

Kinetic and mechanistic studies of the reactions of diarylgermylenes and tetraaryldigermenes with carbon tetrachloride

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Abstract: The mechanisms of the reactions of diphenylgermylene (GePh_2) with CCl_4 in hydrocarbon solvents and in THF solution have been studied, employing 3,4-dimethyl-1,1-diphenylgermacyclopent-3-ene (**6a**) and 1,1-diphenylgermacyclobutane (**17**) as photochemical precursors to GePh_2 . In hydrocarbon solvents, the reaction produces Ph_2GeCl_2 (**10**) and $\text{Ph}_2\text{Ge}(\text{Cl})\text{CCl}_3$ (**12**) in a ratio of $\mathbf{10:12} \approx 7$, along with a variety of other radical-derived products and small amounts of $\text{Ph}_2\text{GeH}(\text{D})\text{Cl}$ (**11**), which is formed partly by reaction of GePh_2 with adventitious HCl. The reaction is much cleaner in THF, where **12** is formed as the major product ($\mathbf{10:12} \approx 0.8$); a similar product distribution is obtained in hexanes containing 0.05 mol/L THF, while **12** is the exclusive product in hexanes containing 3 mmol/L NEt_3 . Rate constants for the reactions of CCl_4 with GePh_2 and five ring-substituted derivatives were determined by laser flash photolysis, as well as Arrhenius parameters for reaction of the parent (GePh_2), in the two solvents. The reactions of GePh_2 with CCl_4 and CHCl_3 have also been studied in 3-methylpentane solution at 78–90 K. Different reaction mechanisms are clearly operative in hydrocarbon and complexing solvents, but both involve modest charge donation from germanium to the substrate in the transition state for the rate-determining step. For the reaction in hydrocarbon solvents, the data are consistent with inner-sphere electron transfer following or in concert with weak Lewis acid–base complexation. A similar mechanism is proposed for the reaction in THF solution, in competition with a second involving nucleophilic attack of the germylene–THF complex at a chlorine atom of the substrate. Rate constants were also determined for reaction of CCl_4 with the corresponding tetraaryldigermenes at low halocarbon concentrations in hexanes, along with Arrhenius parameters for the parent (Ge_2Ph_4). These reactions also proceed via initial Cl-atom abstraction, based on the identity of the products formed in the reaction of CCl_4 with tetramesityldigermene.

Key words: germylene, halocarbon, free radical, kinetics, abstraction, electron transfer.

Résumé : On a étudié les mécanismes des réactions du diphenylgermylène (GePh_2) avec le CCl_4 , dans des solvants hydrocarbonés, en utilisant les 3,4-diméthyl-1,1-diphenylgermacyclopent-3-ène (**6a**) et 1,1-diphenylgermacyclobutane (**17**) comme précurseurs photochimiques du GePh_2 . Dans les solvants hydrocarbonés, la réaction conduit à la formation de Ph_2GeCl_2 (**10**) et de $\text{Ph}_2\text{Ge}(\text{Cl})\text{CCl}_3$ (**12**) dans un rapport $\mathbf{10:12}$ approximativement égal à 7, aux côtés d'une variété d'autres produits dérivés de radicaux et de faibles quantités de $\text{Ph}_2\text{GeH}(\text{D})\text{Cl}$ (**11**) dont la formation résulte en partie d'une réaction adventive avec du HCl. La réaction dans le THF est beaucoup plus propre et elle la formation du produit **12** est majoritaire ($\mathbf{10:12} = 0,8$); on obtient une distribution de produit semblable dans les hexanes contenant 0,05 mol/L de THF alors que le produit **12** est le produit exclusif dans les hexanes content 3 mmol/L de NEt_3 . Les constantes de vitesse des réactions du CCl_4 avec le GePh_2 et les dérivés de cycles à cinq chaînons substitués ont été déterminées par photolyse éclair au laser et on a aussi déterminé les paramètres d'Arrhenius de la réaction du germylène parent, GePh_2 , dans les deux solvants. On a aussi étudié les réactions du GePh_2 avec le CCl_4 et le CHCl_3 , en solution dans le 3-méthylpentane et à des températures allant de 78 à 90 K. Il est clair que divers mécanismes de réaction interviennent dans l'hydrocarbure et les solvants complexants, mais les deux comportent une étape cinétiquement déterminante de l'état de un état de transition qui implique un modeste transfert de charge du germanium vers le substrat. Les paramètres d'Arrhenius pour la réaction du germylène libre dans les hexanes indiquent que l'état de transition est bien structuré mais faiblement lié; les données sont en accord avec un transfert d'électron dans la sphère interne à la suite de, ou de concert avec, une faible complexation acide–base de Lewis. On propose un mécanisme similaire pour la réaction en solution dans le THF; il serait en compétition avec un autre impliquant une attaque nucléophile du complexe germylène–THF au niveau de l'atome de chlore du substrat. On a aussi déterminé les constantes de vitesse pour la réaction du CCl_4 avec les tétraaryldigermènes correspondants à des faibles concentrations d'halocarbonés dans les hexanes et on a aussi déterminé les paramètres d'Arrhenius pour le (Ge_2Ph_4) parent. Sur la base de l'identité des produits qui se forment dans la réaction du CCl_4 avec le tétramésityldigermène, ces réactions se produisent aussi par le biais d'un enlèvement initial d'un atome de chlore.

