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Kinetic and Mechanistic Studies of the Formal (1+2)- and (1+4)-Cycloadditions of Germylenes to Conjugated Dienes

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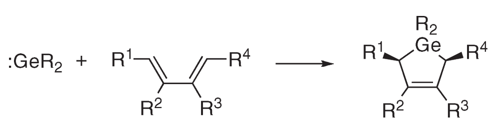
Fast kinetic studies of the reactions of isoprene and 2,3-dimethyl-1,3-butadiene (DMB) with diphenylgermylene ($GePh_2$, **2a**) and of isoprene with a series of diarylgermylenes bearing polar ring substituents ($GeAr_2$, **2b**−**g**) have been carried out in hexanes solution. Though the major stable products of the reactions with isoprene are the corresponding 1,1-diarylgermacyclopent-3-ene derivatives, the results indicate that the major initial products are the corresponding transient 1,1-diaryl-2-vinylgermiranes (**6a**−**g**) resulting from formal (1+2)-cycloaddition to the less-substituted C=C bond of the diene. These compounds are formed reversibly and with rate constants in excess of 10^9 M^{-1} s^{-1}, and appear as discrete reaction intermediates exhibiting λ_{max} = 285 nm and lifetimes of 2−670 μs depending on the identity of the germylene and the diene. The variations in the lifetimes with aryl substituents are shown to be most consistent with a stepwise mechanism for vinylgermirane → germacyclopent-3-ene isomerization, involving (reversible) dissociation to the free germylene and diene followed by (irreversible) (1+4)-cycloaddition. The bimolecular rate constants for (1+4)-cycloaddition to isoprene, calculated from the data on the basis of this model, vary over the range of 5×10^6 to 3×10^8 M^{-1} s^{-1} depending on the aryl ring substituent(s). The variation in the rate and equilibrium constants for reaction of **2a**−**g** with isoprene indicates that the germylene plays the role of an electrophile in both the (1+2)- and (1+4)-cycloaddition processes and demands the involvement of a polarized steady-state intermediate in the (1+2)-addition reaction. The temperature dependence of the experimental rate and equilibrium constants for reaction of $GePh_2$ with isoprene, and of the rate coefficient for decay of the corresponding vinylgermirane, allows most aspects of the potential energy surface to be defined quantitatively.

Introduction

One of the best known and most frequently used trapping reactions of reactive germylene derivatives is the formal (1+4)-cheletropic addition of conjugated dienes, which affords the corresponding germacyclopent-3-ene derivative in high chemical yields (eq 1).[1,2] Early studies of the reactions of thermally generated dimethylgermylene ($GeMe_2$) with dienes showed that the reaction proceeds stereospecifically,[3−6] which led to the proposal that it proceeds via a concerted (1+4)-cycloaddition mechanism.



(1)

While the (1+4)-cycloadduct is the only product observed from reaction of $GeMe_2$ and many other germylene derivatives with 2,3-dimethylbutadiene (DMB),[1,2,7,8] less highly substituted alkyl- and phenyl-substituted acyclic dienes also afford products derived from addition of two molecules of the diene to $GeMe_2$, in addition to the 1:1 cycloadduct.[9] Analogous (1:2)-cycloadducts are also known to be formed upon reaction of $GeMe_2$ with styrene[10,11] and were proposed to result from reaction of a second molecule of alkene with the corresponding (transient) germirane, formed by (1+2)-cycloaddition in the initial step. The corresponding trappable intermediate in the reaction with dienes would thus be a transient vinylgermirane, whose usual fate is conversion to the isomeric germacyclopent-3-ene in high yield (eq 2). The mechanism of the isomerization has been alternatively formulated as a formal [1,3]-sigmatropic rearrangement and a

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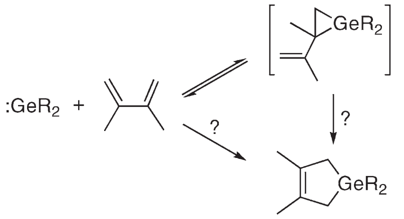
stepwise cycloreversion/(1+4)-cycloaddition process.[1,12,13] Thus, the faster-formed (1+2)-cycloadduct is either a necessary intermediate in the formation of the stable (1+4)-cycloadduct or a reversibly formed bystander that serves mainly as a mediator in the overall reaction. The two mechanisms are kinetically indistinguishable.



(2)

While the corresponding 1-silacyclopent-3-enes are also the major products of reaction of dienes with dimethylsilylene ($SiMe_2$) under high-temperature conditions, their formation was proposed to result from secondary thermal isomerization of the corresponding vinylsiliranes even in the earliest studies of the reaction.[14-18] The reaction of aliphatic dienes with $Si(^tBu)_2$[19] and with diarylsilylenes such as $SiMes_2$ (Mes = 2,4,6-trimethylphenyl),[20] Si(Mes)Tbt (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl),[21] and $SiPh_2$[22] at ambient temperatures affords the corresponding vinylsiliranes as the major products, stereospecifically in the case of $SiMes_2$.[20] Those derived from $SiMes_2$ and Si(Mes)Tbt are stable indefinitely at room temperature, but isomerize stereospecifically to the corresponding silacyclopent-3-enes upon heating,[20,21] while that from $SiPh_2$ does so over a number of hours in solution at room temperature.[22] Tokitoh and co-workers were able to show that the isomerization of the (1+2)-cycloadduct from Si(Mes)Tbt and isoprene proceeds via the stepwise pathway involving (reversible) dissociation to the free silylene and diene followed by direct (1+4)-cycloaddition; thus, in the case of heavily hindered systems at least, the formation of the formal (1+2)- and (1+4)-cycloaddition products occurs competitively.[21] A very recent computational study of the reactions of $SiMe_2$ and $GeMe_2$ with 1,3-butadiene, and of $SiPh_2$ and $GePh_2$ with alkylated dienes, indicates that in all these cases this mechanism provides a significantly lower energy pathway to the corresponding metallacyclopent-3-ene than the one involving [1,3]-sigmatropic rearrangement of the vinylmetallirane intermediate.[13]

Detailed kinetic information on the reactions of isoprene and DMB with transient silylenes and germylenes such as $SiMe_2$,[22] SiMePh,[23] $SiPh_2$,[22] $GeMe_2$,[24] GeMePh,[25] and $GePh_2$[26] under ambient conditions in hexanes solution has been reported, and in all cases the measured absolute rate constant for consumption of the free metallylene by the diene approaches the diffusion-controlled limit. The silylenes are each slightly more reactive than the germylene of homologous structure, as is also the case for the dimethyl- and dihydrometallylenes in the gas phase,[27] but in both series of metallylenes the rate constants for reaction with isoprene vary by only a factor of ca. 2, in the order $MMe_2 \sim MMePh > MPh_2$.[23-25] The results for the germylenes show that the main component of their reactions with isoprene are reversible on the microsecond time scale and are characterized by equilibrium constants ranging from ca. 6000 M^{-1} for $GePh_2$ to ca. 20 000 M^{-1} for $GeMe_2$.[24-26] The kinetic behavior of $GeMe_2$ and GeMePh in the presence of DMB is also consistent with fast, reversible reaction in both cases; accurate values of the equilibrium constants could not be measured, but in the case of GeMePh it is clearly considerably smaller than that for reaction with isoprene.[24,25] In contrast, the results for the silylenes are consistent with equilibrium constants in considerable excess of 10^5 M^{-1} in all cases, such that in fast time-resolved experiments the primary reactions appear to be irreversible.[22,23]

The phenylated metallylenes react with these dienes to form a long-lived transient product exhibiting a UV/vis spectrum centered at $\lambda_{max} \approx 285$ nm, which has been assigned to the corresponding vinylmetallirane derived from the (1+2)-addition reaction. The putative vinylgermiranes exhibit first-order lifetimes of 500−670 μs in hexanes containing 0.01−0.05 M isoprene at 25 °C,[25,26] reflecting (presumably) the rate of isomerization to the corresponding 1-germacyclopent-3-ene derivative.[12,25,26] On the other hand, the corresponding species from reaction of $SiPh_2$ with DMB is sufficiently stable to be detectable in the crude reaction mixture by ^{1}H NMR spectroscopy.[22]

The role of electronic factors associated with either the metallylene or the diene in these reactions has not been extensively explored, save for the early studies of the reactions of thermally generated $GeMe_2$ with various mono- and disubstituted dienes by W. P. Neumann and co-workers.[1,3,5,6,9] These studies led to the conclusion that the reaction is LUMO-diene controlled, the germylene thus playing the role of a *nucleophile* in the transition state of the rate-determining step.[1,6] This seems surprising, given the high degree of electrophilicity that we have come to associate with $GeMe_2$ and other transient germylenes we have studied, not to mention its nearly diffusion- or collision-controlled reactivity toward 1,3-butadiene[28] and alkyl-substituted diene derivatives[24,29] in the gas phase and in solution. Other mechanistic details of the reaction also remain to be elucidated experimentally, such as the possible role of prereaction complexes or other intermediates, activation and thermodynamic parameters, and the mechanism of the vinylgermirane → germacyclopent-3-ene isomerization. The goal of the present work was to explore

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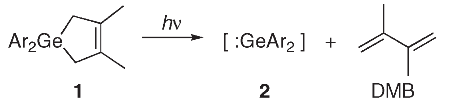
these mechanistic details for the specific case of $GePh_2$, through a study of the effects of polar aryl ring substituents on the kinetics and thermodynamics of its reaction with isoprene.

