Substituent Effects on the Reactions of Diarylgermylenes and Tetraaryldigermenes with Acetic Acid and Other Lewis Bases in Hydrocarbon Solution

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A series of three 1,1-diaryl-3,4-dimethylgermacyclopent-3-ene derivatives bearing polar substituents in the *para*-positions of the 1,1-diphenyl rings have been synthesized, and their photochemistry has been studied by steady state and laser flash photolysis methods. Photolysis in hydrocarbon solvents affords the corresponding diarylgermylenes in chemical and quantum yields similar to those of the parent (1,1-diphenyl) compound, as shown by the results of trapping experiments with methanol (MeOH) and acetic acid (HOAc). The germylenes exhibit UV/vis absorption spectra ($\lambda_{max} = 480-500$ nm) and kinetic behavior ($\tau \approx 2$ μs) similar to that of the parent, diphenylgermylene ($GePh_2$), in hexane solution. Their decay results in the formation of new transient products assigned to the corresponding tetraaryldigermenes (Ge_2Ar_4), whose absorption spectra ($\lambda_{max} = 440$ nm) and lifetimes are also similar to those exhibited by the parent, Ge_2Ph_4. Both the germylenes and the corresponding digermenes are quenched rapidly by added HOAc and Et_2NH, with rate constants that increase with increasing electron-withdrawing power of the aryl substituents, consistent with reaction mechanisms that involve initial nucleophilic attack at germanium in all cases. The Lewis acid−base complexation of the three germylenes with THF and ethyl acetate (EtOAc) has also been studied and supports a two-step mechanism for the reaction with HOAc that involves initial, rate-determining nucleophilic attack at germanium followed by rapid proton transfer. A similar mechanism is proposed for reaction of this substrate with Ge_2Ph_4 on the basis of the measured Hammett ρ-value. Tetramesityldigermene reacts with HOAc in toluene or THF solution to afford the 1,2-addition product, 1-acetoxy-1,1,2,2-tetramesityldigermane, while no reaction could be detected with Et_2NH.

Introduction

The chemistry of germylenes has been of great interest for many years, and a great deal of work has been done toward defining the scope and mechanisms of many of their characteristic reactions.[1] All known examples of these typically highly reactive, electrophilic species possess singlet ground states,[2] which calculations indicate to be more than 20 kcal mol^{-1} below the lowest triplet state in the parent molecule (GeH_2) and simple substituted derivatives.[3] With only one recent exception,[4] the same is true of their organosilicon counterparts, silylenes,[5] whose chemistry has been even more extensively studied.[6]

Not surprisingly, the reactivity of transient silylenes and germylenes shares many common qualitative features with those of singlet carbenes. For example, they all undergo facile insertion into the O−H bonds of alcohols and carboxylic acids, form Lewis acid−base complexes ("ylides") with ethers, amines, and other Lewis bases, and undergo (2+1)-cycloaddition reactions with alkynes, alkenes, and dienes.[1,6,7] It is generally recognized that one of the main variables throughout the series, all else being equal, is a systematic variation in overall reaction thermodynamics, with reaction exothermicities decreasing down the group.[8−10] One particularly good example of this is the (2+1)-cycloaddition with alkenes. While cyclopropanes are a common structural motif in organic chemistry, most of the known silacyclopropane derivatives enjoy only marginal stability, and only two germacyclopropane derivatives have ever been reported,[11] to our knowledge; (2+1)-cycloreversion to generate

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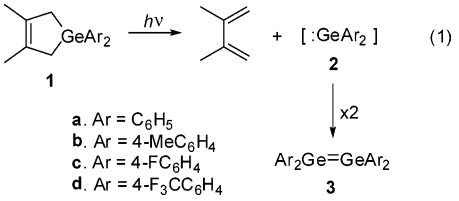
an alkene and the corresponding metallylene is the prevalent mode of decomposition of sila- and germacyclopropane derivatives in the absence of secondary trapping reactions.[8,12−14]

The direct detection and study of transient organogermylenes in solution by laser flash photolysis methods has been of considerable interest. In solution, the direct detection of the dimethyl ($GeMe_2$[15−18]), methylphenyl ($GeMePh$[15b,c,19]), diphenyl ($GePh_2$[16,20−23]), and dimesityl ($GeMes_2$;[16,23,24] Mes = 2,4,6-trimethylphenyl) derivatives by time-resolved UV/vis spectrophotometry has been widely reported, using variety of oligogermane, silyl- and disilylgermane, benzo(7-germanorbornadiene), and germacyclopent-3-ene derivatives as germylene precursors. These compounds are all well established to undergo photochemical germylene extrusion in moderate to high quantum and/or chemical yields. However, most are known to afford other transient photoproducts as well, which has made conclusive identification of the weakly absorbing germylene of interest problematic.[3a] Of these, germacyclopent-3-enes appear to be uniquely suited as precursors for the study of transient germylenes in solution by time-resolved UV/vis methods, as germylene extrusion characteristically proceeds in high quantum yield and essentially quantitative chemical yield from these compounds, and without the competing formation of other (detectable) transient photoproducts in the primary photochemical event. Compounds of this type have recently allowed the definitive identification of, and detailed kinetic studies to be carried out for, all four of the "simple" transient germylene derivatives listed above,[16,17,19b,21,23] affording results that correlate quite well with those of earlier studies of the parent and dimethyl derivatives in the gas phase.[25]

In this paper, we report the synthesis of three new diarylgermylene precursors, the characterization of their photochemistry by steady state and laser flash photolysis techniques, and absolute rate and/or equilibrium constants for the reactions of the corresponding diarylgermylenes with tetrahydrofuran (THF), *N*,*N*-diethylamine (Et_2NH), ethyl acetate (EtOAc), and acetic acid (HOAc). The compounds in question, the 1,1-diaryl-3,4-dimethylgermacyclopent-3-ene derivatives **1b**−**d** (eq 1), were designed to enable the study of the effects of polar substituents on various aspects of the reactivity of diphenylgermylene ($GePh_2$, **2a**) in solution. The substituents (*para*-methyl, -fluoro, and -trifluoromethyl, respectively) were chosen to provide a reasonable span in electron-donating/-withdrawing ability throughout the series, while minimizing the likelihood of any specific effects on either the photochemical yield of the desired diarylgermylenes (**2b**−**d**) or their kinetic behavior due to complexation of the strongly electrophilic germylenes with their precursors. Since the base reaction of $GePh_2$ in solution is dimerization to form tetraphenyldigermene (**3a**),[16,22,26] the effects of substituents on the kinetics and mechanisms of selected reactions of the latter compound, in this case those with HOAc and Et_2NH, can also be studied.