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Mots-clés : germylène, halocarbène, radical libre, cinétique, enlèvement, transfert d'électron.

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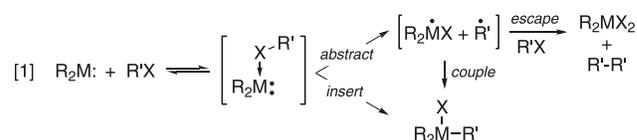
Introduction

There has been great interest over the past few decades in the chemistry of silylenes and germynes, the silicon and germanium analogues of singlet carbenes, respectively. Much of this has been directed toward the synthesis and study of the structures and reactivities of isolable derivatives,^{1–7} which owe their stabilities to electronic stabilization and (or) steric protection of the divalent group 14 atom by substituents. The dimerization process that these effects inhibit occurs at rates within a factor of about 10 of the diffusional limit in solution in the cases of simpler “tetrylenes” such as the dimethyl-, diphenyl-, and dimesityl-substituted derivatives.^{8–12} These simpler derivatives and the parent dihydrides (SiH₂ and GeH₂) thus require fast time-resolved spectroscopic methods to be studied directly,¹³ but they can be expected to provide a more precise definition of the range of chemical behavior inherent to silicon and germanium in their divalent states. They are also key intermediates in many thermal and photochemical reactions of organosilicon^{14,15} and –germanium^{16,17} compounds and are important ligands in a number of metal-catalyzed processes.¹⁸

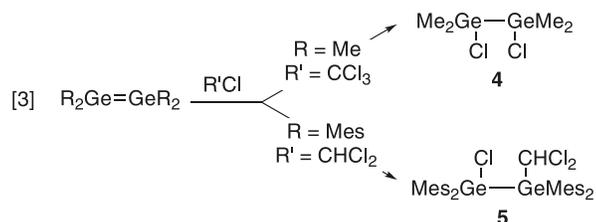
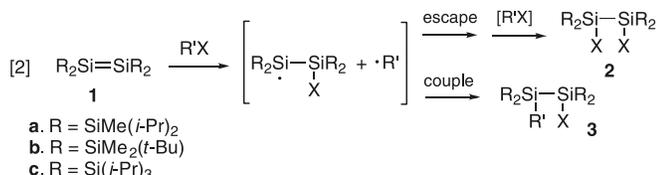
Tetrylenes bearing hydrido or simple alkyl or aryl substituents are voracious electrophiles, reacting exceedingly rapidly with even weak nucleophiles such as alcohols and alkenes.^{9,11,13,19–23} The large majority of the reactions these species undergo, particularly those with heteroatom (i.e., O–, N–, S–, etc.) containing substrates, are thought to begin with the formation of a Lewis acid–base complex between the tetrylene and the substrate.⁴ Indeed, transient silylene^{9,19,22–25} and germylene^{20,21,25–27} donor complexes have been detected directly in a large number of instances, both in low-temperature matrix experiments and in solution at ambient temperatures by laser flash photolysis methods. Complexation with a nonreactive Lewis base such as THF reduces the reactivity of the tetrylene toward both dimerization and reactions with other substrates that require access to the vacant p orbital on the (ground-state singlet) tetrylene to proceed.^{19,28–31} Complexation can also be expected to increase the nucleophilic character of the tetrylene, and hence promote reactions with electrophilic substrates that might be relatively unreactive toward the free species.^{30,32–36}

The reactions of silylenes^{3–5} and germynes^{4,16} with halocarbons are particularly fascinating, as they proceed in one of two directions depending on the halocarbon: C–X insertion and X-atom abstraction. Singlet carbenes behave similarly.^{37,38} Halogen atom abstraction is the main process that occurs with benzyl halides and carbon tetrachloride, whereas C–X insertion predominates with allyl, vinyl, and (in the case of silylenes) aliphatic halides. Again, the reactions are generally thought to proceed via an initially formed tetrylene–halocarbon Lewis acid–base complex, which can then react by concerted insertion into the C–X bond or by homolytic C–X cleavage to form the corresponding singlet radical pair via an electron transfer process (eq. [1]).^{3,39} The caged

radical pair either couples to generate the formal R'–X insertion product or undergoes cage escape; the resulting halo-silyl or halogermyl free radical then abstracts a halogen atom from a second molecule of the halocarbon to form the corresponding dihalosilane or –germane. Interestingly, the reaction of GeMe₂ with CCl₄ also proceeds in THF solution, with a rate constant only slightly smaller than that for reaction with the free germylene in hydrocarbon solvents.³⁰ While product studies were not carried out, it is relevant to note that the reaction of GeMe₂ with CCl₄ is known to afford the C–Cl insertion product essentially exclusively in the presence of catalytic amounts of triphenylphosphine.⁴⁰ This suggests that the presence of a “spectator” donor opens up yet another mechanistic pathway for reaction of the germylene with this halocarbon.