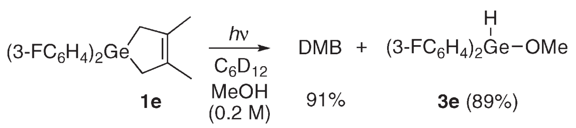
Results

The transient germylenes studied in this work (**2a−g**) were prepared and detected directly by laser flash photolysis of the 1,1-diaryl-3,4-dimethylgermacyclopent-3-ene derivatives **1a−g** (eq 3). Six of these compounds have been reported previously,[30−33] while the seventh (**1e**) was prepared, purified, and characterized by similar methods to those employed for the others.[30−33] Its photochemical behavior was established by photolysis (254 nm) of the compound as a 0.02 M solution in cyclohexane-d_{12} containing methanol (MeOH; 0.2 M) and hexamethyldisilane (2 mM; internal standard), with periodic monitoring of the photolysate over the 0−10% conversion range by ^{1}H NMR spectroscopy. This led to the formation of DMB and a single germanium-containing product, which was tentatively identified as diarylmethoxygermane **3e** (eq 4) on the basis of comparisons to those obtained in similar experiments with the other compounds in the series.[30−33] The photolysis was carried out in parallel with that of a similar solution of **1a** as actinometer.[30] The experiment afforded a quantum yield of Φ = 0.62 ± 0.09 for the formation of **3e** and DMB from **1e**, indicating that the presence of the ring substituent has no discernible effect on the efficiency of germylene photoextrusion, as we found previously for **1b−d**,**f**,**g**.[31−33] Further details of these experiments are provided in the Supporting Information.



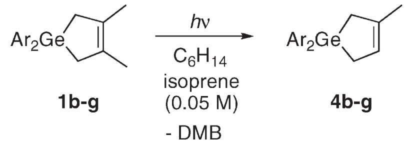
(3)

a. Ar = C_6H_5
b. Ar = 3,4-$Me_2C_6H_3$
c. Ar = 4-MeC_6H_4
d. Ar = 4-FC_6H_4
e. Ar = 3-FC_6H_4
f. Ar = 4-$CF_3C_6H_4$
g. Ar = 3,5-$(CF_3)_2C_6H_3$



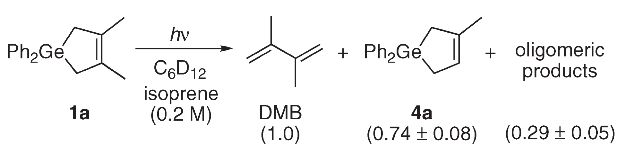
(4)

Photolysis of deoxygenated hexanes solutions of **1b−g** (0.02 M) containing isoprene (0.05 M) led to the formation of the corresponding 1,1-diaryl-3-methylgermacyclopent-3-enes (**4b−g**) as the only products detectable by GC/MS up to ca. 40% conversion of the starting materials. Compounds **4b**[33] and **4e** were identified by comparison of their mass spectra and retention times to those of independently prepared authentic samples, while the others (**4c**, **4d**, **4f**, and **4g**) were tentatively identified on the basis of their mass spectra and GC retention times.



(5)

The course of the photolysis of **1a** in the presence of isoprene was studied in greater detail by ^{1}H NMR spectroscopy. Spectra recorded at periodic intervals during photolysis (254 nm; 25 °C) of a solution of **1a** (0.032 M) in cyclohexane-d_{12} containing isoprene (0.2 M) and Si_2Me_6 (2 mM) confirmed the formation of **4a** and DMB as the major products.[30] The relative slopes of concentration vs time plots constructed for the two products over the 0 to ca. 12% conversion range in **1a** indicate them to be formed in relative yields of [**4a**]:[DMB] = (0.74 ± 0.08):1.0 (see eq 6 and Figure S2, Supporting Information). The NMR spectra also showed broad baseline absorptions in the aromatic and aliphatic regions, which increased in intensity as the photolysis progressed, indicative of the accompanying formation of oligomeric material. The plot of oligomer concentration (calculated in terms of $GePh_2$ equivalents) vs time exhibited a slope of 0.29 ± 0.05 relative to DMB and exhibited slight positive curvature, indicating the yield relative to the other products increases with increasing light exposure. A MALDI mass spectrum of the crude photolysate showed evidence of at least 10 germanium-containing compounds with molecular weights in the range 500−900 Da, of which the major product exhibited a series of isotopic molecular ions consistent with the formula $Ge_2Ph_4(C_5H_8)_4$ (see Figure S3, Supporting Information). A second experiment, carried out under identical conditions but at a reaction temperature of 51 ± 2 °C, afforded **4a**, DMB, and oligomeric material in relative yields of (0.70 ± 0.06):1.0:(0.48 ± 0.07), indicating that the yield of the oligomeric material also increases with increasing reaction temperature. Unfortunately, the change in concentration of **1a** with time could not be monitored in these experiments because of overlap of its NMR signals with those due to **4a**, and thus material balances could not be determined.



(6)

Laser flash photolysis of a flowed, deoxygenated solution of the new compound **1e** (ca. 0.003 M) in anhydrous hexanes, using the pulses from a KrF excimer laser (~20 ns, ~100 mJ, 248 nm) for excitation, resulted in the prompt formation of a transient exhibiting absorption bands centered at λ_{max} ~300 nm and ~490 nm, which decayed over 2−3 μs with the concomitant growth of a substantially longer lived species ($\tau \approx 20$ μs) exhibiting absorptions centered at λ_{max} = 440 nm (see Figure 1). The behavior is closely analogous to that exhibited by **1a−d**,**f** under similar conditions,[30,31] and we thus assign the two

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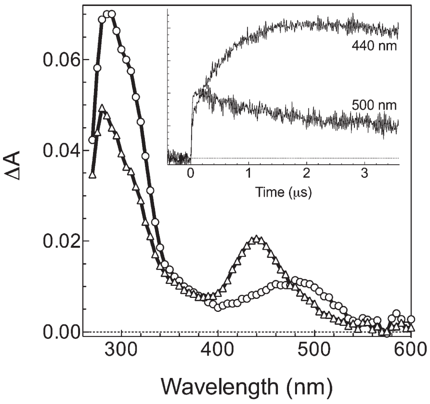
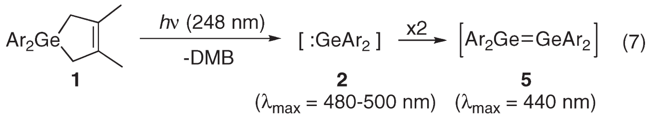


Figure 1. Transient absorption spectra recorded by laser flash photolysis of a 0.003 M solution of 3,4-dimethyl-1,1-bis-[3-fluorophenyl]germacyclopent-3-ene (**1e**) in deoxygenated hexanes, recorded 96−128 ns (○) and 2.78−2.81 μs (Δ) after the laser pulse. The inset shows transient absorption vs time profiles recorded at 500 and 440 nm.

species to germylene **2e** and tetraaryldigermene **5e**, respectively (eq 7).



a. Ar = C_6H_5
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e. Ar = 3-FC_6H_4
f. Ar = 4-$CF_3C_6H_4$
g. Ar = 3,5-$(CF_3)_2C_6H_3$

Flash photolysis of hexanes solutions of **1a**−**f** containing isoprene (0.1−2.0 mM) afforded behavior similar to that reported by us previously in our initial study of **1a** in the presence of this substrate.[26] The germylene decays assumed a bimodal form in the presence of the diene, consisting of a fast initial decay and a much slower decaying residual absorption. The initial decay accelerated and the contribution of the residual component of the overall transient decay profile decreased with increasing isoprene concentration, consistent with reversible reaction with the diene.[24−26] The fast initial decay is due to the pseudo-first-order approach to equilibrium, for which the first-order rate coefficient is given by eq 8, where k_Q is the second-order ("forward") rate constant for the reversible reaction with the germylene and k_{-Q} is the first-order rate constant for the reverse process. The long-lived residual absorption is due to free germylene remaining after equilibrium has been attained; its decay is due predominantly to dimerization to the corresponding digermene, which (as evidenced by growth decay/profiles recorded at its absorption maximum of 440 nm) is formed in successively decreasing overall yields and with a decreasing time constant as the diene concentration is increased.[26] At a given diene concentration [Q], the intensity of the residual signal at the end of the fast initial decay ($\Delta A_{res,Q}$) is related to the equilibrium constant for reaction by eq 9, where ΔA_0 is the initial transient absorbance in the absence of diene.