(1)

The first objective was to define the effects of polar substituents on the absolute rate and/or equilibrium constants for the reactions of $GePh_2$ with representative oxygen- and nitrogen-based nucleophilic substrates such as THF and Et_2NH. These are simple, well-known Lewis acid−base complexation reactions,[27−32] which proceed at rates close to the diffusion limit in hexane solution;[21,23] thus, the substituent effect on the forward rate constant can be anticipated to be small, if observable at all. Both reactions are reversible on the time scale of our experiments because further unimolecular rearrangement of the complexes to tetravalent product is thermodynamically and(or) kinetically unfavorable, according to early studies of the chemistry of hydridogermylamines[33] and recent theoretical calculations.[34,35] We thought it would be particularly interesting to examine the effect of substituents on the equilibrium constant for the reaction of $GePh_2$ with THF, as it is of the right magnitude to be measurable under the conditions of our experiments and might be expected to be somewhat more

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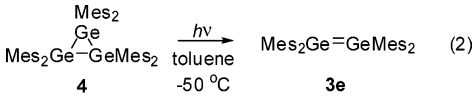
sensitive to polar substituents than the forward rate constant for the process.

The second objective was to examine the effects on the O−H insertion reaction with HOAc. This reaction is closely related to that with alcohols, which was first discovered by Lappert and co-workers[36] and has since been shown to proceed via initial Lewis acid−base complexation followed by rate-determining H-migration,[23,30,37] the second step most likely proceeding catalytically.[23,37] Both steps in the sequence are reversible, as has been known since the work of Satgé and co-workers on the chemistry of hydridoalkoxygermanes.[26] The primary question to be answered in the case of the analogous reaction with carboxylic acids, which in contrast to the reaction with alcohols proceeds irreversibly,[16] is whether the mechanism is similar to that of the reaction with alcohols (with the carboxylic acid playing the role of the base in the initial step) or involves protonation of the germylene in the initial (or perhaps only kinetically significant) step. Presumably, the two mechanisms can be expected to lead to quite different responses of the absolute rate constant to aryl substituent. Our study of this reaction was further expanded to include an examination of the Lewis acid−base complexation of **2a**−**d** with ethyl acetate (EtOAc), to provide additional relevant mechanistic information on the reaction.

The effects of ring substituents on the rate constants for quenching of Ge_2Ph_4 by HOAc and Et_2NH are also reported. These processes occur at measurable rates under the conditions of our experiments,[16] although the products are unknown and cannot be easily determined using **1a**−**d** as precursors because the digermene is produced by germylene dimerization; anything that one might add to react with it reacts with the germylene faster and quenches the formation of the digermene altogether. We have thus carried out product studies of the reactions of the two substrates with tetramesityldigermene (**3e**), a well-known, relatively stable tetraaryldigermene that can be synthesized in good yields by low-temperature photolysis of hexamesitylcyclotrigermane (**4**; eq 2),[38−40] as a model for the evidently rapid reactions of the less hindered tetraaryldigermenes with these substrates.

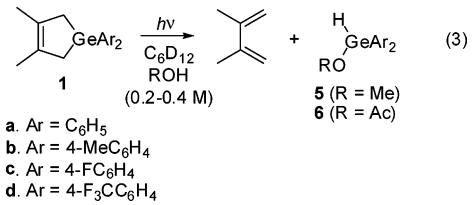


(Mes = 2,4,6-trimethylphenyl)

Results

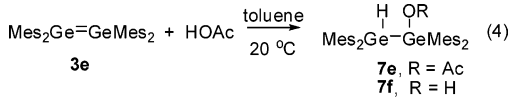
Compounds **1b**−**d** were synthesized by reaction of 1,1-dichloro-3,4-dimethylgermacyclopent-3-ene with the corresponding substituted phenylmagnesium bromides[16] and were obtained in analytically pure form after column chromatography and several recrystallizations from hexanes.

Steady state photolysis of deoxygenated 0.02 M solutions of **1b**−**d** in cyclohexane-d_{12} containing methanol (0.2 M) afforded equal amounts of 2,3-dimethylbutadiene (DMB) and the corresponding diarylmethoxygermanes (**5b**−**d**) in estimated chemical yields of 77−88%, as determined from the relative slopes of concentration versus time plots for the starting materials and products (eq 3). The reactions were monitored by ^{1}H NMR spectroscopy as a function of photolysis time over the 0−25% conversion range, above which the spectra became increasingly complex owing (presumably) to secondary photolysis of the primary products. None of the three methoxygermanes survived either column or gas chromatography of the reaction mixtures without substantial decomposition, so they were identified by comparison of the ^{1}H NMR spectra of the crude photolyzates to that of methoxydiphenylgermane (**5a**), with additional support from high-resolution mass spectrometry. Quantum yields for the formation of **5b**−**d** were determined using the formation of **5a** from **1a** as a secondary actinometer ($\Phi = 0.55 \pm 0.07$[16]) and were found to be the same within experimental error as that for the parent compound in each case.



Similar results were obtained from photolyses of the three compounds in hexane containing HOAc (0.4 M), which led to the formation of DMB and the corresponding acetoxygermanes **6b**−**d** (eq 3) as the major products. The latter showed similar sensitivities to attempted column or gas chromatographic isolation as **5a**−**d**, so their identification was also made spectroscopically using the crude reaction mixtures. However, considerably higher conversions were possible before the ^{1}H NMR spectra began to show signs of secondary photolytic decomposition of the primary products, compared to the experiments with MeOH as the scavenger. This allowed additional confirmation of the product structures to be obtained by ^{13}C NMR and infrared spectroscopy.

Product studies were also carried out on the reaction of tetramesityldigermene (**3e**) with HOAc. The digermene was prepared by photolysis of a 1.6 mM solution of **4** in anhydrous toluene at ca. −50 °C (eq 2), following the procedure of Baines and co-workers.[40] Addition of HOAc (90 mM) as a cooled solution in toluene to the resulting solution of **3e** at ca. −50 °C, followed by warming to room temperature, resulted in disappearance of the intense yellow color characteristic of the digermene over a period of ca. 10 min. The mixture, after evaporation of solvent and excess HOAc, contained residual **4**, 1-hydroxy-1,1,2,2-tetramesityldigermene (**7f**), and 1-acetoxy-1,1,2,2-tetramesityldigermane (**7e**; eq 4), which was isolated and identified on the basis of its ^{1}H and ^{13}C NMR, infrared, and mass spectra. The yield of **7f** depended on the rigor with which the solvent was dried prior to use and did not change during column chromatography of the crude reaction mixture. The compound thus appears to be formed by reaction of **3e** with traces of water present in the solvent;[41] lower yields of **7e**



relative to **7f** were obtained when the reaction was carried out in THF solution.

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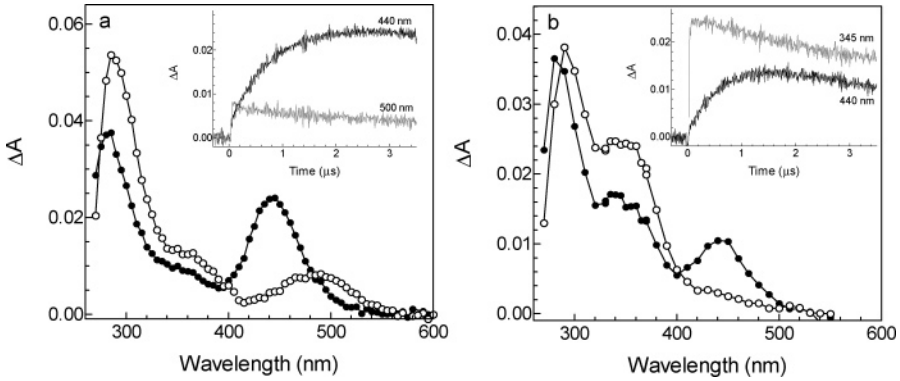


Figure 1. Transient UV/vis absorption spectra from laser flash photolysis of dry, deoxygenated solutions of **1d** (0.003 M) at 25 °C, (a) in hexane 30−100 ns (○) and 3.50−3.52 μs (●) after the laser pulse and (b) in hexane containing 4.3 mM THF 115−140 ns (○) and 3.49−3.54 μs (●) after the laser pulse. The insets show transient absorption profiles recorded at selected wavelengths within the ranges monitored.