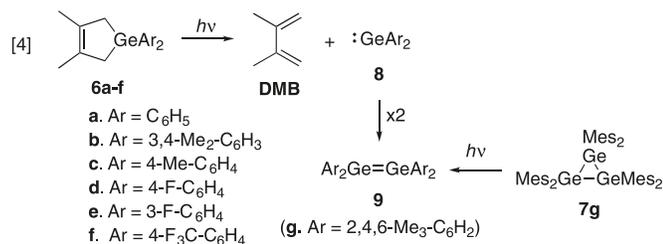


The reactions of halocarbons with disilenes^{41,42} and digermenes,^{43–45} the M=M doubly bonded dimers of silylenes and germynes, respectively, also appear to proceed via initial halogen atom abstraction in most known cases. Kira et al.⁴² carried out a detailed experimental study of the reactions of a series of three kinetically stable tetrasilyldisilenes (**1**) with CCl₄, CHCl₃, and various other chloro- and bromocarbons in hexane solution (eq. [2]), and found the product distributions and rate constants to vary systematically as a function of both the halocarbon and steric bulk in the disilene. Through a combination of kinetic, electron paramagnetic resonance (EPR), and electrochemical studies on these systems, they concluded that the reaction proceeds by simple chlorine atom abstraction to generate the corresponding halodisilanyl and R' radicals (eq. [3]), which they proposed is promoted by a significant degree of 1,2-biradical character of the Si=Si bond. Mochida et al.⁴³ reported the major product of the reaction of (transient) tetramethyldigermene (Ge₂Me₄) with CCl₄ to be the corresponding 1,2-dichlorodigermene (**4**), whereas Baines and co-workers⁴⁵ isolated the formal Cl–R' addition product (**5**) from the reaction of the sterically stabilized digermene Ge₂Mes₄ with CHCl₃ (eq. [3]). A similar difference in product distribution was also observed by Kira et al.⁴² for the reactions of tetrasilyldisilenes **1a** and **1b** with these two halocarbons, CCl₄ being the more reactive of the two by roughly three orders of magnitude. The reactions of several simple disilenes and digermenes with CCl₄ have been studied computationally by Su,⁴⁶ the results of which indicate that Cl abstraction is indeed the lowest energy reaction pathway in these systems.



Kinetic studies of the reactions of CCl₄ with Ge₂Me₄,^{11,43} Ge₂Et₄,⁴³ (GeMePh)₂,⁴⁷ and Ge₂Ph₄²⁰ in hydrocarbon solvents reveal a ca. 20-fold span in the rate constants, which decrease in the order $k_{\text{Ge}_2\text{Et}_4} \approx 2k_{\text{Ge}_2\text{Me}_4} \approx 6k_{\text{GeMePh}_2} \approx 20k_{\text{Ge}_2\text{Ph}_4}$. The trend may be indicative of a modest degree of charge transfer from the Ge=Ge bond to the halocarbon in the transition state for Cl abstraction, as Kira et al.⁴² concluded from a kinetic study of the reactions of a series of substituted benzyl chlorides with disilene **1c**.

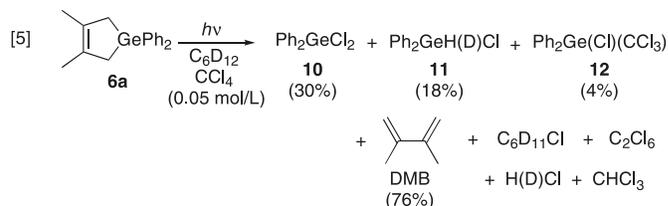
In the present paper, we report the results of product, kinetic, and low-temperature spectroscopic studies of the reactions of GePh₂ and its (digermene) dimer (Ge₂Ph₄) with CCl₄ in hexanes and THF solution, which was carried out with the goal of elucidating the detailed mechanisms of these reactions in both noncomplexing and (for GePh₂) complexing solvents. Arrhenius parameters have been determined, and the role of electronic factors in the transition states for the rate-determining steps of these reactions have been assessed through an examination of the effect of polar ring substituents on the absolute rate constants. As in earlier kinetic studies,^{27,30,48} we employed the substituted 1,1-diaryl-3,4-dimethylgermacyclopent-3-enes **6a–6f** as photochemical precursors to the corresponding diarylgermylenes (**8a–8f**) and tetraaryldigermenes (**9a–9f**; eq. [4]), each pair of which can be studied in the same experiment. It is not practical to carry out product studies of the digermene reactions using these precursors because formation of the digermene requires dimerization of the significantly more reactive germylene, so tetramesityldigermene (**9g**) has been employed as a model compound. The latter was generated by low-temperature photolysis of hexamesitylcyclotrigermene (**7g**).^{49,50}



Results

Product studies

Steady-state photolyses of deoxygenated solutions of **6a** (0.02 mol/L) in C₆D₁₂ containing varying initial concentrations of CCl₄ (0.02–0.5 mol/L) and hexamethyldisilane (ca. 0.002 mol/L; internal standard) were monitored over the 0%–10% conversion range (in **6a**) by ¹H NMR spectroscopy and GC–MS, which allowed the identification of chlorogermenes **10–12** (eq. [5]), DMB, chlorocyclohexane-*d*₁₁, chloroform, and trace amounts of hexachloroethane (C₂Cl₆). The yields of DMB and **10–12** were determined relative to consumed **6a** from the slopes of concentration vs time plots, constructed for the five compounds from the NMR integrals. Significant amounts of unidentified products giving rise to resonances in the allylic (δ 3.4–3.7) and aliphatic (δ 1.5–2.2) regions of the NMR spectrum were also detected; their yields relative to the other products increased with increasing photolysis times, consistent with them being derived from (secondary) radical reactions involving (mainly) DMB, whose concentration vs time plots displayed significant downward curvature. Broad baseline absorptions in the aromatic region of the NMR spectra were also observed and became more pronounced with increased photolysis times, consistent with the formation of oligomeric material containing phenyl groups. The yields of these unidentified materials increased with increasing initial CCl₄ concentration, as did the severity of the curvature in the concentration vs time plots for DMB. This suggests that they arise to a large extent from secondary radical reactions resulting from photolysis of CCl₄,^{51–53} which absorbs weakly at 254 nm ($\epsilon_{254\text{nm}} = 0.44 \text{ (mol/L)}^{-1} \text{ cm}^{-1}$ compared with $\epsilon_{254\text{nm}} = 340 \text{ (mol/L)}^{-1} \text{ cm}^{-1}$ for **6a**). Indeed, H(D)Cl was also detected qualitatively in the photolyzed mixtures in the head space above the solutions. Table 1 lists the yields of **10–12** and DMB (the latter calculated from the initial slopes of the curved plots) that were obtained in the experiments using initial CCl₄ concentrations in the 0.02–0.1 mol/L range (see Supplementary data).