$$k_{decay} \approx k_{-Q} + k_Q[Q] \tag{8}$$

$$(\Delta A_o / A_{res,Q}) = 1 + K_{eq}[Q] \tag{9}$$

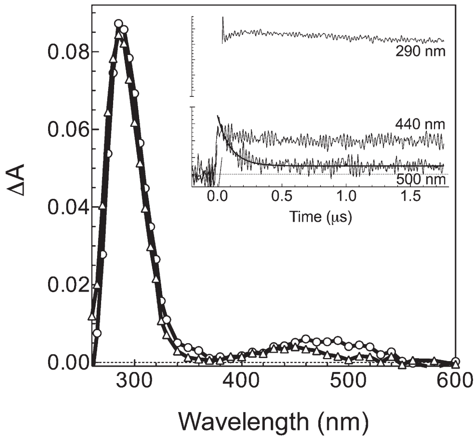
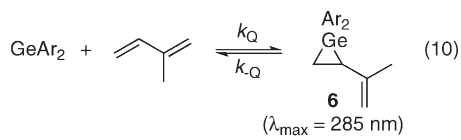


Figure 2. Transient absorption spectra recorded by laser flash photolysis of a 0.003 M solution of 3,4-dimethyl-1,1-diphenyl-germacyclopent-3-ene (**1a**) in deoxygenated hexanes containing 1.5 mM isoprene, recorded 48−54 ns (○) and 1.74−1.76 μs (Δ) after the laser pulse. The inset shows transient absorption vs time profiles recorded at 500, 440, and 290 nm.

Figure 2 shows representative transient spectra and decays recorded with a solution of **1a** in hexanes containing 1.5 mM isoprene. Under these conditions the lifetime of germylene **2a** is reduced to ca. 100 ns, the growth of the digermene absorption is completely quenched due to the competing reaction of the germylene with the diene, and the presence of the major product of the latter reaction is evident from the strong long-lived absorption centered at λ_{max} = 285 nm; much of the expected growth of the latter absorption is masked by strong sample fluorescence that obscures the short-wavelength region of the spectrum in the first ca. 50 ns after excitation. Similar long-lived absorptions were observed with each of the compounds studied in this work in the presence of the diene, and we assign them to the corresponding vinylgermiranes, **6a**−**g** (eq 10; *vide infra*). The UV/vis spectral maxima of these compounds are red-shifted by ca. 20 nm relative to those of **1a**−**g** and **4a**−**g** (see Supporting Information).



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e. Ar = 3-FC_6H_4
f. Ar = 4-$CF_3C_6H_4$
g. Ar = 3,5-$(CF_3)_2C_6H_3$

Owing to the modest overlap between the spectra of the germylenes and corresponding digermenes, the determination of meaningful values of k_{decay} and $\Delta A_{res,Q}$ from data recorded at various concentrations of diene required correction of the raw 500 nm decay profiles, subtracting the minor contribution due to the corresponding digermene. At each diene concentration ([Q]) that was studied, corrected transient absorbance data for the germylene ($\Delta A_{corr,t}$) were calculated by scaled subtraction of a growth/decay trace recorded at the digermene absorption maximum of 440 nm from that for the germylene at 500 nm, employing a scaling factor of 0.15, the ratio of the extinction coefficients at 500 and 440 nm in the UV/vis absorption spectrum of digermene **5a**;[26] the scaling factor varies only slightly from compound to

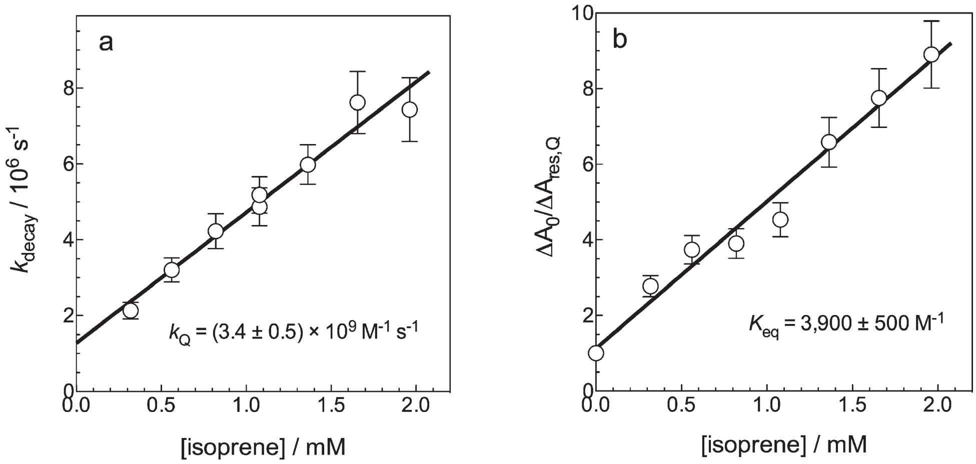


Figure 3. Plots of (a) k_{decay} vs [Q] and (b) $(\Delta A_o/\Delta A_{res,Q})$ vs [Q], for the reaction of germylene **2b** with isoprene in deoxygenated hexanes at 25.0 °C. The solid lines are the linear least-squares fits of the data to eqs 8 and 9, respectively.

Table 1. Second-Order Rate Constants (k_Q) and Equilibrium Constants (K_{eq}) for the Reactions of Diarylgermylenes 2a−g with Isoprene and First-Order Rate Coefficients for Decay of the Corresponding Vinylgermiranes 6a−g ($k_{6\text{-decay}}$) and the Products $K_{eq}k_{6\text{-decay}}$ in Deoxygenated Hexanes Solution at 25 °C (except where otherwise noted, errors are reported as ±2σ)

		$k_Q/10^9$ M^{-1} s^{-1}	$K_{eq}/10^3$ M^{-1}	$k_{6\text{-decay}}/10^3$ s^{-1} [a]	$K_{eq}k_{6\text{-decay}}/10^6$ M^{-1} s^{-1}
2a	H	5.2 ± 0.5	6.0 ± 1.5	2.52 ± 0.18	15.1 ± 4.6
2b	3,4-Me_2	3.4 ± 0.5	3.9 ± 0.5	1.34 ± 0.01	5.2 ± 0.7
2c	4-Me	4.3 ± 0.5	3.3 ± 0.6	1.82 ± 0.07	7.8 ± 1.7
2d	4-F	6.6 ± 1.4	1.7 ± 0.3	7.43 ± 0.07	12.6 ± 2.3
2e	3-F	4.8 ± 1.6	4.0 ± 1.0	9.54 ± 0.54	38 ± 12
2f	4-CF_3	2.5 ± 0.4	5.0 ± 0.5	14.5 ± 0.6	72 ± 9
2g	3,5-$(CF_3)_2$	1.6 ± 0.7 [b]	0.6 ± 0.3 [b]	487 ± 3	290 ± 145

[a] Decay rate constants were determined by nonlinear least-squares analysis of decays recorded in the presence of 30−50 mM isoprene, and are each the average of several determinations; errors are reported as ± 1 standard deviation of the mean. [b] Mean ± 1 standard deviation of three independent determinations.

compound within the series. Representative examples of raw and corrected decay profiles for germylene **2b** (from **1b**) in the presence of 0, 0.32, and 0.82 mM isoprene are shown in Figure S4 of the Supporting Information. The corrected decay profiles obtained with isoprene concentrations at the upper end of the concentration range studied ([Q] > 0.5 mM), where the decay of the residual absorption was substantially slower than the initial fast decay, were analyzed as single-exponential decays according to eq 11. Those recorded at the lower end of the concentration range were generally analyzed as two-exponential decays, in which case k_{decay} was taken as the decay rate coefficient of the fast component, and an approximate $\Delta A_{res,Q}$ value was obtained by visual extrapolation of the slow decay component back to the "end" of the fast initial decay (see Supporting Information). The resulting $(\Delta A_o/\Delta A_{res,Q})$ values were then corrected for minor screening of the excitation light by the diene, which absorbs weakly at the laser wavelength ($\varepsilon_{248nm} = 81 \pm 8$ M^{-1} cm^{-1}).