No evidence of reaction could be discerned upon addition of Et_2NH to similarly prepared THF solutions of **3e**. The same was true of experiments using *n*-butylamine as the potential co-reactant.

Laser Flash Photolysis Studies. Laser flash photolysis studies were carried out on flowed, deoxygenated solutions of **1a**−**d** (ca. 0.003 M) in anhydrous hexane using a pulsed KrF excimer laser (∼25 ns, ∼100 mJ, 248 nm) for excitation. As with the parent compound (**1a**),[16] laser photolysis of **1b**−**d** resulted in the formation of two transient species, one that is formed with the laser pulse ($\lambda_{max} \approx 300$ nm and 480−500 nm; $\tau \approx 2$ μs) and one that is considerably longer-lived ($\lambda_{max} \approx 440$ nm; $\tau \approx 20$ μs) and is formed over a similar time scale to the decay of the first-formed species. The former are assigned to the corresponding diarylgermylenes (**2b**−**d**), while the second-formed species are assigned to the corresponding tetraaryldigermenes (**3b**−**d**), formed by dimerization of **2b**−**d**. Figure 1a shows transient absorption spectra from flash photolysis of **1d** under these conditions, recorded at selected time intervals after the laser pulse, along with representative growth/decay traces recorded at monitoring wavelengths of 500 and 440 nm.

The germylene decays, after scaled subtraction of traces recorded on the same time scale at 440 nm in order to remove the underlying growth/decay component due to the corresponding digermene absorptions, fit acceptably to second-order decay kinetics (eq 5) and afforded rate coefficients of $k_{dim}/\epsilon_{500} = (8 \pm 2) \times 10^6$ cm s^{-1} for **2b** and $(2.8 \pm 0.8) \times 10^7$ cm s^{-1} for **2c** and **2d**. A value of $k_{dim}/\epsilon_{500} = (9 \pm 2) \times 10^6$ cm s^{-1} was obtained for **2a**, which is in acceptable agreement with the value of $k_{dim}/\epsilon_{530} = (1.1 \pm 0.9) \times 10^7$ cm s^{-1} reported by us earlier from (similarly corrected) decays recorded at 530 nm,[16] given the difference in extinction coefficients at the two monitoring wavelengths. The scaling factors used for subtraction of the underlying digermene absorptions were determined from transient spectra recorded for hexane solutions of **1b**−**d** containing 4−15 mM THF, as described below. The results suggest that the absolute rate constants for dimerization of **2c**,**d** are slightly larger than those for **2a**,**b**, barring large variations in extinction coefficient throughout the series. A value of $k_{dim} = (1.2 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1} for **2a** (hexane; 23 °C) was reported in our earlier study of the parent diarylgermylene,[16] which is within a factor of 2 of the diffusional limit in hexane at these temperatures.

$$\Delta A_t = \Delta A_0/(1 + 2k_{dim}(\Delta A_0/\epsilon l)t) \qquad (5)$$

While the UV/vis spectra of **3b**−**d** are all essentially identical to that of tetraphenyldigermene (Ge_2Ph_4, **3a**), the absorption maxima of the germylenes appear to be blue-shifted from that of the unsubstituted derivative (**2a**, $\lambda_{max} = 500$ nm), with the largest differences being observed for the *para*-fluoro (**2c**, $\lambda_{max} = 480$ nm) and *para*-trifluoromethyl derivatives (**2d**, $\lambda_{max} = 490$ nm); that for **2b** appears at $\lambda_{max} = 495$ nm and is not significantly different from that of **2a**. While the spectra were recorded on reasonably short time scales (3.6 μs full scale) and those for the germylenes were taken over a very narrow time window at the peak of the laser pulse, it is difficult to ensure that there is no distortion in the spectra due to small contributions from the corresponding digermenes, whose formation is fastest when the germylene concentration is highest. In an attempt to check for such contributions, a spectrum of **2c** was recorded in hexane containing 2 mM HOAc, where the lifetime of the germylene is reduced to ca. 100 ns and formation of the digermene is quenched almost entirely. The spectrum was found to be essentially identical to that obtained in the absence of added acid. The possibility of a spectral shift due to complexation of **2c** with the precursor was ruled out on the basis of a spectrum recorded with a 30 μM solution of **1c** in hexane using an ArF laser (193 nm) for excitation, which again exhibited $\lambda_{max} = 480$ nm.

Addition of small amounts of tetrahydrofuran (THF) to the solutions of **1b**−**d** led to distinct changes in the form of the transient signals at 500 nm, causing them to develop a distinct initial rapid decay component superimposed on the growth/decay profile of the corresponding digermene (**3b**−**d**); the latter was in all cases essentially unaltered in the presence of low concentrations of THF compared to its form in pure hexane solution. The initial decay became unresolvable from the laser pulse in the presence of ∼2 mM THF, as we found previously for **2a**.[23] Accompanying this behavior was the appearance of new transient absorptions centered at $\lambda_{max} \approx 350$ nm in all three cases, which exhibited a resolvable growth that quickened as successively higher concentrations of THF were added; the growth became unresolvable from the laser pulse at roughly the same THF concentrations as did the germylene decays. Figure 1b shows transient spectra and representative transient growth/decay profiles recorded by laser photolysis of the solution of **1d** in the presence of 4.3 mM THF. Transient absorption spectra recorded for **1b** and **1c** in the presence of 15.0 and 7.3 mM THF, respectively, are shown in the Supporting Information along with the spectra in neat hexane solution. Relative extinction coefficients at 500 and 440 nm ($\epsilon_{500}/\epsilon_{440}$) of 0.150, 0.110, and 0.135 for **3b**, **3c**, and **3d**, respectively, were determined from the spectra of the digermenes obtained in these experiments. The behavior exhibited by the three derivatives in the presence of THF is consistent with reversible scavenging

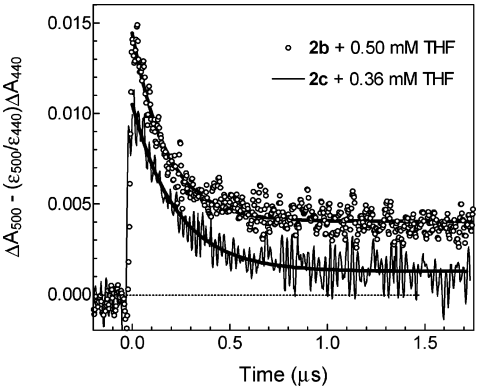
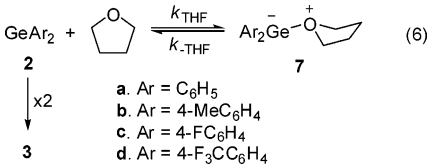


Figure 2. Corrected transient decay profiles for germylenes **2b** and **2c** in hexane containing 0.50 and 0.36 mM THF, respectively, at 25 °C. The solid lines are the nonlinear least-squares fits of the data to eq 9.

of **2b**−**d** by the ether to yield the corresponding **2**-THF Lewis acid−base complexes (**7**; eq 6),[23] which exhibit their own discrete absorptions centered at $\lambda_{max} \approx 350$ nm.



