

First Detection of Methylgermylene in the Gas Phase and Time-Resolved Study of Some of Its Reactions

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Summary: A new transient species has been produced and detected by the gas-phase, 193 nm laser flash photolysis of 1,3,4-trimethylgermacyclopent-3-ene, TMGCP. The species has strong visible absorptions in the wavelength region 450–520 nm (maximum at 485 nm) and is attributed to the germylene, MeGeH. Time-resolved kinetic studies have led to the first rate constants for its reactions with GeH₄, Me₂GeH₂, C₂H₂, C₂H₄, C₃H₆, *i*-C₄H₈, TMGCP, MeOH, HCl, and SO₂. The reactivity of MeGeH is compared to those of GeH₂ and GeMe₂. The Me-for-H substituent effect varies according to reaction type and is not constant from GeH₂ to MeGeH to GeMe₂.

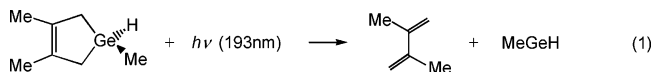
Introduction

There has been considerable and growing interest in the so-called heavy carbenes, reactive intermediates of formula MX₂, where M = Si, Ge, and Sn and X is a substituent such as H, halogen, or an alkyl or aryl group. This arises in large part because of their involvement in the thermal and photochemical breakdown mechanisms of the group 14 organometallic compounds MX₄. In recent years our knowledge of the behavior of such species has been greatly increased by direct time-resolved kinetic studies of their reactions both in the gas phase^{1–5} and in solution.^{6–10}

Both SiH₂ and GeH₂, studied in the gas phase by two of our groups,^{2–5} are found to be very reactive, with rate constants close to the collision limit with many species. By contrast,

SiMe₂³ and GeMe₂^{4,10} are considerably less reactive than the parent molecules. For example, GeMe₂ is ca. 10³ times less reactive than GeH₂ toward Ge–H insertion into Me₂GeH₂.¹¹ This shows that the replacement of H by Me can have dramatic effects on germylene reactivity. Similar but smaller effects are found in a comparison of the reactivities of SiH₂ and SiMe₂.³ To investigate these substituent effects further, we decided to explore the kinetic behavior of methylgermylene, MeGeH, a heavy carbene for which no kinetic data have yet been reported. The replacement of only one H by Me (in GeH₂) offers the benefit that rates should be less drastically reduced (thus making measurements easier) and also permits us to probe the issue of whether substituent effects on germylene reactivity are additive. There is already considerable evidence that this is not the case with silylenes,^{3,12,13} and MeSiH exhibits reactivity much closer to that of SiH₂ than to SiMe₂ in Si–H insertion reactions. The question has not yet been addressed for germylenes.

In this paper, we report the direct detection of MeGeH in the gas phase by laser flash photolysis methods, and a study of its reactivity toward Ge–H insertion (GeH₄, Me₂GeH₂), acetylene (C₂H₂), alkenes (C₂H₄, C₃H₆, *i*-C₄H₈), MeOH, HCl, and SO₂. The germylene has been generated by 193 nm photolysis of the germacyclopent-3-ene derivative TMGCP (eq 1), which was chosen because of the well-established utility of compounds of this general type for study of reactive germylenes in the gas phase^{14,15} and in solution.^{7,8,10}



Experimental Section

The intermediate of interest was generated by laser flash photolysis of 1,3,4-trimethylgermacyclopent-3-ene, TMGCP. The apparatus and equipment for these studies have been described previously;^{5,14,15} additional details relevant to the present work are