The identities of **10–12** were confirmed by spiking the photolyzed mixtures with independently prepared authentic samples. Compound **12** was prepared by reaction of 2 equiv of PhMgBr with **13**⁵⁵ (eq. [6]), and was obtained as a viscous, moisture-sensitive liquid. Unintentional hydrolysis of the compound afforded germanol **14** (eq. [7]), whose structure was determined by single crystal X-ray crystallography (see Supplementary data). The crystallographic data are of fairly low quality, but nevertheless clearly establish the connectivity and identity of the compound.

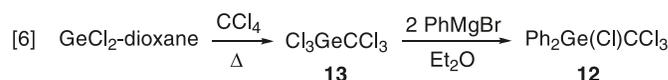
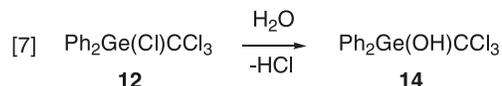
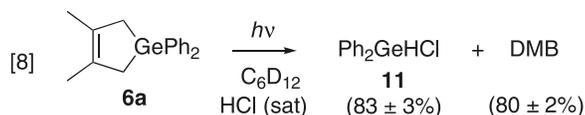


Table 1. Product yields (%) from 254 nm photolysis of 3,4-dimethyl-1,1-diphenylgermacyclopent-3-ene (**6a**; 0.02 mol/L) with CCl₄ in deoxygenated C₆D₁₂ or THF-*d*₈ solution under various conditions.

Solvent	[CCl ₄] (mol/L)	Product yields (%)				%D (11)
		Ph ₂ GeCl ₂ (10)	Ph ₂ GeH(D)Cl (11)	Ph ₂ Ge(Cl)CCl ₃ (12)	DMB	
C ₆ D ₁₂	0.02	20±4	22±3	3.3±0.7	96±6	67
C ₆ D ₁₂	0.05	30±5	18±3	4.1±0.7	76±6	56
C ₆ D ₁₂	0.10	33±4	27±4	3.9±0.5	78±8	44
THF- <i>d</i> ₈	0.05	33±4	20±5	49±6	87±7	25

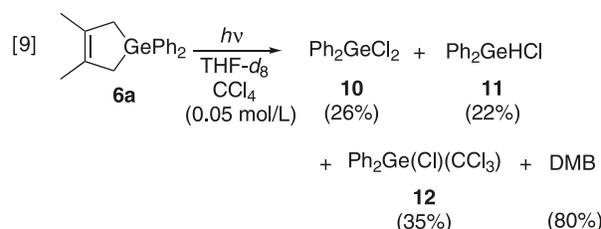


Chlorodiphenylgermane (**11**) was readily recognizable in the NMR spectra of the photolysis mixtures owing to its characteristic Ge–H resonance at δ 6.76, which was present even after ca. 1% conversion of **6a**; its intensity relative to those of the (ortho) aromatic protons indicated the compound was ca. 50% deuterated. The concentration vs time plots for this product exhibited good linearity throughout the (ca. 10%) conversion range in most experiments, but exhibited mild upward curvature in those carried out at higher (>0.1 mol/L) CCl₄ concentrations. The yield of the compound relative to the other products also increased with increasing CCl₄ concentration >0.05 mol/L. One possible route for the formation of the compound is by reaction of GePh₂ with H(D)Cl,⁵⁶ produced by H(D) abstraction by chlorine atoms formed by competing photolysis of CCl₄. Indeed, photolysis of a solution of **6a** (0.04 mol/L) in C₆D₁₂ saturated with HCl(g) resulted in the clean formation of **11** and DMB in high yields (eq. [8]). This mechanism is consistent with the significantly higher yields of the product that were obtained in runs carried out with the higher CCl₄ concentrations, where >0.5% of the incident light is absorbed by the halocarbon. HCl might also be formed by hydrolysis of **10** or **12** by water introduced inadvertently throughout the course of the photolysis; this seems a less likely possibility, but it cannot be ruled out.