$$\Delta A_{corr,\,t} = \Delta A_0 \exp(-k_{decay}t) + \Delta A_{res} \qquad (11)$$

Plots of the pseudo-first-order rate coefficients for approach to equilibrium (k_{decay}) vs isoprene concentration exhibited excellent linearity in each case, allowing the second-order rate constants (k_Q) for reaction of **2a−f** with the diene to be determined by analysis of the data according to eq 8. Excellent linearity was also exhibited by the corresponding plots of $(\Delta A_o/\Delta A_{res,Q})$ vs [isoprene], although in several cases the best-fit value of the intercept was significantly greater than the value of unity predicted by eq 9; as a result, we consider the K_{eq} values to have an error of ca. 25%. Figure 3 shows representative plots of this type from experiments with germylene **2b**, and Table 1 lists the values of k_Q and K_{eq} for the reactions of **2a−f** with isoprene in hexanes solution at 25 °C. Those obtained for germylene **2a** are in excellent agreement with the earlier reported values.[26]

The kinetic behavior of germylene **2g**, from photolysis of hexanes solutions of **1g** containing isoprene, was more difficult to analyze than the others because growth/decay profiles recorded for the corresponding digermene (between 420 and 460 nm) all showed an initial short-lived decay component superimposed on the slow growth of the digermene signal.[32] This precluded the use of the correction procedure that was employed for the other derivatives for determination of k_{decay} values for the germylene and required that they be determined from the raw decay profiles, treating the digermene component as a nondecaying residual absorption. This leads to a distorted estimate of the decay rate coefficient at each diene concentration, which is ultimately transmitted to the k_Q value determined from the plot of k_{decay} vs [isoprene]; a raw value of $k_Q = (2.7 \pm 0.7) \times 10^9$ M^{-1} s^{-1} was obtained from the average of three independent experiments. The correction factor that needs to be applied to this value was estimated by analyzing the raw decays from the experiments with **1b**, **1d**, and **1f** and comparing the resulting raw k_Q values to the true ones. This afforded an average correction factor of 0.6 ± 0.1, which in turn affords a value of $k_Q = (1.6 \pm 0.7) \times 10^9$ M^{-1} s^{-1} for the rate constant for reaction of isoprene with germylene **2g**. A value of $K_{eq} = 600 \pm 300$ M^{-1} s^{-1} was determined for the equilbrium constant using the same procedure as was employed for the others, as the presence of the fast initial decay in the digermene signals does not affect the validity of the correction procedure required to estimate the residual absorbances due to the germylene after equilibrium has been attained.

Transient UV/vis spectra recorded with solutions of **1a**−**g** in hexanes containing 15−60 mM isoprene verified that the vinylgermiranes (**6a**−**g**) are the only species detectable at high concentrations of the diene; in each case, the species exhibited λ_{max} = 285 nm and decayed with first-order kinetics. The lifetimes varied with the aryl ring substituent, from $\tau \approx 2$ μs in the case of **6g** to $\tau \approx 740$ μs for **6b**; representative transient spectra and decay profiles, recorded with hexanes solutions of **1b** and **1f** in the presence of 50 mM isoprene at 25 °C, are shown in Figure S5 of the Supporting Information. In each case, there was no detectable variation in lifetime over the 15−60 mM concentration range in added isoprene. Table 1 includes the first-order decay rate coefficients ($k_{6\text{-decay}}$) of the seven compounds, measured in hexanes containing 50 mM isoprene at 25 °C, along with the products of the vinylgermirane decay coefficients and the corresponding equilibrium constants for their formation ($K_{eq}k_{6\text{-decay}}$). The significance of the latter parameters will be discussed later in the paper.

Rate and equilibrium constants for the reactions of isoprene with germylenes **2a**, **2c**, and **2f** were also determined at two or three additional temperatures over the 14−61 °C temperature range. Figure 4 shows the resulting Arrhenius and van't Hoff plots of the data obtained for germylene **2a**, while the corresponding plots for **2c** and **2f** are shown in Figure S6 of the Supporting Information; the resulting activation and thermodynamic parameters are listed in Table 2. The Arrhenius plot for **2a** shows distinct curvature, but was analyzed as a straight line because of the modest number of points. The rate constants obtained for the other two compounds also did not vary substantially with temperature and were also analyzed as straight lines.

First-order decay coefficients for vinylgermirane **6a** were also determined as a function of temperature in hexanes containing 50 mM isoprene. Both the lifetime of the species and its initial absorption intensity were found to decrease with increasing temperature between 11 and 52 °C, as the spectra of Figure 5 illustrate. The figure also shows the resulting Arrhenius plot of the first-order decay coefficients ($k_{6a\text{-decay}}$), from which were obtained values of E_a = 11.8 ± 0.5 kcal mol^{-1} and $\log(A/s^{-1})$ = 12.0 ± 0.4.

In contrast to the behavior observed for **1a** in the presence of isoprene, addition of DMB to hexanes solutions of the $GePh_2$ precursor resulted in behavior consistent with fast but relatively inefficient reaction of **2a** with the diene, and relatively high concentrations of the substrate were required in order to elicit discernible effects on the germylene signals. Decay traces recorded on longer time scales appeared merely to be reduced in overall signal intensity with increasing concentrations of diene, and to an extent that was barely differentiable from that predicted on the basis of competing absorption of the excitation light by the substrate (ε_{248nm} = 161 ± 15 M^{-1} cm^{-1}). Bimodal decays could be detected over the 3−7.3 mM concentration range in added diene, but required the use of relatively fast time scales in order to resolve the initial fast decay component. A value of k_Q = (2.3 ± 1.0) × 10^9 M^{-1} s^{-1} was estimated from a three-point plot of k_{decay} vs [DMB], while a value of K_{eq} = 150 ± 20 M^{-1} was obtained from analysis of the residual signal intensities

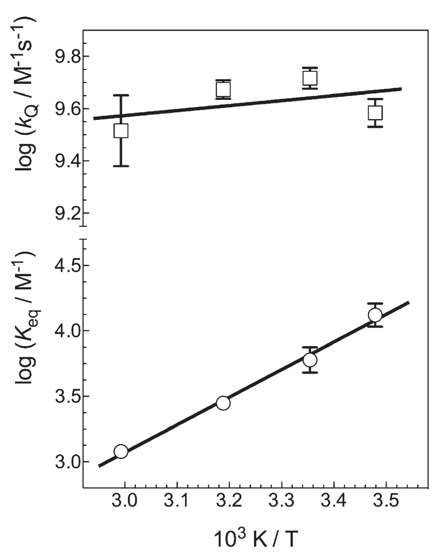


Figure 4. Arrhenius (○) and van't Hoff (□) plots for the reaction of $GePh_2$ (**2a**) with isoprene in deoxygenated hexanes.

Table 2. Arrhenius and van't Hoff Parameters for the Reactions of Germylenes 2a, 2c, and 2f with Isoprene in Deoxygenated Hexanes Solution[a]

	2a (H)	**2c** (4-Me)	**2f** (4-CF_3)
E_a/kcal mol^{-1}	−0.9 ± 2.4	+1.5 ± 0.9	+3.7 ± 4.2
$\log(A/M^{-1}\ s^{-1})$	+9 ± 2	+11 ± 1	+12 ± 3
ΔG/kcal mol^{-1}	−5.2 ± 0.2	−4.8 ± 0.1	−5.0 ± 0.2
ΔH/kcal mol^{-1}	−9.7 ± 1.1	−10.5 ± 0.9	−12 ± 6
ΔS/cal K^{-1} mol^{-1}	−15 ± 4	−19 ± 3	−21 ± 20

[a] The standard state is a 1M hexanes solution at 298.15 K; see Table S4 of the Supporting Information for the corresponding values employing the gas phase at 1 bar and 298.15 K as standard state. Errors are quoted as ±2σ.

