerization of silenes and germenes of analogous structure have comparable overall exothermicities, consistent with the similarities in the absolute rate constants for dimerization of **16a** and **16b**. Nucleophilic addition, on the other hand, maintains a strong exothermicity in silenes, but is significantly less exothermic in the case of germenes. This too is reflected in the relative reactivities of **16a** and **16b** toward methanol addition.

Scheme 1



The near-zero activation energies for dimerization of both **16a** and **16b** are similar to those reported previously for **2a** in the gas phase[26,29] and, given the high degree of exothermicity associated with the process, are consistent with either concerted[46–48] or stepwise[9] mechanisms for the reaction. The preexponential factors are associated with entropies of activation of $\Delta S^\ddagger = -18 \pm 2$ and -13 ± 2 cal/mol·K for **16a** and **16b**, respectively, at 300 K.

While we cannot yet conclusively decide between concerted and stepwise dimerization mechanisms in either case, it is possible to define for the stepwise mechanism what the kinetic behavior of the putative reaction intermediates must be in order to be consistent with the experimentally observed activation energies. Scheme 1 defines the form of a stepwise mechanism involving a single intermediate, analogous to the mechanisms that have been previously established for the addition of alcohols[49] and other nucleophiles to transient silenes in solution.[50] Mechanisms of this type, when the reaction is strongly exothermic, will exhibit a bell-shaped Arrhenius behavior provided that a large enough temperature range can be spanned experimentally.[9] This behavior is caused by the fact that the rates of the two reaction pathways available to the intermediate—reversion to reactants ($k_{-\mathrm{I}}$) and collapse to products (k_{P})—vary in different ways with temperature. The activation energy is negative over the (high) temperature range where $k_{-\mathrm{I}} > k_{\mathrm{P}}$, positive over the (low) temperature range where $k_{-\mathrm{I}} < k_{\mathrm{P}}$, and zero at the temperature where $k_{-\mathrm{I}} \approx k_{\mathrm{P}}$. If the dimerizations of both **16a** and **16b** are nonconcerted, then the near-zero activation energies that are observed indicate that $k_{-\mathrm{I}}$ and k_{P} must be of similar magnitudes to one another over the 0–60 °C temperature range; however, the intermediate from **16a** must revert to reactants marginally faster than collapse to products (since its E_a is slightly negative), while the opposite must be true for the intermediate from **16b**.

In our view, the most reasonable stepwise reaction mechanism for dimerization of the 1,1-diphenyl-substituted metallaenes **16a** and **16b** is one that involves the intermediacy of the 1,3-dimetalla-1,4-butanediyl biradicals **18**, and so further examination of the viability of this mechanism requires that we have independent information on how such biradicals behave. In principle, this information should be available from studies of the photochemistry of the corresponding 1,3-dimetallacyclobutanes, since the photolysis of these compounds is

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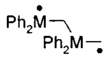
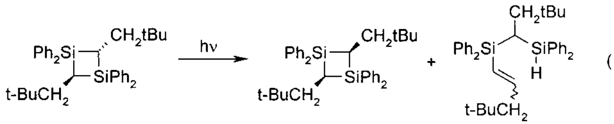
thought to proceed via initial scission of one of the ring C−M bonds.[36,51,52] The only example available that gives information on both cleavage and coupling of 1,3-disila-1,4-butanediyl biradicals is the report by Jones and coworkers of the photolyses of *cis*- and *trans*-1,1,3,3-tetraphenyl-2,4-dineopentyl-1,3-disilacyclobutane (**19**), each of which results in the formation of the other geometric isomer and the acyclic isomers **20** (eq 11).[51] These products are those expected from bond rotation/recoupling and hydrogen migration within the 1,4-biradical intermediate **21**. Photolysis of *cis*- and *trans*-**19** in the presence of methanol resulted in the additional formation of methoxysilane **23**, the methanol-trapping product of silene **22**. Thus, it is at least clear that 1,4-biradicals of this type undergo competitive ring closure and β-scission to silene, as expected. Unfortunately, the crucial question of the relative rates of these processes cannot be answered quantitatively without careful product analyses at low conversions, and data of this type were not reported. The photolysis of disilacyclobutane **17a** has been shown to lead to the formation of **16a**, but in very low quantum yield ($\Phi_{\mathbf{16a}} = 0.007$).[36]