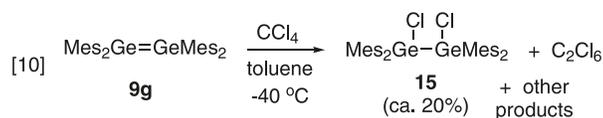
Photolysis of **6a** (0.02 mol/L) in THF-*d*₈ containing CCl₄ (0.05 mol/L) afforded the same products as were obtained in C₆D₁₂, but the material balance was considerably higher and the formal C–Cl insertion product (**12**) was formed as the major product (eq. [9]) (see Supplementary data). The broad baseline absorptions in the aromatic region of the NMR spectrum were much less pronounced, the unidentified resonances in the δ 1.5–2.2 and δ 3.4–3.7 regions of the spectrum were absent, and the concentration vs time plot for DMB exhibited only slight nonlinearity over the 0%–10% conversion range in **6a**, indicating a significantly smaller contribution to the overall product distribution from radical-derived side reactions. The yield of **11** (relative to **11-d**) was also higher than in the C₆D₁₂ photolyses, which we interpret as being due mainly to increased amounts of HCl being

formed during the experiment. This could be due in part to hydrolysis of the other chlorogermane products by adventitious water in the solvent, the presence of which could be detected by NMR. The water peak broadened throughout the course of the experiment, an effect consistent with the formation of HCl in the product mixture,⁵⁷ and the concentration vs time plot for **11** exhibited upward curvature. These observations are all consistent with the main source of **11** (in this experiment) being via reaction of GePh₂ with HCl.

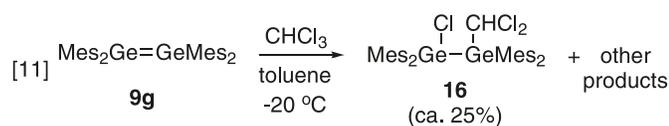


A similar product distribution was obtained upon photolysis of a cyclohexane solution of **6a** (0.02 mol/L) containing CCl₄ (0.05 mol/L) and THF (0.06 mol/L), which afforded **10** and **12** in an approximate 1:1 ratio, according to GC–MS analysis of the mixture. Another experiment employing the same concentrations of **6a** and CCl₄ in cyclohexane containing triethylamine (NEt₃, 0.003 mol/L) afforded **12** as the major germanium-containing product, and only trace amounts of **10** and **11** could be detected by GC–MS.

The course of the reaction of CCl₄ with tetramesityldigermene (**9g**) was also studied, following the reported procedure for the synthesis of the digermene by low-temperature photolysis of hexamesitylcyclotrigermene (**7g**; 1.3 mmol/L) in deoxygenated toluene containing triethylsilane.^{45,58} Addition of a cold solution of CCl₄ in toluene to a prepared solution of **9g** at –40 °C ([CCl₄] ≈ 0.35 mol/L) caused the characteristic yellow colour of the digermene to decolorize within a few seconds. The solvent was evaporated and the ¹H NMR spectrum of the residue showed evidence for the formation of several products (see Supplementary data), amongst which 1,2-dichlorotetramesityldigermene (**15**; eq. [10]) was identified by spiking the mixture with an independently prepared sample.⁵⁹ The yield of **15** was estimated to be ~20% from the contribution of the area of its aromatic proton resonance to the total area of the aromatic proton region of the spectrum (δ 6.50–8.85), excluding the contributions from residual **7g** and Mes₂Ge(H)SiMe₃.⁶⁰ Attempts to identify the other products by GC–MS allowed only C₂Cl₆ (in trace amounts) to be unambiguously identified in the mixture.



Only trace amounts of **15** could be detected in the product mixture obtained in a similar experiment employing CHCl_3 as substrate. In this case, addition of a cold solution of CHCl_3 to a toluene solution containing **9g** at $-40\text{ }^\circ\text{C}$ ($[\text{CHCl}_3] \approx 0.8\text{ mol/L}$) resulted in no change in the yellow colour of the solution, even after standing at $-40\text{ }^\circ\text{C}$ for 30 min. Raising the temperature to ca. $-20\text{ }^\circ\text{C}$ caused the yellow colour to disappear within ~ 5 min. The ^1H NMR spectrum of the evaporated mixture was similar to that described previously by Baines and co-workers,⁴⁵ and verified the formation of compound **16** (eq. [11]) as the major product of the reaction of the digermene with CHCl_3 .



Laser flash photolysis studies

Laser flash photolysis experiments were carried out using flowed, deoxygenated solutions of **6a–6f** (ca. 0.003 mol/L) in anhydrous hexanes and the pulses from a KrF excimer laser ($\sim 25\text{ ns}$, $\sim 100\text{ mJ}$, 248 nm) for excitation. The behaviour observed for the six compounds in the absence of added CCl_4 has been described previously.^{10,27,30,48} Briefly, the photolysis pulse results in the prompt formation of the characteristic absorptions owing to the corresponding transient diarylgermylenes (**8a–8f**; $\lambda_{\text{max}} = 300\text{ nm}$ and $480\text{–}500\text{ nm}$), which decay with second-order kinetics with the concomitant growth of absorptions centered at ca. 440 nm owing to the corresponding digermenes (**9a–9f**). In each case, addition of CCl_4 causes the decay of the germylene absorptions (monitored at 500 nm) to accelerate and produces concomitant reductions in the maximum signal intensities and apparent lifetimes of the digermene absorptions, as we reported previously for **6a**.²⁰ The digermenes could be detected and their decay kinetics characterized in the presence of lower concentrations of CCl_4 , over a range that varied depending on the reactivity of its germylene precursor toward the substrate. The germylenes remained detectable at much higher ($0.1\text{–}1.0\text{ mol/L}$) CCl_4 concentrations, where their decays proceeded completely to baseline and followed clean first-order kinetics. Rate constants for reaction of CCl_4 with each of the germylenes (**8a–8f**) and the corresponding digermenes (**9a–9f**) were obtained from the slopes of plots of the first-order decay rate coefficients (k_{decay}) vs $[\text{CCl}_4]$ according to eq. [12], where k_0 is the hypothetical pseudo-first-order rate coefficient for decay of the monitored species in the absence of substrate and k_{CCl_4} is the second-order rate constant for reaction with the substrate, respectively. These plots exhibited good to excellent linearity in each case (see Supplementary data). For example, Fig. 1 shows selections of representative transient absorbance vs time profiles obtained for digermene **9c** and germylene **8c** in the presence of varying amounts of CCl_4 , along with the corresponding plots of k_{decay} vs $[\text{CCl}_4]$ as insets. The absolute rate constants ob-