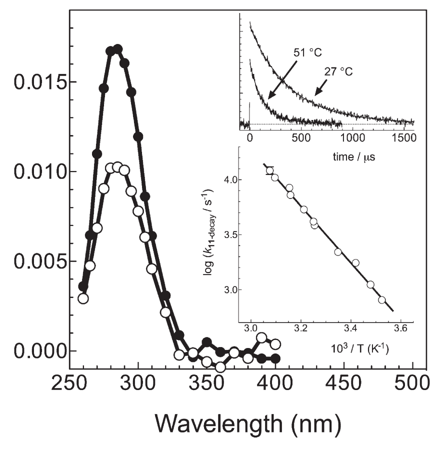
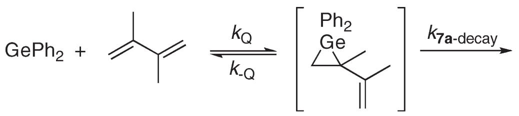


Figure 5. Transient absorption spectra of vinylgermirane **6a**, recorded by laser photolysis of **1a** in deoxygenated hexanes containing 50 mM isoprene at 27 °C (●) and 51 °C (○). The insets show transient decay profiles recorded at 290 nm at the two temperatures (top) and the Arrhenius plot of the first-order decay coefficients over the 11−52 °C temperature range.

after correction for screening of the excitation light by the diene (see Figure S16, Supporting Information). A spectrum recorded in the presence of 30 mM DMB showed a single transient absorption, also centered at λ_{max} = 285 nm, which we assign to vinylgermirane **7a**; it decays with clean first-order kinetics and lifetime τ = 8.3 μs. The spectrum is quite similar to that obtained after photolysis of **1a** in a 3-methylpentane matrix at 78 K, which was also assigned to this compound.[12]

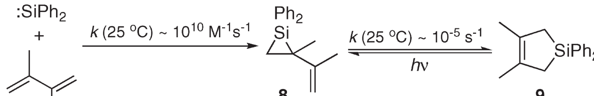


(12)

7a
λ_{max} = 285 nm
τ = 8.3 μs

Discussion

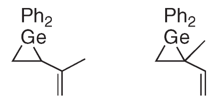
The structural assignments of the long-lived transient products observed in laser photolysis experiments with **1a**–**g** in the presence of isoprene and (for **1a**) with DMB, to the corresponding vinylgermiranes **6a**–**g** and **7a**, respectively, are supported by several independent observations. First, the formation of transient products with similar spectral and kinetic characteristics has been found to be a general feature of the reactions of both $GePh_2$ (**2a**) and GeMePh with terminal alkenes and dienes; for example, reaction of $GePh_2$ with 4,4-dimethyl-1-pentene (DMP) yields a transient product exhibiting λ_{max} = 275 nm (τ = 1.2 ms),[26] while GeMePh affords transient products exhibiting λ_{max} = 285 nm (τ = 670 μs) and λ_{max} = 275 nm (τ = 2.6 ms) in the presence of isoprene and DMP, respectively.[25] Second, photolysis of **1a** in a hydrocarbon matrix at 78 K results in the formation of a species exhibiting an essentially identical UV/vis spectrum to that obtained in solution phase experiments with **1a** in the presence of 30 mM DMB; the species disappears rapidly upon warming the matrix above its softening point.[12] The formation of **7a** on photolysis of **1a** under these conditions has been proposed to be due to the rigid solvent cage preventing diffusive separation of the germylene and its diene coproduct; between this and the low temperature of the medium, the equilibrium mixture is forced essentially entirely in the direction of the vinylgermirane.[12] Third, the major product of reaction of $SiPh_2$ with DMB, whose early identification as vinylsilirane **8**[34] has been more recently confirmed by NMR evidence,[22] exhibits a very similar UV/vis spectrum (λ_{max} = 280 nm) to those of the transient products from $GePh_2$ with DMB and isoprene;[22] the same compound is also formed as the major product of photolysis of 1-silacyclopent-3-ene **9** in solution (eq 13).[12] Consistent with the significantly greater thermodynamic stabilities of siliranes compared to germiranes,[35] vinylsilirane **8** exhibits a lifetime of several hours, isomerizing slowly in the dark at room temperature to generate **9**.[22] The similarity between the UV/vis spectra of **8** and those assigned to **6a** and **7a** provides reasonable evidence against a possible assignment of the latter spectra to other reactive intermediates that might be considered, such as a germylene←diene π-complex. The π-complex assignment is also mitigated against by the higher K_{eq} value estimated for the reaction of $GeMe_2$ with isoprene[24] compared to that for reaction of $GePh_2$ with the same diene, to the extent that variations in the magnitude of K_{eq} for complex formation with germylene structure can be expected to mirror germylene Lewis acidity; the equilibrium constants for Lewis acid–base complexation of $GeMe_2$ and diarylgermylenes with O- and N-donors indicate that $GeMe_2$ is a significantly weaker Lewis acid than $GePh_2$.[24,26,33,36] Furthermore, the log K_{eq} values for Lewis acid–base complexation of diarylgermylenes with O-donors such as tetrahydrofuran and ethyl acetate correlate well with Hammett σ-values,[31] while those for reaction of **2a**–**g** with isoprene do not (*vide infra*).



(13)

8 (major) **9**

Two regioisomers are of course possible for the vinylgermirane derived from reaction of $GePh_2$ with isoprene (**6a** and **6a′**), depending on which of the two C=C bonds in the diene (if either) is the preferred site of reaction. The structures of the 1:2 adducts isolated by Neumann and co-workers from the reaction of thermally generated $GeMe_2$ with isoprene indicate that the less-substituted C=C bond is the preferred site of reaction with this germylene;[9] we have found no evidence for the formation of the analogous products from **2a** at room temperature, however, with isoprene concentrations as high as 0.2 M. Our identification of **6a** as the preferred regioisomer is based on a comparison of the rate and equilibrium constants for its formation to those for formation of **7a** from $GePh_2$ and DMB, for which only a single structure is possible. The difference in K_{eq} values is particularly significant, with that for formation of **7a** being ca. 40 times smaller than that for formation of the isoprene adduct. This is consistent with a free energy difference $\Delta(\Delta G)$ $\approx$ 2.2 kcal mol^{-1}, which is significantly larger than what one would reasonably expect for regioisomer **6a′** given that the only difference between it and **7a** is the methyl group at the 1-position of the vinyl substituent. We had hoped there might be a detectable difference between the UV/vis spectra of the two vinylgermirane derivatives that would lend additional support to the assignment, but none is evident.



6a **6a′**

Equilibrium constants have now been measured or estimated for the reactions of a number of transient germylenes with isoprene, the trends in which provide some indication of the variation in the thermodynamic stabilities of the corresponding vinylgermirane derivatives as a function of substitution at germanium. Those for reaction of isoprene with $GeMe_2$ (K_{eq} $\approx$ 20000 M^{-1}; ΔG $\approx$ −5.9 kcal mol^{-1}),[24] GeMePh (K_{eq} $\approx$ 15000 M^{-1}; ΔG $\approx$ −5.7 kcal mol^{-1}),[25] and $GePh_2$ (K_{eq} = 6000 M^{-1}; ΔG = −5.2 kcal mol^{-1}) indicate that aryl substitution at germanium results in a modest decrease in thermodynamic stability, relative to dimethyl substitution. Substituents in the *meta*- and/or *para*-positions of the aryl rings have only small effects on ΔG, and there is no systematic variation with Hammett substituent constants (see Figure 6b). This is also true of ΔH, where the measured values for the 4-Me and 4-CF_3

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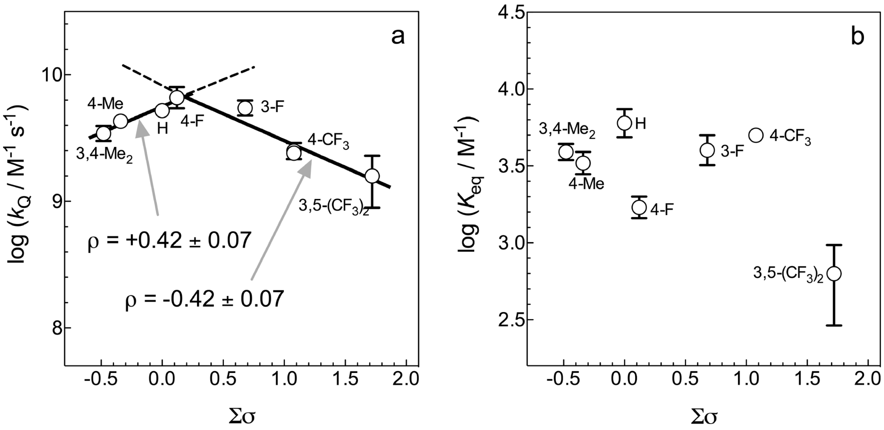
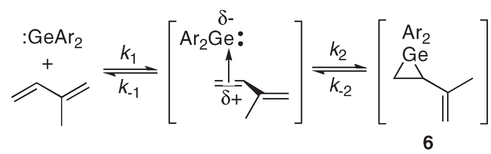


Figure 6. Hammett plots of the (a) rate and (b) equilibrium constants for reaction of diarylgermylenes **2a−g** with isoprene in hexanes solution at 25 °C.

derivatives (**6c** and **6f**, respectively) are the same within experimental error as that of the parent compound (ΔH = -9.6 ± 1.1 kcal mol^{-1}). Interestingly, it appears that these effects are dwarfed by those of substitution at the germirane ring-carbons (*vide supra*); increasing steric bulk at germanium can also be anticipated to exert a substantial stabilizing effect, judging from the results noted in the Introduction for 1,1-diaryl-2-vinylsilirane derivatives.[20−22] Quantifying these effects are the subject of further work in our laboratory.