In addition to the behavior noted above, decay profiles for germylenes **2b** and **2c**, after correction for the underlying absorptions due to the corresponding digermenes, exhibited a bimodal form in the presence of sub-millimolar concentrations of THF. The decays consisted of a fast initial decay component and a very slowly decaying residual absorption, similar to that reported by us previously for **2a** in the presence of THF.[23] The fast initial decay component is associated with the approach to equilibrium with **7**, for which the pseudo-first-order rate constant is given by eq 7, where k_Q and k_{-Q} are the absolute rate constants for the forward and reverse components of the process and Q is the scavenger (THF). The slowly decaying residual absorption is associated with that due to free germylene remaining after equilibration is complete and undergoing slow dimerization; the equilibrium constant ($K_{eq} = k_Q/k_{-Q}$) is approximately related to the initial and residual transient absorbances (ΔA_0 and ΔA_{res}, respectively) as defined by eq 8, where ΔA_0 and ΔA_{res} are obtained from analysis of ΔA_t versus time profiles according to eq 9.[23] Corrected decay traces for **2b** and **2c** in hexane containing 0.50 and 0.36 mM THF, respectively, are shown in Figure 2. Nonlinear least-squares fitting of the two decay profiles afforded decay rate constants of $k_{decay} = (5.6 \pm 0.3) \times 10^6$ and $(4.4 \pm 0.3) \times 10^6$ s^{-1}, respectively, leading to an estimate of $k_{THF} \approx 1.1 \times 10^{10}$ M^{-1} s^{-1} in both cases. Similarly, the ΔA_0 and ΔA_{res} values obtained from the analyses afforded estimates of $K_{eq} \approx 5200$ M^{-1} for **2b** and $K_{eq} \approx 20\,000$ M^{-1} for **2c**. Germylene **2d** appeared to decay completely to the pre-pulse level in the presence of 0.35 mM THF (consistent with $K_{eq} > 25\,000$ M^{-1}), with a k_{decay} value corresponding to $k_{THF} \approx 1.2 \times 10^{10}$ M^{-1} s^{-1}. For comparison, a similar analysis of data recorded for **2a** in hexane containing 0.40 mM THF afforded estimates of $k_{THF} \approx 9 \times 10^9$ M^{-1} s^{-1} and $K_{eq} \approx 16\,000$ M^{-1}, 25−30% higher and lower, respectively, than the (more accurate) values determined by us previously from data recorded at several THF concentrations over the 0.2−0.8 mM range.[23] We thus conclude that k_{THF} varies only slightly throughout the series of germylenes, if at all. On the other hand, K_{eq} varies quite significantly, increasing in size as the electron-withdrawing power of the aryl substituents increases, from a low of $K_{eq} \approx 5000$ M^{-1} in the case of **2b** to a value in excess of 25 000 M^{-1} in the case of **2d**.

$$k_{decay} = k_{-Q} + k_Q[Q] \tag{7}$$

$$\Delta A_0/\Delta A_{res} = 1 + K_{eq}[Q] \tag{8}$$

$$\Delta A_t = \Delta A_{res} + (\Delta A_0 - \Delta A_{res}) \exp(-k_{decay}t) \tag{9}$$

Addition of HOAc and Et_2NH to hexane solutions of **1b**−**d** had very different effects on the germylene and digermene decay profiles; the results were again quite similar to those found in our previous study of **1a** in the presence of these reagents.[16] Addition of small amounts of these substrates resulted in marked decreases in the peak intensities of the digermene signals and concomitant acceleration of both their initial growth and subsequent decay, all in proportion to the concentration of added reagent; the decays fit acceptably to pseudo-first-order kinetics in the presence of the two substrates over the concentration ranges in which they could be detected. Decays recorded at 500 nm, where **2b**−**d** are the dominant absorbers, also clearly accelerated in the presence of the two substrates and followed good first-order kinetics once the concentrations were high enough to reduce the peak intensity of the digermene absorptions (at 440 nm) to less than ca. 25% of their values in the absence of the scavenger.

Plots of k_{decay} versus [Q] according to eq 10, where Q is the substrate and k_0 is the hypothetical first-order decay rate constant at [Q] = 0, were linear for each of the germylenes and digermenes, as illustrated in Figure 3 for the experiments with HOAc as scavenger. The digermene decays fit acceptably to pseudo-first-order kinetics in the presence of the two substrates over the concentration ranges in which they could be detected. Rate constants for reaction of $GePh_2$ (**2a**) and Ge_2Ph_4 (**3a**) by HOAc were redetermined; the value obtained for **2a** ($k_{HOAc} = (4.4 \pm 0.6) \times 10^9$ M^{-1} s^{-1}) matches that reported in our earlier study,[16] while the value for **3a** ($k_{HOAc} = (7.0 \pm 0.4) \times 10^7$ M^{-1} s^{-1}) is somewhat higher than our previously estimated upper limit ($k_{HOAc} < 4 \times 10^7$ M^{-1} s^{-1}), which was based on a single decay rate constant obtained at the highest HOAc concentration that was studied.[16] Quenching by acetic acid-*Od* (DOAc) was also studied for three of the germylenes (**2a**, **2b**, and **2c**) and two of the digermenes (**3b** and **3d**) and found to proceed with the same rate constant as HOAc within experimental error in each case. The absolute rate constants obtained in these experiments are listed in Table 1, along with the absorption maxima of the germylenes (**2a**−**d**) and their THF complexes (**7a**−**d**).

$$k_{decay} = k_0 + k_Q[Q] \tag{10}$$

As was also found for **2a**,[16] quenching of **2b**−**d** by diethylamine was accompanied by the formation of transient products absorbing at $\lambda_{max} \approx 320$ nm, which can be assigned to the Ar_2-Ge−Et_2NH Lewis acid−base complexes **8** (eq 11). The species decayed with mixed-order kinetics over several tens of microseconds. As was found for the THF complexes **7**, there was no discernible variation in the position of the absorption maxima of these species throughout the series.