tained in the experiments with the six compounds are listed in Table 2; the values obtained for **8a** and **9a** are in excellent agreement with the previously reported values.²⁰

$$\text{[12]} \quad k_{\text{decay}} = k_0 + k_{\text{CCl}_4}[\text{CCl}_4]$$

Co-absorption of the excitation light by the substrate ($\epsilon_{248\text{nm}} = 1.23\text{ mol/L}^{-1}\text{ cm}^{-1}$ for CCl_4 , compared with $\epsilon_{248\text{nm}} = 290\text{ mol/L}^{-1}\text{ cm}^{-1}$ for **6a**) was impossible to avoid in these experiments, and so a control experiment was carried out to assess the possible contributions to the germylene and digermene decay kinetics owing to the formation of HCl , trichloromethyl, and solvent-derived radicals^{61,62} within the reaction volume owing to competing CCl_4 photolysis. We chose germacyclopentene **6d** for the experiment because the corresponding germylene and digermene exhibit reactivity toward CCl_4 that is roughly in the middle of the ranges exhibited by the six germylenes and corresponding digermenes that were studied in this work. Decay rate coefficients were determined for **8d** and **9d** at several CCl_4 concentrations between 0.03 and 0.5 mol/L as a function of excitation laser intensity, on which the concentrations of these CCl_4 -derived species should depend. The decay rate coefficients for both species were found to be approximately constant over a two- to four-fold range in laser intensity at each CCl_4 concentration that was examined, indicating that co-absorption of the excitation light by the substrate has minimal effects on the measured rate constants for reaction of CCl_4 with **8a–8f** and **9a–9f** owing to the presence of HCl , CCl_3 , and solvent-derived radicals produced in the laser pulse. The presence of CCl_4 did cause modest reductions in the intensities of the transient signals, but no more than would be expected because of simple screening of the excitation light by the substrate. It can thus be further concluded that CCl_4 does not quench the excited (singlet) states of **6a–6f** within the concentration ranges that were studied.

A transient absorption spectrum recorded with a solution of **6a** in hexanes containing 0.5 mol/L CCl_4 , conditions under which the lifetime of GePh_2 is reduced to $\tau \approx 165\text{ ns}$ and digermene formation is completely suppressed, showed no difference in the relative intensities of the GePh_2 absorption maxima (500 and ca. 300 nm) compared to those in the absence of added substrate, and no new absorptions (transient or stable) that could be ascribed to intermediates or products of reaction of GePh_2 with the halocarbon.

We also attempted to measure a rate constant for the reaction of CCl_4 with tetramesityldigermene (**9g**) in hexanes, employing **7g** ($1.3 \times 10^{-5}\text{ mol/L}$) as precursor. Laser photolysis of **7g** produces the strong absorptions owing to **9g** ($\lambda_{\text{max}} = 405\text{ nm}$) both within the laser pulse and (in the absence of added substrates) over a $20\text{–}30\text{ }\mu\text{s}$ time period after the pulse owing to dimerization of GeMes_2 (**8g**), the photolysis co-product;⁶³ the latter was not monitored in these experiments. Addition of small amounts of CCl_4 to the solution caused the signal owing to **9g** to decay, exhibiting lifetimes that decreased from ca. 1.4 to 0.8 ms over the $1.3\text{–}5\text{ mmol/L}$ concentration range in added halocarbon. A plot of k_{decay} vs $[\text{CCl}_4]$ afforded $k_{\text{CCl}_4} = (2.0 \pm 0.1) \times 10^5\text{ (mol/L)}^{-1}\text{ s}^{-1}$ (see Supplementary data), which should be considered an upper limit of the true value; the lifetimes showed a modest dependence on laser intensity, suggesting

Fig. 1. Transient absorbance vs time profiles for (a) tetraaryldigermene **9c** and (b) diarylgermylene **8c**, from laser flash photolysis of **6c** in deoxygenated hexanes containing (a) 0–0.04 mol/L CCl_4 and (b) 0.24 mol/L (—) and 0.56 mol/L (○) at 25 °C. The insets show the plots of k_{decay} vs $[\text{CCl}_4]$ obtained from the two sets of data.