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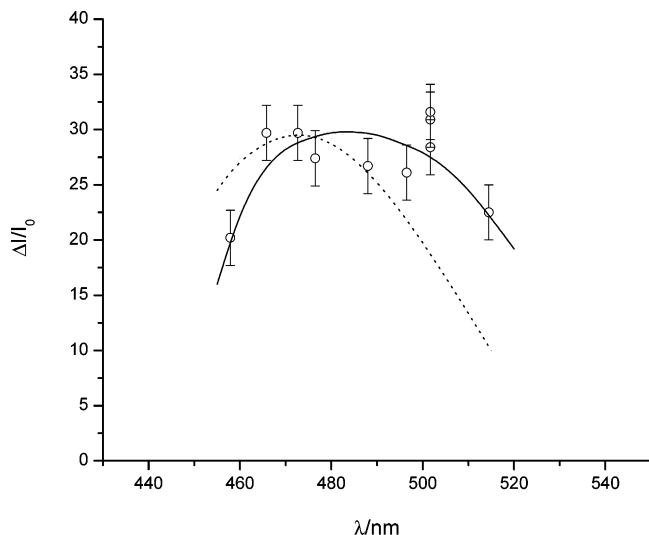


Figure 1. Zero time absorption spectrum of transient obtained from 193 nm laser flash photolysis of TMGCP. The solid line is the surmised spectral fit (see text). The dashed line is the gas-phase spectrum of GeMe₂ from ref 14.

given in the Supporting Information. The transient monitoring procedure, which is also standard, is given in the Supporting Information as well. The data analysis provides values for the first-order rate coefficients, k_{obs} , for removal of the transient species in the presence of excess reactive substrate gas. The dependence of k_{obs} on substrate partial pressure then defines the absolute rate constant for reaction, under the particular conditions of temperature and total pressure employed.

TMGCP was prepared in >95% purity (by GC analysis) by monochlorination of 3,4-dimethyl-1-germacyclopent-3-ene followed by methylation of the resulting chlorogermane with methylmagnesium bromide. Details of the synthesis and characterization of the compound are given in the Supporting Information.

Results

General Considerations. TMGCP was found to possess a strong UV absorption at wavelengths below 210 nm ($\lambda_{\text{max}} < 190$ nm). Preliminary (193 nm) gas-phase photolysis experiments with GC analysis of the photolyzates established the formation of 2,3-dimethylbutadiene (DMB) as the only volatile hydrocarbon product.

Flash photolysis of mixtures consisting of ca. 40 mTorr TMGCP, diluted in 5–10 Torr SF₆ to ensure rapid thermalization of the system after each laser pulse, afforded reasonably strong transient signals over the available monitoring wavelength range of 458–514 nm. The signals decayed with good first-order kinetics under these conditions. Transient formation in most experiments was accompanied by the formation of solid particulate (“dust”), although this occurred sufficiently slowly relative to the decay of the transient signal that it caused no discernible deviation from clean pseudo-first-order decay kinetics. For averaging purposes, it was necessary to wait several minutes between shots to allow the dust to settle.

Identity of the Transient. The transient absorption spectrum was obtained by monitoring the zero time absorbance (obtained by computer fitting of exponential decay curves) at eight of the nine available wavelengths of the argon ion probe laser. In these experiments 40 mTorr of precursor was photolyzed in the presence of SF₆ at a total pressure of 5 Torr and a photolysis laser energy of 60 ± 5 mJ/pulse. Figure 1 shows the resulting spectrum. The highest transient absorbance value was obtained

at 501.7 nm, and the results suggest a possible second peak at ca. 470 nm; however, the signal variation over the range 465 to 505 nm was very slight, and so the data are reasonably represented by a broad featureless absorption centered at ca. 485 nm, within the experimental scatter. For comparison, the gas-phase visible absorption spectrum of GeMe₂ ($\lambda_{\text{max}} = 470$ nm),¹⁵ scaled to the same maximum absorbance, is also shown in Figure 1. The comparison suggests a very slight red shift of the spectrum of MeGeH relative to that of GeMe₂. This is the expected result, considering that the corresponding maximum in the gas-phase laser-induced fluorescence excitation spectrum of GeH₂ occurs at $\lambda_{\text{max}} \approx 514$ nm.¹⁶