To assist in the interpretation of the results for HOAc, we also examined the behavior of $GePh_2$ and the three substituted derivatives in the presence of ethyl acetate (EtOAc). Steady-

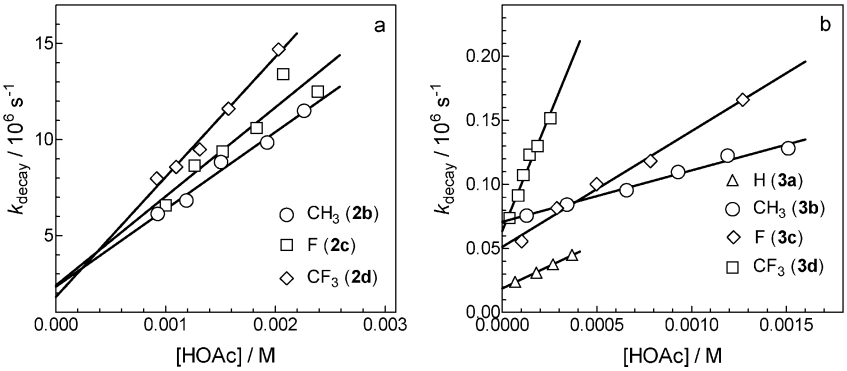
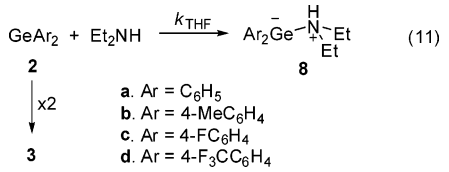


Figure 3. Plots of the pseudo-first-order rate constants for decay of (a) diarylgermylenes **2b**−**d** and (b) tetraaryldigermenes **3a**−**d** in hexane at 25 °C in the presence of HOAc.

Table 1. Quantum Yields for Formation of Diarylgermylenes (2a−d), UV/vis Absorption Maxima, and Absolute Rate or Equilibrium Constants for Reaction of Diarylgermylenes (2a−d) and Tetraaryldigermenes (3a−d) with Acetic Acid (HOAc), *N,N*-Diethylamine (Et_2NH), and Ethyl Acetate (EtOAc) in Hexane Solution at 25 °C

			$GeAr_2$ (**2**)			Ge_2Ar_4 (**3**)	
precursor	Φ_2[a]	λ_{max} (nm)	k_{HOAc} (10^9 M^{-1} s^{-1})	k_{Et_2NH} (10^9 M^{-1} s^{-1})	K_{EtOAc} (M^{-1})	k_{HOAc} (10^7 M^{-1} s^{-1})	k_{Et_2NH} (10^9 M^{-1} s^{-1})
1a	0.55 ± 0.07	500	3.9 ± 0.7 (4.4 ± 0.6) [b]	7.3 ± 0.9	405 ± 7	7.0 ± 0.4	2.4 ± 0.4
1b	0.50 ± 0.09	495	3.4 ± 0.6 (3.1 ± 0.8) [b]	6.9 ± 0.8	129 ± 5	4.0 ± 0.5 (4.5 ± 0.8) [b]	3.1 ± 0.3
1c	0.47 ± 0.12	480	4.1 ± 0.8	7.3 ± 0.4	460 ± 80	9.0 ± 1.0	4.9 ± 0.5
1d	0.55 ± 0.12	490	6.2 ± 1.0 (7.2 ± 0.9) [b]	9.4 ± 1.0	900 ± 25	36 ± 6 (28 ± 3)[b]	5.8 ± 0.6

[a] Quantum yields for the formation of methoxygermanes **5a**−**d** from photolysis of **1a**−**d** in C_6D_{12} containing 0.2 M MeOH. The values for **1b**,**c** employed the photolysis of **1a** as secondary actinometer. [b] Value obtained using acetic acid-*Od* as scavenger.



state photolysis of a solution of **1a** in C_6D_{12} containing EtOAc (0.3 M) resulted in the formation of DMB and germanium-containing polymers and showed no evidence for the formation of products that might be ascribable to trapping of **2a** by the ester. Flash photolysis of hexane solutions of **1a** in the presence of 1.5−15 mM EtOAc afforded germylene absorptions whose initial intensities decreased systematically with increasing substrate concentration, but with no change in the form of the transient decay profiles. No effect of any sort was observed on the digermene absorptions at 440 nm. New transient absorptions centered at λ_{max} = 350 nm were observed to appear, which increased in initial intensity as that of the germylene signal (at 500 nm) decreased; at no concentration was an initial growth in the signal resolvable from the laser pulse, however. These new absorptions decayed over 10−20 μs, concomitantly with the growth of the digermene absorptions at 440 nm; the latter were slowed significantly in the presence of EtOAc compared to the growth rates in the absence of the substrate. Only the digermene and the 350 nm absorptions could be detected in the presence of 30 mM EtOAc, as the transient spectra of Figure 4a illustrate. The behavior is consistent with reversible complexation of **2a** with EtOAc, under conditions where the equilibrium constant is sufficiently small and the forward rate constant sufficiently large that the approach to equilibrium cannot be detected on the time scale of our experiments.[23] The signal detected for $GePh_2$ at 500 nm in the presence of low concentrations of EtOAc thus corresponds to free germylene in equilibrium with the complex and is related to the equilibrium constant by eq 12, where $(\Delta A_0)_0$ and $(\Delta A_0)_Q$ are the initial signal intensities in the absence and presence of Q (EtOAc, in this

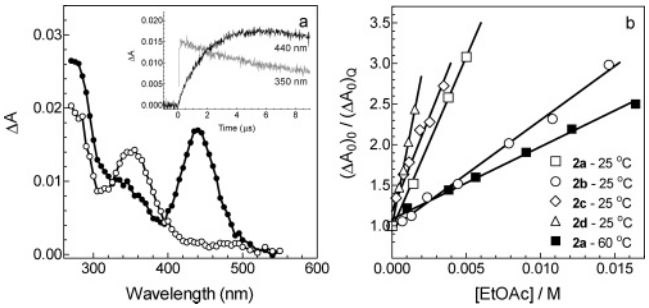
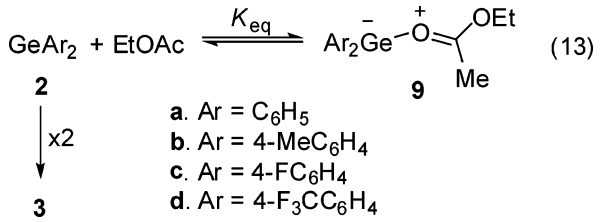


Figure 4. (a) Transient UV/vis absorption spectra recorded by flash photolysis of a deoxygenated 0.003 M solution of **1a** in hexane containing 0.03 M EtOAc at 25 °C, 100−160 ns (○) and 6.6−6.7 μs (●) after the laser pulse; the inset shows transient absorption profiles recorded at 350 and 440 nm. (b) Plots of $(\Delta A_0)_0/(\Delta A_0)_Q$ for quenching of the peak signal intensities due to **2a**−**d** by EtOAc in hexane at 25 °C and for **2a** at 60 °C. The solid lines are the least-squares fits of the data to eq 12.

case).[23] Similar behavior was observed for each of the germylene/digermene systems studied in this work, and plots of $(\Delta A_0)_0/(\Delta A_0)_Q$ versus [EtOAc] were in each case linear, as shown in Figure 4b. The species absorbing at 350 nm are assigned to the Lewis acid−base complexes of germylenes **2a**−**d** with the ester (**9a**−**d**; eq 13). The K_{eq} values determined in these experiments are collected with the other kinetic data in Table 1.

$$(\Delta A_0)_0/(\Delta A_0)_Q = 1 + K_{eq}[Q] \qquad (12)$$

Complexation of $GePh_2$ (**2a**) with EtOAc and THF was also studied at 60 °C, where the effects of added substrate on the germylene signal intensities were found to be similar in form but significantly less pronounced than at room temperature. The (corrected) germylene decay in the absence of added substrate was significantly faster at this temperature than at 25 °C, but followed clean second-order kinetics with a decay coefficient