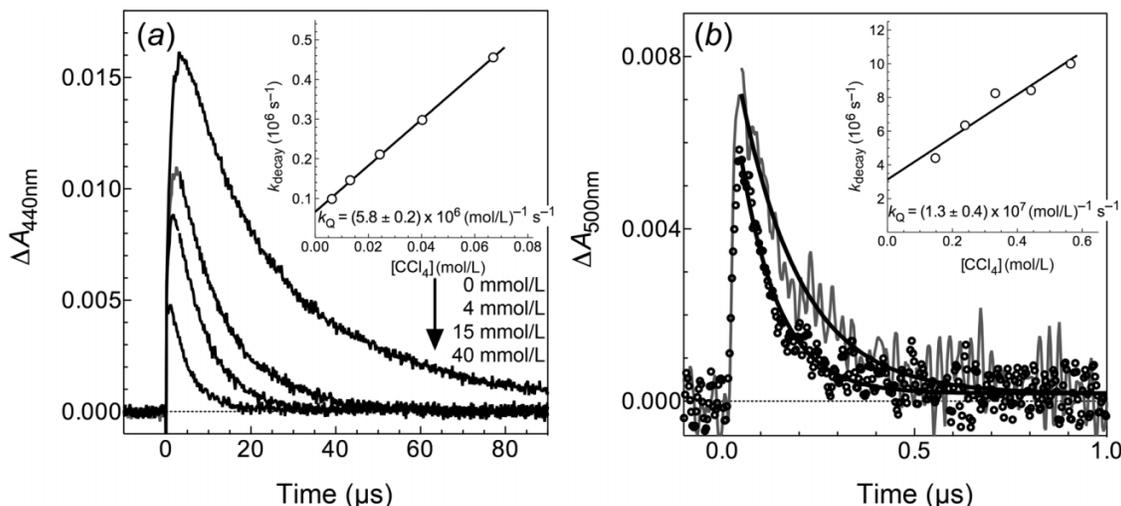


Table 2. Second-order rate constants for the reactions of CCl_4 with germylenes **8a–8f** and digermenes **9a–9g** in deoxygenated hexanes solution and with the corresponding germylene–THF complexes in THF at 25 °C.

8 or 9	Second-order rate constant		
	$k_{\text{CCl}_4^8}$ (10^6 (mol/L) $^{-1}$ s $^{-1}$)	$k_{\text{CCl}_4^9}$ (10^6 (mol/L) $^{-1}$ s $^{-1}$)	$k_{\text{CCl}_4^{8\text{-THF}}}$ (10^6 (mol/L) $^{-1}$ s $^{-1}$)
a (H)	12±1	3.9±0.5	4.3±0.3
b (3,4-Me ₂)	12±2	8.9±1.0	6.4±0.6
c (4-Me)	13±4	5.8±0.2	2.3±0.2
d (4-F)	6.9±1.6	2.5±0.1	0.86±0.07
e (3-F)	8.0±0.8	1.3±0.1	0.56±0.08
f (4-CF ₃)	2.6±1.2	0.91±0.08	1.3±0.2
g (2,4,6-Me ₃)	—	≤0.20	—

Note: Errors are reported as twice the standard error from linear least-squares analysis according to eq. [10].

they may be affected by competing photolysis of the substrate, as discussed above.

Laser photolysis experiments with **6a–6f** in deoxygenated THF solution afforded the strong, long-lived transient absorptions owing to the corresponding germylene–THF complexes, as reported previously for **6a**, **6c**, **6d**, and **6f**.³⁰ The spectra and lifetimes measured for the THF complexes with **8b** and **8e** (see Supplementary data) were quite similar to those of the other four; the complexes exhibited absorption maxima in the 340–350 nm range and decayed over several tens of microseconds, coincident with the growth of weak absorptions (centered at 440 nm) owing to the corresponding digermenes.³⁰ Addition of 0.01–0.4 mol/L CCl_4 to the solutions caused the absorptions owing to the complexes to decay with clean pseudo-first-order kinetics and quenched the formation of the corresponding digermenes; again, plots of k_{decay} vs $[\text{CCl}_4]$ according to eq. [10] were linear in each case (see Supplementary data), and afforded the absolute rate constants listed in Table 2. Figure 2a shows a series of representative transient decay profiles for the **8a**–THF complex at various substrate concentrations, whereas Fig. 2b shows the plot of k_{decay} vs $[\text{CCl}_4]$. Chloroform was also found to shorten the lifetime of the **8a**–THF complex, and a plot of k_{decay} vs $[\text{CHCl}_3]$ was linear with slope $k_{\text{CHCl}_3} = (2.4 \pm 0.5) \times 10^4$ (mol/L) $^{-1}$ s $^{-1}$ (see Supplementary data).

Rate constants were determined at four additional temperatures over the 10–60 °C range, for the reactions of CCl_4 with **8a** and **9a** in hexanes and with the **8a**–THF complex in THF (see Supplementary data). The resulting Arrhenius plots afford activation parameters of $E_a = -0.7 \pm 0.7$ kcal/mol (1 cal = 4.184 J) and $\log(A/(\text{mol/L})^{-1} \text{s}^{-1}) = 6.5 \pm 0.5$ for the reaction of free **8a** in hexanes, $E_a = +4.3 \pm 0.8$ kcal/mol and $\log(A/(\text{mol/L})^{-1} \text{s}^{-1}) = 9.6 \pm 0.6$ for that of **9a** in hexanes, and $E_a = +5.9 \pm 0.4$ kcal/mol and $\log(A/(\text{mol/L})^{-1} \text{s}^{-1}) = 10.9 \pm 0.3$ for the reaction of the **8a**–THF complex in THF. Figure 3a shows the plots for **8a** (in hexanes) and **8a**–THF (in THF) and that for **9a** in hexanes is shown in Fig. 3b.