Hammett plots of the rate and equilibrium constants for reaction of isoprene with $GePh_2$ and **2b−g** are shown in Figure 6. As mentioned above, there is no systematic variation in K_{eq} with Hammett σ-values (see Figure 6b); this indicates that the transient products of the reactions have no appreciable polar (or dipolar) character, hence supporting the vinylgermirane assignment. On the other hand, the corresponding plot for the (forward) reaction rate constants (k_Q; Figure 6a) displays a smooth but distinctly *curved* correlation with $\sum\sigma$, with the maximum rate occurring with the *para*-F derivative (**2d**) and decreasing as the substituents are made more electron-donating or electron-withdrawing relative to this substituent. The behavior is consistent with a two-step mechanism in which the rate-determining step changes with substituent and where the individual rate constants for the two steps are affected in opposite ways by polar substituents.[37] The limiting slopes defined by the two extremes of the plot ($\rho = +0.42 \pm 0.07$ on the donor side and $\rho = -0.42 \pm 0.07$ on the acceptor side; the 4-F derivative was included in both analyses) indicate a significant dipolar character for the intermediate in the reaction. The curved Arrhenius plot and resulting negative average activation energy that is exhibited by the parent compound are also consistent with a two-step reaction mechanism, in which the identity of the slower step changes as a function of temperature, from the first step at low temperatures to the second step at the other extreme.

A mechanism consistent with this behavior involves the initial formation of a polarized π-complex as a steady-state intermediate, which undergoes competing dissociation to the free reactants and collapse to vinylgermirane, the latter also reversibly. Equation 14 illustrates the proposed mechanism for formation of **6**, showing one of the two possible regioisomers of the π-complex. The first step in the sequence is essentially a Lewis-acid−base reaction and, hence, would be expected to exhibit a positive Hammett ρ-value, as it should be assisted by increased electrophilicity in the germylene.[31] The second step involves nucleophilic attack of the germanium lone pair at carbon within the complex; it should exhibit a negative Hammett ρ-value since it proceeds with neutralization of formal negative charge at germanium.[33,38] The observed Hammett behavior is consistent with step 1 being rate-determining in those derivatives bearing substituents more electropositive than 4-fluoro (H, 4-Me, 3,4-Me_2) and step 2 being rate-determining in those bearing substituents more electronegative than 4-fluoro (3-F, 4-CF_3, 3,5-$(CF_3)_2$). The change in the overall activation energy to (small) positive values for **2c** and **2f**, which are situated on either side of the apex in the Hammett plot of Figure 6a, is also consistent with this interpretation.



(14)

The recent computational study of Nag and Gaspar on the reaction of $GeMe_2$ with 1,3-butadiene provides mixed support for the involvement of a reactive π-complex as an intermediate.[13] A reactive complex was found to exist as a discrete intermediate at the B3LYP/6-31G(d,p)-6-311G(d,p) level of theory, separated by a free energy barrier of 3.0 kcal mol^{-1} from the corresponding vinylgermirane, but ca. 5.7 kcal mol^{-1} higher in free energy than the isolated reactants; the complex is more stable than the free reactants by 1.2 kcal mol^{-1} at a higher level of theory (CCSD(T)/cc-pVTZ//B3LYP/6-31G(d,p)-6-311G(d,p)), but the (free energy) barrier for its conversion to the vinylgermirane disappears. The results of the higher level calculations are in better agreement with experimental kinetic data for the reactions of $GeMe_2$ with aliphatic dienes in the gas phase and in solution, which are consistent with a very small but significant barrier to reaction; they proceed with rate constants close to, but clearly less than, the diffusional (or collisional) limit at 25 °C.[24,27−29] The involvement of reactive π-complexes as intermediates in the addition of GeH_2 and $GeMe_2$ to

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ethylene and other alkenes is a common feature of all of the various theoretical studies of these reactions that have been reported[39−45] and is consistent with experimental kinetic studies of the reaction of GeH_2 with ethylene in the gas phase.[27,41]

Our data also provide information on the factors affecting the lifetime of vinylgermirane **6a**, which was monitored in the presence of sufficiently high concentrations of isoprene (50−60 mM) to make it the only species detectable by laser photolysis methods. The species was found to decay with clean pseudo-first-order kinetics and a lifetime of $\tau = 400 \pm 25$ μs at 25 °C, in reasonable agreement with the value reported earlier.[26] The lifetime did not vary significantly over the 15−60 mM concentration range in isoprene, indicating that it does not react with a second molecule of the diene at rates exceeding ca. 10^4 M^{-1} s^{-1}. The lifetime was found to decrease by a factor of ca. 15 as the temperature was increased over the 10.6−52.0 °C temperature range, leading to a linear Arrhenius plot (Figure 5) and overall activation parameters of $E_a = 11.8 \pm 0.5$ kcal mol^{-1} and $\log(A/s^{-1}) = 12.0 \pm 0.4$, the latter corresponding to a value of $\Delta S^{\ddagger} = -5.6 \pm 1.8$ cal K^{-1} mol^{-1} for the entropy of activation at 25 °C. The maximum transient absorbance due to **6a** also decreased significantly with increasing temperature (see Figure 5), roughly in the manner expected from the variation in K_{eq} over the same temperature range. For example, the intensity ratio of the absorbances at 285 nm at 27 and 51 °C (ca. 1.65 from the data of Figure 5) is in reasonable agreement with the value of 1.82 predicted from the ratio of the equilibrium constants at the two temperatures, determined by interpolation of the van't Hoff plot of Figure 4.

We assign the first-order decay of vinylgermirane **6a** to its thermal conversion to the corresponding germacyclopent-3-ene derivative, **4a**, and thus the measured activation parameters to those associated with this process. Two mechanisms have been discussed for the isomerization, which is common to both vinylgermirane and vinylsilirane derivatives: a direct, single-step [1,3]-rearrangement pathway and a two-step mechanism proceeding via metallylene extrusion followed by concerted (1+4)-cycloaddition (eq 15).[13] Put another way, the first mechanism is the one that would hold if the formation of **4** from the free germylene and isoprene requires the *intermediacy* of vinylgermirane **6**, while the second is the one that would hold if the two products are formed *competitively*, and **6** acts merely as an unstable spectator in mobile equilibrium with the free germylene and diene; the latter mechanism is the one predicted to be correct on the basis of computational studies of the reaction of both silylenes and germylenes with aliphatic dienes.[13] Experimentally, the two mechanisms are kinetically indistinguishable from the context of either the free germylene or the vinylgermirane. Thus, our kinetic data for the reactions of **2a** with isoprene and DMB, combined with those for the subsequent decay of the corresponding vinylgermiranes, indicate only that formation of the thermodynamically stable products of these reactions (the corresponding germacyclopent-3-enes, **4a** and **1a**, respectively) proceeds substantially more slowly than formation of the corresponding vinylgermiranes (**6a** and **7a**, respectively). A value of $k_{(1+4)} = (1.5 \pm 0.5) \times 10^7$ M^{-1} s^{-1} can be calculated for the bimolecular rate constant of the putative (1+4)-cycloaddition reaction in the case of $GePh_2$ and isoprene at 25 °C, from the first-order rate coefficient for decay of **6a** and the K_{eq} value for its formation. This is roughly 350 times slower than the rate constant for the (1+2)-cycloaddition process that yields **6a** (k_Q in Table 1), corresponding to a difference in free energy of activation of ca. 3.5 kcal mol^{-1}. Similar treatment of the rate coefficients for decay of **6a** over the ca. 11−52 °C temperature range with interpolated values of K_{eq} (from the van't Hoff plot of Figure 4) leads to the Arrhenius plot of Figure 7, from which is obtained values of $E_a = +2.2 \pm 0.5$ kcal mol^{-1} and $\log(A/M^{-1}\ s^{-1}) = 8.8 \pm 0.4$, and hence $\Delta S^{\ddagger} = -20 \pm 2$ cal K^{-1} mol^{-1} at 25 °C. The treatment thus affords an enthalpy of activation for (1+4)-cycloaddition that is ca. 3 kcal mol^{-1} higher than the (average) $\Delta H^{\ddagger}$ for (1+2)-cycloaddition. The entropies of activation for the two pathways are the same within experimental error and in the range expected for cycloaddition processes.[46]