The same trend in the UV/vis spectral maxima of GeH₂, MeGeH, and GeMe₂ is predicted by time-dependent DFT calculations, which have been carried out at the PW91/TZ2P level of theory using the statistical average of orbital potentials (SAOP) exchange–correlation function and zero-order relativistic corrections, as employed previously for calculation of the spectra of GeH₂ and GeMe₂.⁷ The calculations predict $\lambda_{\text{max}} = 486$ nm for MeGeH, which can be compared to the corresponding calculated absorption maxima of $\lambda_{\text{max}} = 493$ nm and $\lambda_{\text{max}} = 463$ nm for GeH₂ and GeMe₂, respectively.⁷

Further support for the identity of the transient was obtained by the finding of a Ge–H insertion product (see below).

Kinetic Studies. Preliminary experiments showed that the values of the decay constants, k_{obs} , were independent of both the excitation pulse energy and the number of photolysis shots employed for signal averaging. They were, on the other hand, dependent on the partial pressure of TMGCP, indicative of reaction of MeGeH with the precursor. A plot of k_{obs} versus precursor partial pressure was linear, affording a rate constant of $k = (3.1 \pm 0.2) \times 10^{10}$ dm³ mol⁻¹ s⁻¹ for reaction of MeGeH with TMGCP at a total pressure of 10 Torr. The magnitude of the rate constant suggests that the main mode of reaction is with the C=C bond, rather than the Ge–H bond in the molecule (vide infra).

The substrates were chosen to explore the various known reaction types open to germynes and to allow comparisons to previously reported data for GeH₂ and GeMe₂. For each substrate a set of runs was carried out with varying substrate pressures but a fixed pressure of precursor, made up to a total pressure of 10 Torr with SF₆. Selected runs were made at different monitoring wavelengths in order to confirm that the measured decay constants did not vary with wavelength, although the bulk of the data was obtained at either 501.7 or 514.5 nm. The substrate pressures were varied over suitable ranges to explore the systematic dependences of k_{obs} upon them; representative plots of k_{obs} versus substrate partial pressure are shown in Figure 2 for the decay of MeGeH in the presence of C₂H₂, MeOH, and Me₂GeH₂. All the plots show reasonable linearity within the experimental scatter ($\pm 10\%$), indicating a first-order dependence of k_{obs} on substrate and hence overall second-order reaction kinetics. Runs were carried out at three different total pressures for C₂H₂ as substrate; the results of these experiments are shown in Figure 3. The second-order rate constants determined from these experiments are collected in Table 1. The errors are reported as single standard deviations from linear least-squares analysis of the data.

End Product Search. GC analysis was attempted on the reaction products of the transient with hydrocarbon and germane substrates. The most obvious product peak, found in all analyses, was that of DMB, the coproduct of precursor photolysis. In the MeGeH + alkene/C₂H₂ studies, no new product peaks were

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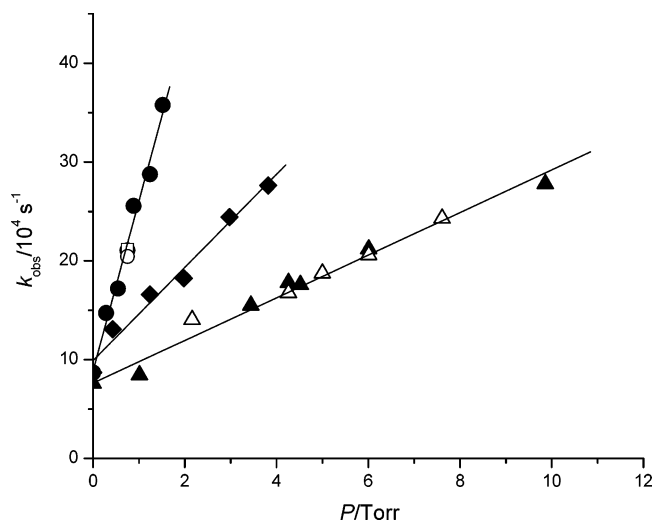


Figure 2. Second-order plots for the reaction of MeGeH with three reactive substrates using a variety of monitoring wavelengths (nm⁻¹): (a) C₂H₂, ●, 501.7; □, 476.5; ○, 465.8; (b) MeOH, ◆, 501.7; (c) Me₂GeH₂, ▲, 514.5; △, 501.7.