(13)

of $k_{dim}/\epsilon_{500} = (2.2 \pm 0.3) \times 10^7$ cm s^{-1}. Addition of EtOAc resulted in reductions in initial germylene signal strength in an analogous manner to those observed at 25 °C, and a plot of $(\Delta A_0)_0/(\Delta A_0)_Q$ versus [EtOAc] according to eq 12 afforded a value of $K_{eq} = 89 \pm 7$ M^{-1} for complexation with EtOAc (see Figure 4b). Decays recorded in the presence of THF were bimodal and were analyzed as two single-exponential decays in order to estimate the decay rate constant of the fast initial component associated with the complexation reaction; the resulting plot of k_{decay} versus [THF] according to eq 7 afforded $k_Q = (9 \pm 2) \times 10^9$ M^{-1} s^{-1}. The ΔA_{res} values required for determination of K_{eq} were estimated as the ΔA values at the break-points in the bimodal decays, and the resulting plot of $\Delta A_0/\Delta A_{res}$ versus [THF] according to eq 8 afforded a value of $K_{eq} = 3100 \pm 200$ M^{-1} (see Supporting Information).

Discussion

The results demonstrate that polar substituents attached to the phenyl rings of $GePh_2$ have small but distinct effects on the rate and equilibrium constants for reaction of the species with nucleophilic substrates. The particular reactions studied here are all very fast, but they all appear to be accelerated by remote electron-withdrawing substituents attached to the phenyl rings. Distinct effects are also observed on the lowest energy UV/vis absorption maximum of the species, which is associated with the n,p electronic transition in the molecule.[1g,42] In contrast, the same substituents have little effect on the UV/vis spectra of the corresponding tetraaryldigermenes or on the course or efficiency of the photochemistry of the 1,1-diarylgermacyclopent-3-ene precursors. Again though, regular effects are observed on the reactivity of the digermenes, particularly in the case of reaction with HOAc, which is the intrinsically slower of the two reactions that have been studied.

The apparent blue shift in λ_{max} exhibited by the *para*-methyl-substituted diarylgermylene (**2b**) relative to that of the unsubstituted compound (**2a**) is too small to be considered really significant, but those for the *para*-CF_3 (**2d**; $\lambda_{max} = 490$ nm) and *para*-F (**2c**; $\lambda_{max} = 480$ nm) derivatives are well outside the limits of error in our measurements. One potential problem in pinpointing the absorption maxima of these compounds precisely is the possibility that the absorption bands are distorted due to small contributions from the corresponding digermenes, as their formation is quite rapid during the first 50−100 ns after the laser pulse, making it difficult to avoid bleed-through of the product transient absorptions in the earliest time window after the laser pulse that can be monitored in our experiments. This can be minimized by working at lower laser intensities in order to reduce the initial germylene concentration and slow the dimerization reaction or by recording spectra at even shorter time scales in the presence of an irreversible scavenger (such as HOAc) at concentrations high enough to eliminate digermene formation altogether. The spectrum of **2c** was re-recorded under both these sets of conditions, but showed no discernible change from that recorded with higher laser intensities and in the absence of germylene scavengers. Another potential explanation for the spectral shifts is complexation of the germylene with its precursor, which is present at a concentration of ca. 3 mM. This too can be ruled out for **2c**, since the spectrum recorded by 193 nm flash photolysis of a 30 μM solution of **1c** was identical to that obtained with the 248 nm laser at the ca. 100-fold higher precursor concentration. On the basis of the fact that the magnitude of the spectral shift correlates roughly with the *inductive* electron-withdrawing power of the aryl substituents (as characterized by the σ_I values for fluoro and trifluoromethyl[43]), we speculate that the effect may originate in an inductive effect on the energy of the nonbonding molecular orbital in $GePh_2$.

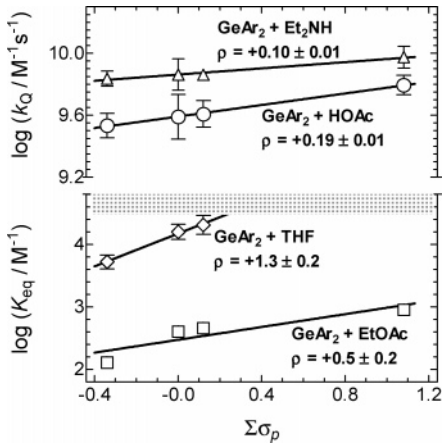


Figure 5. Hammett plots of the absolute rate and equilibrium constants for Lewis acid−base complexation of diarylgermylenes **2a**−**d** with Et_2NH (k_Q; Δ), THF (K_{eq}; ◇), and EtOAc (K_{eq}; □), and of the absolute rate constants for reaction of **2a**−**d** with AcOH (k_Q; ○) in hexane solution at 25 °C. The shaded area in the lower portion of the graph represents the indeterminable range in log K_{eq}, where K_{eq} is too large to be measured (i.e., $K_{eq} > 25\,000$ M^{-1}); the point for **2d** lies in this range.

The equilibrium constants for complexation of **2a**−**c** with EtOAc are ca. 50 times smaller than the corresponding ones for complexation with THF, matching the trends in the solution phase Brønsted and hydrogen-bond basicities of the two compounds.[44,45] The corresponding thermodynamic parameters can be estimated from the measured equilibrium constants at 25 and 60 °C, which yields values of $\Delta H° \approx -11 \pm 2$ kcal/mol and $\Delta S° \approx -24 \pm 5$ cal K^{-1} mol^{-1} for complexation with THF and $\Delta H° \approx -8.5 \pm 0.6$ kcal/mol and $\Delta S° \approx -23 \pm 2$ cal K^{-1} mol^{-1} for complexation with EtOAc, with the gas phase at 298 K and 1 bar as standard reference state. It is interesting to note that the Ph_2Ge−THF and Ph_2Ge−EtOAc complexes exhibit very similar UV/vis absorption maxima, in keeping with the similar thermodynamic stabilities of the two species.

Plots of the rate and equilibrium constants for the four reactions of **2a**−**d** studied in this work versus Hammett substituent constants[43] are collected together in Figure 5. Excellent correlations are observed for the reactions with HOAc and Et_2NH, affording Hammett ρ-values of $+0.19 \pm 0.01$ and $+0.10 \pm 0.01$, respectively, with the smaller value being obtained for the faster of the two reactions. The largest ρ-values are exhibited by the complexation equilibria with THF ($\rho =$

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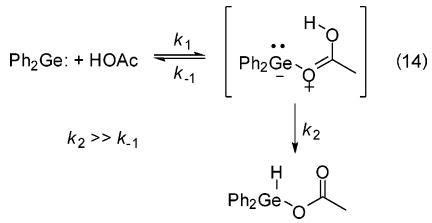
+1.3 ± 0.2; three data points) and EtOAc ($\rho = +0.51 \pm 0.18$; four data points). The substantial substituent effect on the equilibrium constants for complexation with THF contrasts sharply with the minimal variation in the forward rate constants for the process, which results from the fact that formation of the complex occurs at rates close to the diffusion limit. The same limitation applies to the rate constants for complexation with Et_2NH, which is also reversible but has equilibrium constants that are too large to be measured under the conditions of our experiments.[16] The germylene must clearly play the role of an electrophile in these complexation reactions, and thus the positive ρ-values that characterize them confirm the expectation that this aspect of germylene reactivity should be enhanced by the presence of electron-withdrawing substituents in the molecule.