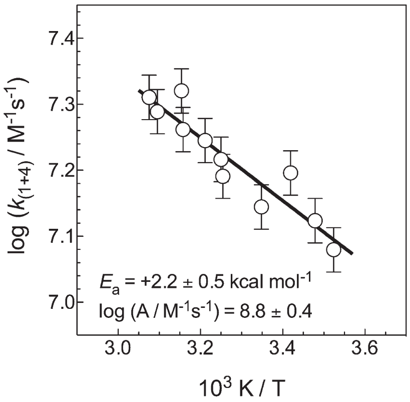
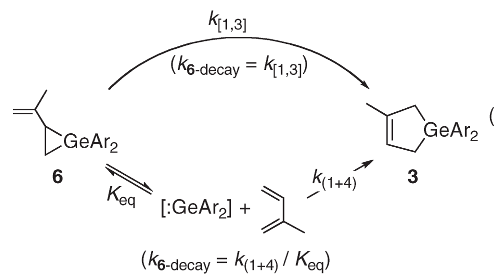


Figure 7. Arrhenius plot of the hypothetical second-order rate constants for (1+4)-cycloaddition of $GePh_2$ (**2a**) and isoprene, calculated from the first-order decay coefficients of vinylgermirane **6a** and interpolated values of the equilibrium constants for formation of **6a** as a function of temperature ($k_{(1+4)} = K_{eq}k_{\mathbf{6a}\text{-decay}}$).



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The resulting free energies of activation, calculated from the experimental rate constants, are $\Delta G^{\ddagger}_{(1+2)} = +4.2 \pm 0.1$ kcal mol^{-1} and $\Delta G^{\ddagger}_{(1+4)} = +7.7 \pm 0.1$ kcal mol^{-1} in hexanes

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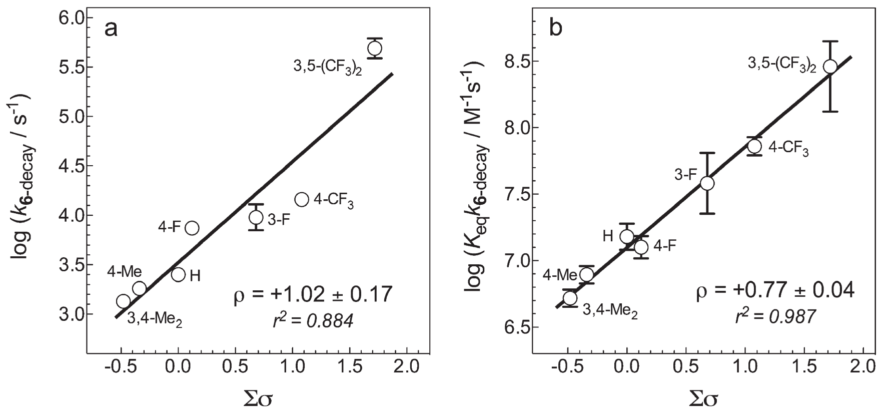
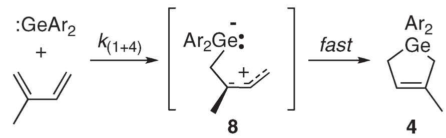


Figure 8. Hammett plots of (a) the first-order rate coefficients for decay of vinylgermiranes **6a**–**g** ($k_{\mathbf{6}\text{-decay}}$) and (b) the calculated rate constants for (1+4)-cycloaddition of **2a**–**g** with isoprene ($k_{(1+4)} = K_{eq}k_{\mathbf{6}\text{-decay}}$), in hexanes solution at 25 °C.

solution at 298 K, corresponding to values of $\Delta G^{\ddagger}_{(1+2)} = +6.1 \pm 0.1$ kcal mol^{-1} and $\Delta G^{\ddagger}_{(1+4)} = +9.6 \pm 0.1$ kcal mol^{-1} employing the gas phase at 1 bar and 298.15 K as standard state. These are both ca. 9 kcal mol^{-1} smaller than those computed by Nag and Gaspar for the same reaction pathways at the B3LYP/6-31G(d,p)-6-311G(d,p) level of theory, but as they pointed out, B3LYP significantly overestimates the stability of the free germylene relative to that indicated at higher levels of theory.[13] Interestingly, the computed (B3LYP) free energy difference between the transition state for (1+4)-cycloaddition and the most stable conformer of **6a**, which eliminates the errors specifically associated with the computed energy of the free germylene as much as possible, is $\Delta G^{\ddagger} = 10.4$ kcal mol^{-1}.[13] This is in quite good agreement with the value calculated from the experimental (first-order) rate coefficient for the decay of **6a** at 298 K in hexanes ($\Delta G^{\ddagger} = 12.8$ kcal mol^{-1}). The difference in the calculated (B3LYP) free energies of activation for the (1+2)- and (1+4)-cycloadditions of $GePh_2$ and isoprene ($\Delta(\Delta G^{\ddagger}) = 3.6$ kcal mol^{-1})[13] is in outstanding agreement with the experimentally derived value.

The effects of substituents in both the diene and the germylene on the rate and equilibrium constants lend more concrete experimental support for the dissociation/(1+4)-cycloaddition mechanism. The first-order rate coefficient for decay of vinylgermirane **7a**, from the reaction of $GePh_2$ with DMB, is close to 50 times larger than that of **6a**, a rather large and unexpected difference in reactivity in the context of a direct [1,3]-sigmatropic rearrangement mechanism.[47] This difference all but disappears, however, if the rate coefficient is considered in the context of the dissociation/cycloaddition mechanism. The product of the $k_{\mathbf{7a}\text{-decay}}$ and K_{eq} values affords $k_{(1+4)} = (1.8 \pm 0.3) \times 10^7$ M^{-1} s^{-1} for the rate constant for (1+4)-cycloaddition, which is roughly 100 times smaller than the rate constant for (1+2)-cycloaddition to the same substrate, but the same within experimental error as that calculated above for the formation of **4a** via (1+4)-cycloaddition of **2a** to isoprene. It thus appears that the key difference between the reactions of $GePh_2$ with the two dienes lies in the equilibrium constant for vinylgermirane formation, which is 40 times smaller for DMB than for isoprene; the individual free energy barriers for formation of the two competing products appear to be quite similar for these two dienes. Similarly, a Hammett plot of the first-order rate coefficients for the decay of vinylgermiranes **6a**–**g** ($k_{\mathbf{6}\text{-decay}}$) shows a strong but significantly scattered positive correlation of the rates with substituent constants, as shown in Figure 8a. The correlation improves quite considerably when the equilibrium constants are included in the analysis (Figure 8b). Thus, consideration of the pseudo-first-order decays of the vinylgermiranes in terms of the stepwise dissociation/(1+4)-cycloaddition mechanism, which requires that $k_{\mathbf{6}\text{-decay}} = k_{(1+4)}/K_{eq}$, provides a significantly better and more easily rationalizable explanation of the trends in reactivity as a function of substitution than is possible in the context of the sigmatropic rearrangement mechanism.

The Hammett correlation of Figure 8b ($\rho = +0.77 \pm 0.04$) suggests there to be significant negative charge development at germanium in the transition state of the rate-determining step for (1+4)-cycloaddition of $GePh_2$ to isoprene and is consistent with a concerted process driven largely by interactions between the germylene LUMO and diene HOMO. The indication of charge polarization during the rate-determining step could be the result of asynchronous bonding in the transition state, as Nag and Gaspar found in their computational study of the reaction of $GeMe_2$ with 1,3-butadiene.[13] The behavior is also consistent with a stepwise mechanism proceeding via electrophilic addition of the germylene to one of the termini of the diene substrate, leading to a zwitterionic intermediate that undergoes rapid collapse to the (1+4)-cycloadduct (eq 16); if such an intermediate is involved, however, it must be different than the one involved in the formal (1+2)-addition process, as the latter reaction proceeds more than 2 orders of magnitude faster. The involvement of such an intermediate in the reaction of $GeMe_2$ with electron-rich dienes requires that the lifetime of the intermediate be too short to allow bond rotations in the carbon framework of the species, to be compatible with the fact that the (1+4)-cycloaddition of $GeMe_2$ to electron-rich dienes proceeds stereospecifically;[4] no such information is yet available for $GePh_2$, to our knowledge.



(16)

In any event, the electronic effects on the two competing cycloaddition pathways in $GePh_2$ have dramatic consequences on the relative rate constants for the two processes

(47) Baldwin, J. E. *Chem. Rev.* **2003**, *103*, 1197.