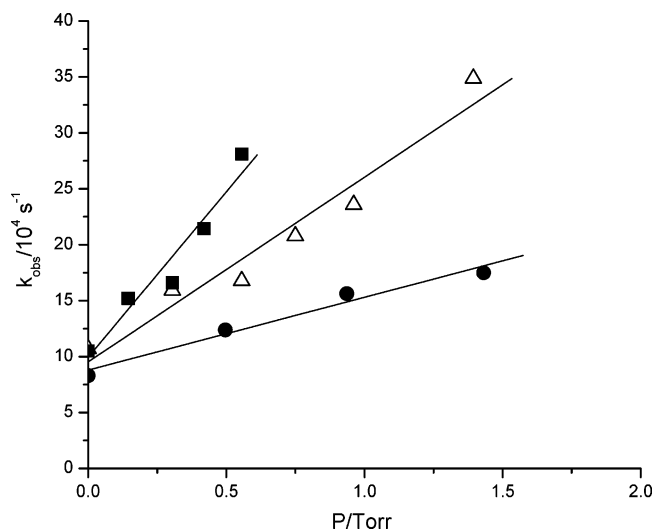
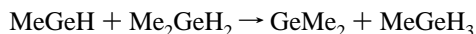


Figure 3. Second-order plots for the reaction of MeGeH with C₂H₄ using the 501.7 nm monitoring wavelength at three different pressures/Torr (SF₆): ■, 30; △, 10; ●, 3.

detected. However we note that the probable germirane/germirene products are not likely to be stable enough to survive GC analysis.^{14,15}

A product peak was observed upon photolysis of TMGCP in Me₂GeH₂. This was characterized as that of MeGeH₂GeHMe₂, the anticipated Ge–H insertion product. A sample of the latter compound was prepared by Hg-photosensitized decomposition of a mixture of MeGeH₃ and Me₂GeH₂ (see Supporting Information). Additionally the possible formation of MeGeH₃ from reaction of MeGeH with Me₂GeH₂ was specifically ruled out by absence of a GC peak at the known retention time. This was important because it eliminates the possibility of the reaction



which might have occurred via the intermediacy of MeGeH₂-GeHMe₂* (vibrationally hot 1,2,2-trimethyldigermene, unstabilized by collision). This in turn rules out the possibility of additional complexities in the kinetic experiments with this substrate from accompanying formation of GeMe₂, which absorbs in the same spectral range as MeGeH (see Figure 1).

Table 1. Second-Order Rate Constants for MeGeH with Various Substrates at 298 (±2) K^a

substrate	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
GeH ₄	$(3.87 \pm 0.72) \times 10^8$
Me ₂ GeH ₂	$(4.02 \pm 0.19) \times 10^8$
C ₂ H ₂	$(3.21 \pm 0.12) \times 10^9$
C ₂ H ₄	$(1.23 \pm 0.12) \times 10^9$ (3 Torr SF ₆)
	$(2.96 \pm 0.28) \times 10^9$ (10 Torr SF ₆)
	$(5.50 \pm 0.58) \times 10^9$ (30 Torr SF ₆)
C ₃ H ₆	$(3.93 \pm 0.14) \times 10^9$
i-C ₄ H ₈	$(8.79 \pm 0.66) \times 10^9$
TMGCP	$(3.14 \pm 0.23) \times 10^{10}$
MeOH	$(9.15 \pm 0.48) \times 10^8$
HCl	$(3.94 \pm 0.37) \times 10^8$
SO ₂	$(2.48 \pm 0.14) \times 10^{10}$

^a At a total pressure of 10 Torr (SF₆) unless otherwise specified.