The rate constants for reaction of **2a**−**d** with HOAc exhibit a sensitivity to substituents similar to the rate and equilibrium constants for Lewis acid−base complexation with the ether, amine, and ester, which is clearly consistent with a mechanism in which the carboxylic acid plays the role of nucleophile in the rate-determining step. A mechanism involving initial, rate-determining complexation of the germylene with the carboxylic acid, followed by rapid migration of the acidic proton to germanium to complete the reaction (eq 14), is consistent with the results. The lack of a significant isotope effect on the rate constants for reaction of **2b** and **2d** with HOAc and DOAc also supports this mechanism, though much less conclusively because the rates are so fast that little effect would be expected even if H-transfer were involved in the rate-controlling step of the reaction. Thus, even though it is relatively small, the observed substituent effect provides mechanistic information that cannot be readily obtained in other ways. If the rate constant for the second (proton migration) step is fast relative to reversion of the complex to free reactants (i.e., $k_2 >> k_{-1}$), then the overall rate constant for the reaction will be defined by the rate constant for complexation, i.e., $k_{HOAc} \approx k_1$. If we assume that the equilibrium constant for complexation of the germylene with EtOAc provides a reasonable model for that associated with the initial step in the reaction with HOAc, then an estimate of $k_{-1} \approx 1 \times 10^7$ s^{-1} is obtained for the rate constant for reversion of the complex to the free reactants. This in turn sets a lower limit of ca. 10^8 s^{-1} for k_2, the rate constant for (intramolecular) H-migration in the complex of $GePh_2$ with HOAc. This can be compared to our recent estimate of $k_2 \approx 10^4$ s^{-1} for the rate constant of the analogous process in the zwitterionic intermediate involved in the O−H insertion reaction of $GePh_2$ with methanol.[23] In the latter case, intramolecular proton transfer is sufficiently slow that the intermediate Lewis acid−base complex can be detected directly by laser flash photolysis methods. Complexation is the initial step in the reaction with both aliphatic alcohols and carboxylic acids and represents the rate-determining step for decay of the germylene in both cases. It is also the rate-determining step for *product formation* in the reaction with HOAc. In the case of alcohol insertions, where H-migration in the intermediate complex is slowed by both lower acidity and tighter geometric requirements in the transition state, the H-migration step represents the rate-determining step for formation of the final product.

The corollary to this conclusion is that the Lewis acid−base complexation of $GePh_2$ with HOAc and EtOAc both proceed very rapidly, with rate constants that are within a factor of ∼10 of the diffusional limit in hexane solution. The behavior exhibited by **2a**−**d** in the presence of EtOAc is in fact consistent with a forward rate constant of this magnitude.[23] Ideally,



(14)

reversible reactions are characterized in kinetic experiments of this type by the detection of both the approach to equilibrium (which provides a measure of the forward rate constant k_Q) and the residual quantity of limiting reactant that remains after the approach to equilibrium is complete (which provides a measure of the equilibrium constant K_{eq}, given the ability to measure the quantity of limiting reactant at the beginning of the approach to equilibrium as well). The fact that only the latter could be detected in our experiments means that k_Q must be on the order of 10^9 M^{-1} s^{-1} or greater, given the maximum time resolution of our instrument and the magnitude of K_{eq} that characterizes the reaction.[23] The behavior in the presence of EtOAc contrasts that observed with Et_2NH and other amines, which also react reversibly with $GePh_2$ in hexane solution; in these cases the equilibrium constants are relatively large (K_{eq} > ca. 2.5×10^4 M^{-1}), and thus only the forward rate constants for complexation can be measured.[16,21] The intermediate ("ideal") situation, where both k_Q and K_{eq} can be measured, is obtained for the reactions of **2a** and **2b** with THF, as the data of Figure 2 illustrate. The same behavior has been reported previously for the reactions of $GePh_2$ with methanol, *tert*-butanol, terminal alkenes, and isoprene.[16,23]

Hammett plots of the rate constants for quenching of digermenes **3a**−**d** by Et_2NH and HOAc are shown in Figure 6. As can be seen from the data, an excellent correlation is observed for the reaction with HOAc, for which the rate constants vary over the range $(4-36) \times 10^7$ M^{-1} s^{-1} throughout the series of compounds studied and lead to a ρ-value of +0.33 ± 0.01. The rate constants for quenching by the amine, which are within a factor of 10 of the diffusion-controlled rate in hexane at 25 °C, vary by a factor of only ca. 2 throughout the series of compounds and correlate relatively poorly with σ-values ($\rho = +0.11 \pm 0.07$). As found for the reactions of these substrates with **2a**−**d**, the results indicate that the effects of remote polar substituents are relatively small in both cases, but are consistent with mechanisms in which the substrate plays the role of nucleophile in the rate-determining step of the quenching process in both cases.

The rapid reactions of these substrates with the precursors to **3a**−**d** (i.e., germylenes **2a**−**d**) preclude the formation of digermene trapping products in tractable yields under the conditions of steady state photolysis experiments with **1a**−**d**. Nevertheless, the most likely course of the reactions with HOAc can be inferred from the identity of the product obtained from reaction of tetramesityldigermene (**3e**) with this substrate: the formal 1,2-addition product **6e** (*vide supra*). It is interesting to note that the latter reaction is on the order of 9 orders of magnitude slower than those of the less sterically hindered derivatives **3a**−**d**; a ballpark estimate of $k_{HOAc} \approx 10^{-1}$ M^{-1} s^{-1} can be derived from the time required for disappearance of the characteristic yellow color due to **3e** in the presence of ca. 0.01 M HOAc in THF at room temperature, which is consistent with the upper limit of ca. 10^2 M^{-1} s^{-1} that was estimated by flash photolysis in our previous kinetic study of **3e** in hexane solution.[16]

Rate constants for reaction of two of the substituted digermenes with acetic acid-*Od* have been determined and found

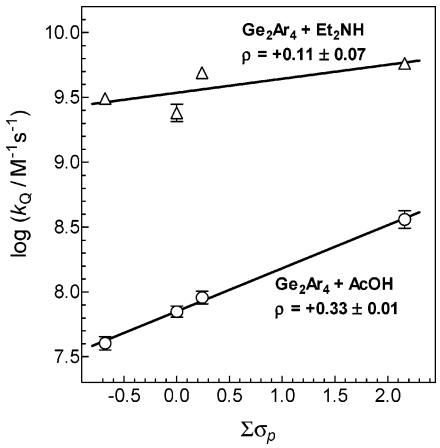
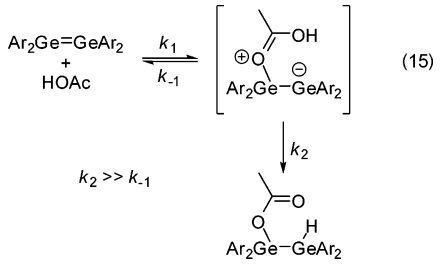