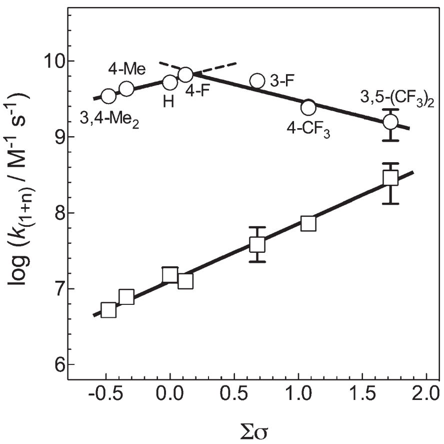


Figure 9. Hammett plots of the rate constants for competing (1+2)- (○) and (1+4)-cycloaddition (□) of diarylgermylenes **2a**−**g** with isoprene in hexanes at 25 °C.

as the electronic characteristics of the germylene are varied. This is illustrated in Figure 9, which combines the individual Hammett plots of Figure 6a (for (1+2)-cycloaddition) and Figure 8b (for (1+4)-cycloaddition) in a single graph. (1+2)-Cycloaddition to isoprene proceeds ca. 350 times more rapidly than (1+4)-cycloaddition in the case of $GePh_2$, and this difference increases (modestly) as germylene electrophilicity is decreased by donor substituents on the aryl rings. In contrast, increasing germylene electrophilicity results in a much more dramatic *reduction* in this difference, to the point where, with germylene **2g**, the rate constants for the two competing reactions are very nearly the same. This presumably occurs mainly because the germylene←diene π-complex becomes a bottleneck in the reaction pathway leading to the (1+2)-cycloadduct as germylene electrophilicity is increased.

The indication that $GePh_2$ plays the role of an electrophile in its (1+4)-cycloaddition reaction with isoprene is opposite Neumann and co-workers' early conclusion for $GeMe_2$.[5,6,9] However, the latter was based on relative product yields obtained in competition experiments with a variety of substituted dienes, which show simply that the (1+4)-cycloadducts of $GeMe_2$ with electron-poor dienes are formed *more efficiently* than those from electron-rich dienes. Given the complexities in the reaction that are now apparent, as well as the fact that $GeMe_2$ is even more reactive than $GePh_2$ toward the electron-rich dienes that have been studied in the present work,[24,33] it is clear that such a statement is an overgeneralization at the very least. What could not be revealed by the early competition kinetics studies is the way in which the unstable (1+2)-cycloadducts, which are undoubtedly formed much faster than the isolable ((1+4)-cycloaddition) products and whose stabilities are now known to be acutely sensitive to substituents on the diene, control the overall relative product yields in a competition experiment involving two different dienes. It seems likely to us that the mechanistic details of the reactions of transient germylenes with dienes and other unsaturated systems will prove to vary quite significantly with the electronic characteristics of the substrate.

Summary and Conclusions

Kinetic and thermodynamic results for the reactions of $GePh_2$ and various aryl-substituted derivatives with isoprene and 2,3-dimethyl-1,3-butadiene (DMB) in hexanes solution indicate that the major stable products of the reaction, the corresponding 1,1-diarylgermacyclopent-3-enes, are formed by a (1+4)-cycloaddition mechanism, which is slow relative to the reversible formation of the kinetic product, the corresponding 1,1-diaryl-2-vinylgermirane derivative, via formal (1+2)-cycloaddition. The results are in broad agreement with the conclusions of a recent theoretical study of the reactions of $GeMe_2$ and $GePh_2$ with 1,3-butadiene and isoprene, respectively, and in addition show that the rate constants for both reactions exhibit a marked sensitivity to the presence of polar substituents on the germylene and to alkyl substitution in the diene. (1+2)-Cycloaddition, which favors formation of the vinylgermirane corresponding to addition to the less-substituted of the two C=C bonds in the diene, proceeds 2 orders of magnitude more rapidly than (1+4)-addition and is *rapidly reversible* at ambient temperatures; in the reaction of $GePh_2$ with isoprene, the corresponding vinylgermirane is more stable than the free germylene and diene by only $\Delta G = -5.2$ kcal mol^{-1}, corresponding to an enthalpy difference of $\Delta H = -9.6$ kcal mol^{-1}. The difference is reduced significantly with DMB as the diene rather than isoprene.

Substituent and temperature effects are consistent with a two-step reaction mechanism for vinylgermirane formation, involving a polarized steady-state intermediate such as the corresponding germylene←diene π-complex; the Arrhenius parameters indicate a small negative overall activation energy for the reaction ($E_a \approx -0.9$ kcal mol^{-1}) and a moderately large, negative entropy of activation ($\Delta S^{\ddagger} \approx -20$ cal K^{-1} mol^{-1}) for the reaction of the parent diarylgermylene ($GePh_2$) with isoprene. The corresponding vinylgermiranes are readily detectable by time-resolved UV/vis spectroscopy, as long-lived transients exhibiting $\lambda_{max} = 285$ nm; the spectrum is insensitive to substitution on either the aryl rings or at (one of) the germirane ring carbons. On the other hand, the lifetime is markedly sensitive to substituents, decreasing substantially with increasing electron-withdrawal at germanium or with methyl-substitution at the germirane ring carbon. These results are best accommodated by a mechanism for vinylgermirane decay that involves (reversible) dissociation to the free germylene and diene, followed by slow (1+4)-cycloaddition to yield the thermodynamically stable product, the corresponding 1,1-diarylgermacyclopent-3-ene. In the case of $GePh_2$ and isoprene, the latter reaction proceeds with activation parameters of $E_a = +2.2$ kcal mol^{-1} and $\Delta S^{\ddagger} \approx -20$ cal K^{-1} mol^{-1}. It too shows a marked sensitivity to polar substituents, the rate constant increasing dramatically with increasing germylene electrophilicity in a manner consistent with a LUMO-germylene/HOMO-diene controlled process. As germylene electrophilicity increases past a certain point, the rate of (1+4)-cycloaddition increases at the expense of that of (1+2)-cycloaddition because the polar intermediate involved in the latter process becomes a bottleneck in the reaction pathway.

Further mechanistic studies of this and other reactions of transient germylenes and their silicon homologues are in progress.

Experimental Section

Germacyclopent-3-enes **1a**−**d**,**f**,**g** were synthesized and purified according to the previously reported procedures;[30−33] the synthesis and characterization of **1e** and **4e** and the basic photochemical behavior of **1e** are described in the Supporting Information. Hexanes (EMD OmniSolv) for laser flash photolysis experiments was dried by passage through activated neutral alumina (250 mesh; Purifry Co., Gramercy LA) under nitrogen using a Solv-Tek solvent purification system. Isoprene and DMB (both Aldrich) were distilled or passed as neat liquids through a short column of silica gel prior to use.

Nanosecond laser flash photolysis experiments were carried out using the pulses from a Lambda-Physik Compex 120 excimer laser, filled with F_2/Kr/Ne (248 nm; ca. 20 ns; 100 ± 5 mJ), and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.[30] Solutions were prepared in a calibrated 100 mL reservoir, fitted with a glass frit to allow bubbling of argon through the solution for at least 30 min prior to and then throughout the duration of each experiment. Concentrations were such that the absorbance at the excitation wavelength was between ca. 0.7 and 0.9. The solutions were pumped from the reservoir through Teflon tubing connected to a 7 × 7 mm Suprasil flow cell using a Masterflex 77390 peristaltic pump. The glassware, sample cell, and transfer lines were dried in a vacuum oven (65−85 °C) before use. In experiments carried out at 25 °C, solution temperatures were measured with a Teflon-coated copper/constantan thermocouple inserted into the thermostated sample compartment in close proximity to the sample cell; those in which the solution temperature was varied were carried out using a flow cell that allowed insertion of the thermocouple directly into the sample solution. Reagents were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Transient absorbance−time profiles at each concentration of scavenger are the signal-averaged result of 7−40 laser shots. Decay rate coefficients were calculated by nonlinear least-squares analysis of the transient absorbance−time profiles using the Prism 5.0 software package (GraphPad Software, Inc.) and the appropriate user-defined fitting equations, after importing the raw data from the Luzchem mLFP software and applying the necessary corrections to remove the minor contributions from the corresponding digermenes at low substrate concentrations.[26,31] Rate constants were calculated by linear least-squares analysis of decay rate−concentration data (generally 4−7 points) that spanned as large a range in transient decay rate as possible. Errors are quoted as twice the standard error obtained from the least-squares analyses. Rate constants determined at temperatures other than 25 °C were corrected for thermal solvent expansion.[48]

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Supporting Information Available: Details of the preparation and characterization of compounds; additional kinetic data determined from laser flash photolysis experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

(48) Density of Solvents as a Function of Temperature. In *CRC Handbook of Chemistry and Physics, Internet Version*, 87th ed.; Lide, D. R., Ed.; CRC Press/Taylor and Francis: Boca Raton, FL, 2007; pp 15−25.