Table 2. Comparison of Gas-Phase Ge–H Insertion Rate Constants^{a,b} for Three Germylenes at Ambient Temperature

substrate	germylene		
	GeH ₂	MeGeH	GeMe ₂
GeH ₄	$3.3 \times 10^{10} \text{ c}$	$3.9 \times 10^8 \text{ e}$	
Me ₂ GeH ₂	$1.4 \times 10^{11} \text{ d}$	$4.0 \times 10^8 \text{ e}$	$1.4 \times 10^8 \text{ d}$

^a Units: dm³ mol⁻¹ s⁻¹. ^b At a total pressure of 10 Torr (SF₆) unless otherwise specified. ^c k_{∞} , ref 18. ^d Ref 11. ^e This work.

Discussion

The measurements reported here represent the first direct observation of MeGeH and the first experimental determination of gas-phase rate constants for some of its reactions, and follow similar studies of the gas-phase kinetics of GeH₂¹⁴ and GeMe₂.¹⁵ The results show that MeGeH inserts into Ge–H bonds, adds to the π-bonds of alkenes and alkynes, and reacts with lone-pair donor species in accordance with the general pattern of behaviour of other simple germylenes.^{4,8,10} We did not study the possible reaction of MeGeH with an alkane since earlier experiments have already shown that neither GeH₂¹⁴ nor GeMe₂¹⁵ exhibits detectable reactivity toward saturated hydrocarbons in the gas phase. It is worth noting that despite the difficulties of identifying reaction products because most of them are too labile to survive GC analysis, in the case of MeGeH + Me₂GeH₂, the product MeGeH₂GeHMe₂ has been identified, thus providing analytical evidence for our identification of the transient as MeGeH.

Insertion Reactions. The absolute rate constants for insertion of MeGeH into the Ge–H bonds of GeH₄ and Me₂GeH₂ are compared to the previously published data for reaction of GeH₂ and GeMe₂ with the same substrates in Table 2. Although the overall pressure dependence of these rate constants was not investigated here, studies of analogous reactions of MeSiH¹² and GeH₂¹¹ suggest no pressure dependences should be expected. It is clear that MeGeH is between 2 and 3 orders of magnitude less reactive toward these substrates than GeH₂ and a factor of ca. 3 times more reactive than GeMe₂ toward Me₂-GeH₂. While recent experiments suggest that this rate constant for GeMe₂ may have been overestimated,¹⁷ its general order of magnitude is nevertheless supported by a recent solution-phase value of $5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the rate constant for reaction of GeMe₂ with Et₃GeH.¹⁰ On a per Ge–H bond basis, MeGeH is a factor of ca. 2 more reactive toward Me₂GeH₂ than GeH₄, which can be compared to the corresponding difference of a factor of ca. 10 in the case of GeH₂.^{4,11,18} Of further interest

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Table 3. Comparison of Gas-Phase Addition Rate Constants^{a,b} for Three Germylenes at Ambient Temperature

substrate	germylene		
	GeH ₂	MeGeH	GeMe ₂
C ₂ H ₄ (3 Torr)	1.0 × 10 ^{10d}	1.2 × 10 ^{9h}	5.4 × 10 ⁸ⁱ
C ₂ H ₄ (10 Torr)	2.4 × 10 ^{10d}	3.0 × 10 ^{9h}	1.0 × 10 ⁹ⁱ
C ₂ H ₄ (30 Torr)	3.9 × 10 ^{10d}	5.5 × 10 ^{9h}	2.4 × 10 ⁹ⁱ
C ₃ H ₆	5.4 × 10 ^{10e}	3.9 × 10 ^{9h}	
i-C ₄ H ₈	7.2 × 10 ^{10f}	8.8 × 10 ^{9h}	
alkene ^c	1.3 × 10 ^{11d}	3.1 × 10 ^{10h}	5.9 × 10 ⁹ⁱ
C ₂ H ₂	7.8 × 10 ^{10g}	3.2 × 10 ^{9h}	7.8 × 10 ⁹ⁱ