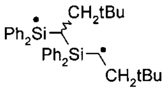


a. M = Si
b. M = Ge

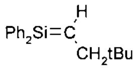
18



trans-**19** *cis*-**19** **20** (11)



21



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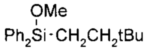

23

The results of similar studies of the photochemistry of **17b** seem more conclusive than in the silicon case, since photolysis of this compound in methanolic hexane solution leads to the formation of methoxygermane **24** with a quantum yield of $\Phi_{\mathbf{24}} = 0.11$.[36] This value corresponds to the quantum yield for formation of **16b** from the excited state of the digermacyclobutane, as the experiment was carried out under conditions of quantitative trapping of the germene by the alcohol. Indeed, **16b** can be readily detected by laser flash photolysis of **17b**, in contrast to the behavior of the silicon analogue **17a** under identical conditions.[36] These results suggest that biradical **18b** undergoes β-scission with reasonable efficiency relative to coupling to regenerate **17b**. We do not know what the relative rates of biradical β-scission ($k_{-\mathrm{I}}$) and coupling (k_{P}) are; nevertheless, the possibility that $k_{-\mathrm{I}}$ is similar to but smaller than k_{P}, as the slightly positive E_a for dimerization of **16b** demands, is certainly a viable one.

Summary and Conclusions

1,1-Diphenylsilene and 1,1-diphenylgermene exhibit similar reactivities toward head-to-tail dimerization in hexane solution. Both reactions are characterized by near-zero Arrhenius activation energies and Arrhenius preexponential factors on the order of 10^9-10^{10} M^{-1} s^{-1}. In neither case do the results allow one to distinguish conclusively between concerted and stepwise mechanisms for the reaction. However, they do provide an indication of what the kinetic behavior of the putative reaction intermediates must be in order for a nonconcerted mechanism, perhaps involving the intermediacy of the corresponding 1,3-dimetalla-1,4-butanediyl biradical, to be consistent with the experimentally observed activation energies. A stepwise mechanism involving a different biradical intermediate, such as the 2,3-disila-1,4-butanediyl recently predicted by theory for the head-to-tail dimerization of the parent silene,[21] seems unlikely, but nevertheless cannot be rigorously excluded as a possibility.

The head-to-tail dimerization of 1,1-diphenylsilene (**16a**) exhibits an Arrhenius activation energy of $E_a = -1.0 \pm 0.4$ kcal/mol and activation parameters of $\Delta H^\ddagger = -1.6 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = -18 \pm 2$ cal/mol·K at 300 K. For this to be consistent with the stepwise mechanism, the biradical intermediate would have to revert to silene somewhat faster than it collapses to product by bond rotation and coupling. In contrast, an Arrhenius activation energy of $E_a = +0.8 \pm 0.4$ kcal/mol ($\Delta H^\ddagger = +0.2 \pm 0.4$ kcal/mol; $\Delta S^\ddagger = -13 \pm 2$ cal/mol·K at 300 K) is observed for the head-to-tail dimerization of 1,1-diphenylgermene (**16b**). This is consistent with a mechanism involving the initial reversible formation of 1,3-digerma-1,4-butanediyl biradical **18b**, which undergoes coupling in preference to cleavage.

Further work in this area will be directed at delineating the chemistry of 1,3-dimetalla-1,4-butanediyl biradicals, in an effort to define the mechanism(s) of the head-to-tail dimerization of transient silenes and germenes more precisely.

Experimental Section

Hexane (BDH Omnisolv) was distilled from sodium under an atmosphere of dry nitrogen. 1,1-Diphenylsilacyclobutane (**15a**) and 1,1-diphenylgermacyclobutane (**15b**) were synthesized according to published methods.[13,53] Nanosecond laser flash photolysis experiments employed the pulses (248 nm; 15−20 ns; 120−140 mJ) from a Lambda Physik Compex 100 excimer laser filled with F_2/Kr/He mixtures and a computer-controlled detection system as described previously.[54] Solutions were prepared at concentrations such that the absorbance at the excitation wavelength was ca. 0.7 (~0.003 M) and were flowed continuously through a 3 × 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple that was inserted directly into the flow cell.

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