Figure 6. Hammett plots of the absolute rate constants for quenching of tetraaryldigermenes **3a**−**d** with Et_2NH (Δ) and HOAc (○) in hexane solution at 25 °C.

to be the same within experimental error as those for reaction with the protiated carboxylic acid in both cases. For rate constants on the order of 10^8 M^{-1} s^{-1}, the lack of a kinetic isotope effect is significant and rules out both a concerted mechanism and a stepwise one initiated by protonation; the latter is also ruled out by the positive Hammett ρ-value. A mechanism involving rate-determining nucleophilic addition to form the zwitterionic addition product, which proceeds to the final product by fast H-migration (eq 15), is consistent with all of the data. The mechanism of eq 15 is related to the one proposed by Baines and co-workers for the reaction of **3e** with aliphatic aldehydes.[46]



(15)

In view of the indication from our kinetic experiments of a very rapid quenching interaction between the transient tetraaryldigermenes (**3a**−**d**) and Et_2NH, we were somewhat surprised to find no evidence for reaction of either Et_2NH or *n*-butylamine with tetramesityldigermene (**3e**), even after 2 days in THF solution at 4 °C. We thus have no information on the likely identity of the product(s) formed upon quenching of **3a**−**d** by the amine. To our knowledge there are no known examples of the reaction, and the only potentially relevant example known in disilene chemistry is that of ammonia with a (sterically stabilized) 1,3-tetrasilabutadiene derivative.[47] The small positive ρ-value suggests that the first (and possibly only) step in the reaction involves the amine acting as a nucleophile, perhaps to form a zwitterionic species analogous to the proposed intermediate for HOAc addition (see eq 15). It remains unclear whether the primary product of the reaction with **3a**−**d** proceeds further to form the 1,2-addition product that might be expected or simply moderates oligomerization of the digermene as a result of it being formed reversibly. In this regard, it should be noted that **3a** is quenched by the tertiary amine Et_3N at least 100 times more slowly than by Et_2NH,[21] and no new transient absorptions that might be assigned to such a species are evident in flash photolysis experiments with **1a**−**d** in the presence of the secondary amine. The failure of **3e** to react with either diethyl- or *n*-butylamine, coupled with the observation of near diffusion-controlled quenching of **3a**−**d** by the secondary amine, indicates that the influence of steric effects on this reaction is much greater than is the case with HOAc addition. Further study of the reaction will clearly be necessary in order to understand these results more completely.

Summary and Conclusions

The effects of polar ring substituents on the rate constant for the O−H insertion reaction of diphenylgermylene ($GePh_2$, **2a**) with acetic acid (HOAc) in hexane solution have been determined and compared to those on the rate and(or) equilibrium constants for Lewis acid−base complexation of the germylene with THF, EtOAc, and Et_2NH under similar conditions. Each of these reactions proceed at rates within a factor of ∼5 of the diffusion limit in hexane at 25 °C, and thus the rate constants are relatively insensitive to remote substitution with polar substituents on the phenyl rings. Nevertheless, small but discrete effects are observed, and the rate constants for reaction of the four germylenes with HOAc and Et_2NH correlate with Hammett substituent constants, affording ρ-values of $+0.19 \pm 0.01$ and $+0.10 \pm 0.01$, respectively. The equilibrium constants for complexation with THF and EtOAc in hexane are affected much more strongly by aryl substituents, with the data affording equilibrium ρ-values of $+1.3 \pm 0.2$ and $+0.5 \pm 0.2$, respectively. The positive ρ-values are consistent with mechanisms in which the germylene plays the role of electrophile in the kinetically significant step in every case. On the basis of these results, a mechanism for HOAc insertion involving initial, rate-determining Lewis acid−base complexation of the germylene at the carbonyl oxygen followed by fast proton transfer is proposed.

Both HOAc and Et_2NH also quench the lifetimes of the corresponding tetraaryldigermenes (**3a**−**d**), which are formed by dimerization of the diarylgermylenes and can be monitored directly at low substrate concentrations. Quenching by HOAc most likely proceeds via 1,2-addition, based on the identity of the product formed from reaction of the carboxylic acid with tetramesityldigermene (**3e**). The second-order rate constants for quenching of **3a**−**d** by HOAc again correlate with Hammett substituent constants, leading to a reaction constant of $\rho = +0.33 \pm 0.07$. This and the lack of a significant kinetic isotope effect on the reaction are consistent with a mechanism involving nucleophilic attack of the substrate at the Ge═Ge bond in the initial (rate-determining) step, to form a zwitterionic intermediate that proceeds to the overall 1,2-addition product by fast proton transfer from oxygen to germanium. The reaction is exquisitely sensitive to steric effects, as shown by the ca. 10^9-fold lower rate constant for reaction of HOAc with tetramesityldigermene (**3e**) compared to that measured for the parent tetraaryldigermene (Ge_2Ph_4; **3a**). An even greater steric effect is evident in the reaction of tetraaryldigermenes with primary and secondary amines, which proceeds at close to the diffusion-controlled rate in the case of **3a** but to no detectable extent whatsoever in the case of the tetramesityl derivative.

Mechanistic studies of several other characteristic reactions of transient diarylgermylenes in solution are in progress.

Experimental Section

Tetrahydrofuran (Caledon) and hexanes were dried by passage through activated alumina under nitrogen using a Solv-Tek solvent

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purification system. Glacial acetic acid (Caledon) and acetic acid-*d* (Aldrich) were used as received from the suppliers. *N*,*N*-Diethylamine (Aldrich) was refluxed over KOH and distilled. Ethyl acetate (Caledon) was dried by passage through activated silica gel. 3,4-Dimethyl-1,1-diphenylgermacyclopent-3-ene (**1a**)[16] and hexamesitylcyclotrigermane (**4**)[48] were prepared as previously described. Details of the synthesis of the other compounds reported in this work are described in the Supporting Information.

Laser flash photolysis experiments employed the pulses from a Lambda Physik Compex 120 excimer laser filled with F_2/Kr/Ne (248 nm; ~25 ns; 100 ± 5 mJ) mixtures, and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.[16] Solutions were prepared at concentrations such that the absorbance at the excitation wavelength was between ca. 0.7 and 0.9 and were pumped continuously through a vacuum oven-dried, thermostated 7 × 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir, fitted with a glass frit to allow bubbling of argon gas through the solution for at least 30 min prior to and then throughout the duration of each experiment, using a Masterflex 77390 peristaltic pump fitted with Teflon tubing (Cole-Parmer Instrument Co.). The glassware, sample cell, and transfer lines were dried in a vacuum oven at 65−85 °C before use. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple inserted into the thermostated sample compartment in close proximity to the sample cell. Reagents were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Transient decay and growth rate constants were calculated by nonlinear least-squares analysis of the absorbance−time profiles using the Prism 3.0 software package (GraphPad Software, Inc.) and the appropriate user-defined fitting equations, after importing the raw data from the Luzchem mLFP software. 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 deviation obtained from the least-squares analyses.

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Supporting Information Available: Details of the preparation and characterization of compounds, representative transient decay and growth/decay profiles, time-resolved UV/vis absorption spectra, and details of kinetic analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0609362

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