^a Units: dm³ mol⁻¹ s⁻¹. ^b At a total pressure of 10 Torr (SF₆) unless otherwise specified. ^c C₂H₄, *k*_∞ (GeH₂), TMGCP (MeGeH), 3,3-dimethylbutene-1 (GeMe₂). ^d Ref 20. ^e Ref 21. ^f Ref 14. ^g Ref 23. ^h This work. ⁱ Ref 15.

here is the contrast with the corresponding silylenes; MeSiH is much closer in reactivity to SiH₂ than to SiMe₂ in the analogous Si–H insertion reactions.¹² The reactivity ratios of SiH₂:MeSiH:SiMe₂ are 1.0:0.20:0.00050 for reaction with SiH₄, and 1.0:0.51:0.017 for reaction with Me₂SiH₂.¹²

The evidence, both kinetic and theoretical, indicates that these insertion reactions all occur via a mechanism involving intermediate complexes of the type [R₂M–H–M(H)R₂].^{3,4} The crucial factor, determining the magnitude of the overall rate constant in each case, is the ratio of the (unimolecular) rate constants for forward reaction and reverse (i.e., back) dissociation of the complex. This in turn is dependent on the relative sizes of the secondary barrier to reaction and the depth of the energy well holding the complex together. It is already known from quantum chemical calculations that there are significant differences between the reactive complexes of GeH₂ and SiH₂ (with GeH₄ and SiH₄, respectively),¹⁸ and calculations are underway to compare the behavior of GeH₂ and GeMe₂ insertion complexes involved in the reactions with Ge–H bonds.¹⁹ Nevertheless, on the basis of the present results it would appear that single Me-for-H substitution affects the reactivity of germylene much more than silylene in σ-bond insertion reactions.

Addition Reactions. Table 3 lists the absolute rate constants determined in the present work for addition of MeGeH to alkenes and alkynes, along with previously published data for reaction of GeH₂ and GeMe₂ with the same substrates. Comparisons here are more difficult because these reactions are in most cases pressure dependent, particularly for the smaller substrate molecules. This can be seen quite clearly in the data for addition to C₂H₄, where all three germynes show strong pressure dependences. These pressure dependences arise from the instability of the product germiranes. In the cases of GeH₂ + C₂H₄ and GeH₂ + C₃H₆, these have been modeled using RRKM theory,^{20,21} while in solution-phase studies of GeMe₂, evidence for reversibility in the addition to 4,4-dimethyl-1-pentene comes from the observation of bimodal decays at low alkene concentrations, coupled with anomalously low reaction efficiencies compared to dimerization.¹⁰ Similar (but even more distinctive) signs of reversibility have also been observed in the solution-phase reaction of GePh₂ with the same alkene.⁸

Under all pressure conditions that have been studied, the order of germylene reactivity toward ethylene is GeH₂ > MeGeH > GeMe₂. Once again it appears that MeGeH is closer in reactivity

Table 4. Comparison of Gas-Phase Rate Constants^{a,b} for Reaction of Three Germylenes with Lone-Pair Donor Molecules at Ambient Temperature

substrate	germylene		
	GeH ₂	MeGeH	GeMe ₂
MeOH	6.6 × 10 ^{8c}	9.0 × 10 ^{8e}	
HCl	1.7 × 10 ^{9d}	3.9 × 10 ^{8e}	
SO ₂	3.9 × 10 ^{10d}	2.5 × 10 ^{10e}	2.6 × 10 ^{10f}

^a Units: dm³ mol⁻¹ s⁻¹. ^b At a total pressure of 10 Torr (SF₆). ^c Ref 24. ^d Ref 25. ^e This work. ^f Ref 17.

to GeMe₂ than to GeH₂, although the Me-for-H substitution effects are less marked than for the Ge–H insertion reaction. While the data are less extensive, the same pattern is seen for the larger alkenes; MeGeH additions to propene and isobutene are roughly an order of magnitude slower than GeH₂ additions at 10 Torr total pressure. Some idea of the true (i.e., high-pressure limiting) bimolecular rate constants for addition of the three germynes to alkenes can be obtained either by extrapolation of pressure-dependent values (e.g., GeH₂ + C₂H₄) or from the data for addition to larger alkenes (e.g., MeGeH + TMGCP and GeMe₂ + 3,3-dimethyl-1-butene), where pressure dependences should be insignificant.²² This assumes that the effects of alkene substituents are small, as has generally been found in the analogous silylene addition reactions.³ Comparison of the rate constants in the context of these assumptions (Table 3) indicates that Me-for-H substitution results in successive reductions of 4–5 in reactivity. In this case the reactivity of MeGeH is close to the geometric mean of those of GeH₂ and GeMe₂. It should be noted that the gas-phase GeMe₂ + alkene rate constants agree quite well with the value of 8.9 × 10⁹ dm³ mol⁻¹ s⁻¹ obtained in one of our labs for GeMe₂ + 4,4-dimethyl-1-pentene in solution.¹⁰

In the reactions with C₂H₂, both MeGeH and GeMe₂ are again slower than GeH₂, but MeGeH is actually less reactive than GeMe₂. Whether or not this reactivity order reflects that in the true bimolecular addition rate constants will have to await pressure dependence studies and extrapolation to the high-pressure limits. It is known that the reaction of GeH₂ with C₂H₂ is pressure independent,²³ which results because the initially formed germirene is capable of fast secondary decomposition to Ge + C₂H₄ via a complex set of intermediates.²³ This may, however, be a special case, and it cannot be assumed that 1-methylgermirene and 2,2-dimethylgermirene, the putative primary products of reaction of C₂H₂ with MeGeH and GeMe₂, respectively, will necessarily behave similarly.

Reactions with Lone-Pair Donor Molecules. Three lone-pair donor substrates, viz., MeOH, HCl, and SO₂, were chosen to provide a variety of reaction types and the possibility of further comparisons. The rate constants for their reactions with the three germynes are shown in Table 4. Comparisons are again complicated by pressure dependences. The reaction of GeH₂ with MeOH is known to be pressure dependent,²⁴ which arises because of the difficulty of stabilizing the weakly bound Lewis acid–base adduct, H₂Ge←O(H)Me, which is the effective end product of the gas-phase reaction. The reaction of MeGeH with MeOH is almost certainly also pressure dependent, but whether the extent of falloff from the high-pressure limit is

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greater or less than for the GeH₂ case will have to await further studies. Thus, although Me-for-H substitution produces a rate constant increase for this reaction at 10 Torr (SF₆), the difference may not persist in the high-pressure limit.

The reaction GeH₂ + HCl,²⁵ like SiH₂ + HCl,²⁶ is not pressure dependent, so it seems unlikely that MeGeH + HCl should be. The Me-for-H rate constant reduction of 4.3 found here for this reaction is therefore probably close to the true value. It is likely that this rate reduction comes about through weaker stabilization of the initially formed Lewis acid–base complex, thus making redissociation of the Me(H)Ge←ClH complex more favorable relative to further reaction.

The products of the reaction of germylenes with SO₂ are unknown, but all three germylenes for which we have data indicate a fairly fast reaction, with negligible Me-for-H substituent effect. This suggests that although the initial step in the reaction probably involves the formation of a complex, this intermediate proceeds rapidly to products without having a significant effect on the rate. The measured rate constants are therefore probably close to the true bimolecular values. They are very close in magnitude to the maximum rate constant value found for other germylene reactions,²⁷ which suggests an upper

limiting collisional efficiency of ca. 1 in 6 for germylene reactions in general.⁴

Further gas-phase studies of these reactions over more extended pressure and temperature ranges are planned. Preliminary studies of MeGeH in hexane solution have revealed unexpected complexities, which are currently under investigation.

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Supporting Information Available: Details of the synthesis and characterization of TMGCP, the laser flash photolysis method, characterization of MeGeH₂GeHMe₂, and the TD-DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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