Low-temperature spectroscopic studies

A study of the reactions of GePh_2 (**8a**) with CCl_4 and CHCl_3 in 3-methylpentane (3-MP) solution at 78–95 K was also carried out. These experiments employed 1,1-diphenylgermacyclobutane (**17**) as the photochemical precursor to GePh_2 , which is produced in ca. 20% chemical yield along with cyclopropane, 1,1-diphenylgermene (**18**; 60%), and ethylene from photolysis of this compound in hexanes at 25 °C (eq. [13]).⁶⁴ We anticipated that GePh_2 should be detectable from **17** under these conditions since its co-product (cyclopropane) is inert; we have previously shown that the photolysis of **6a** in low-temperature glasses does not afford

Fig. 2. (a) Transient decay profiles of the **8a**-THF complex in THF containing various concentrations of CCl₄, recorded at 350 nm. The black lines are the fit of the decays to first-order kinetics. (b) Plot of k_{decay} vs [CCl₄] from the experiment of (a).

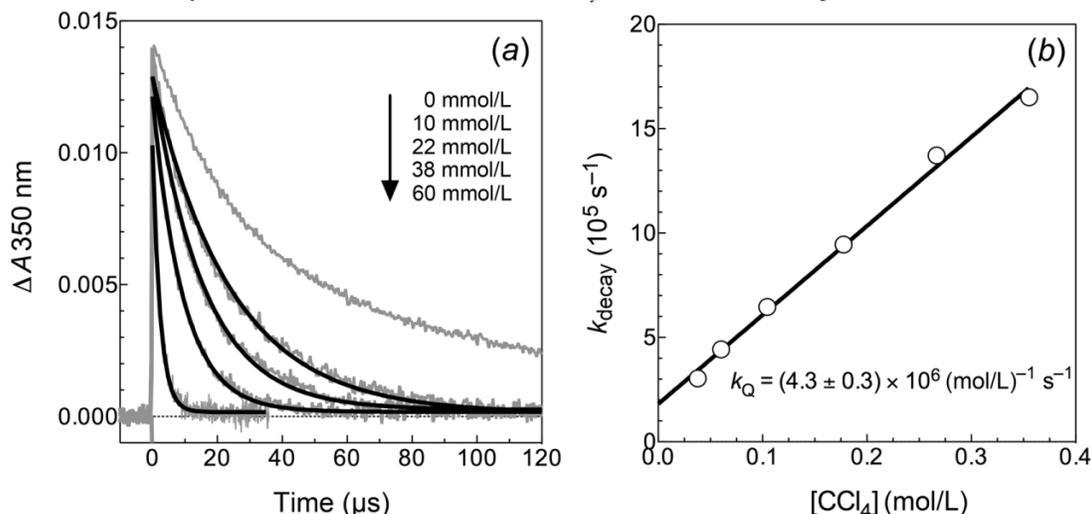
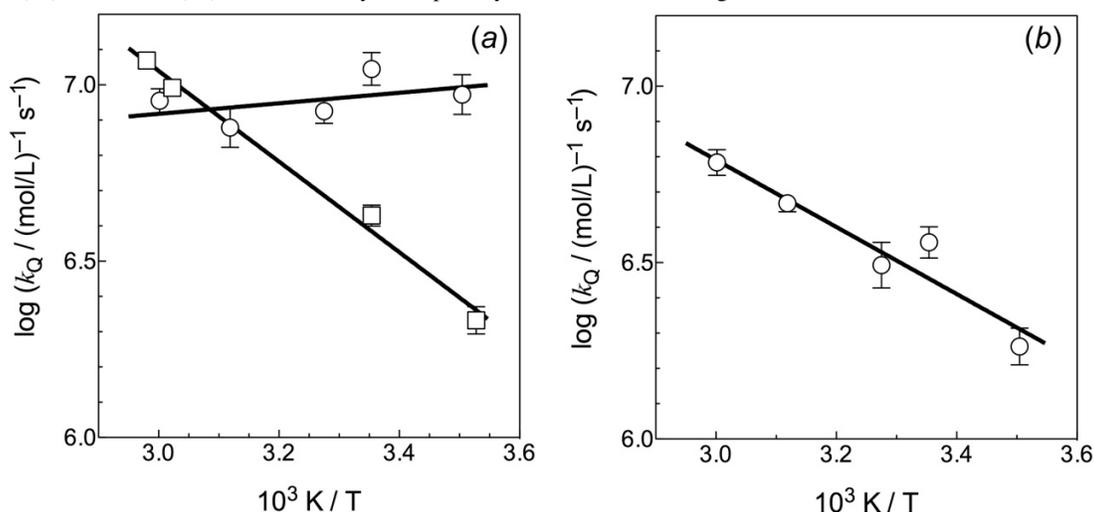
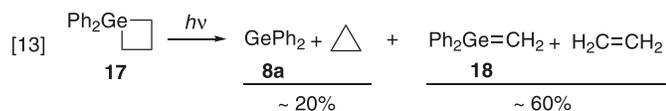


Fig. 3. Arrhenius plots for the reactions of CCl₄ with (a) GePh₂ (**8a**) in deoxygenated hexanes (○) and the **8a**-THF complex in THF (□), and (b) Ge₂Ph₄ (**9a**) in hexanes (○), determined by laser photolysis of **6a** over the range of 10–60 °C.



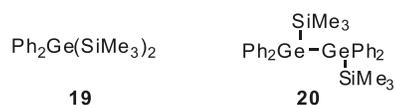
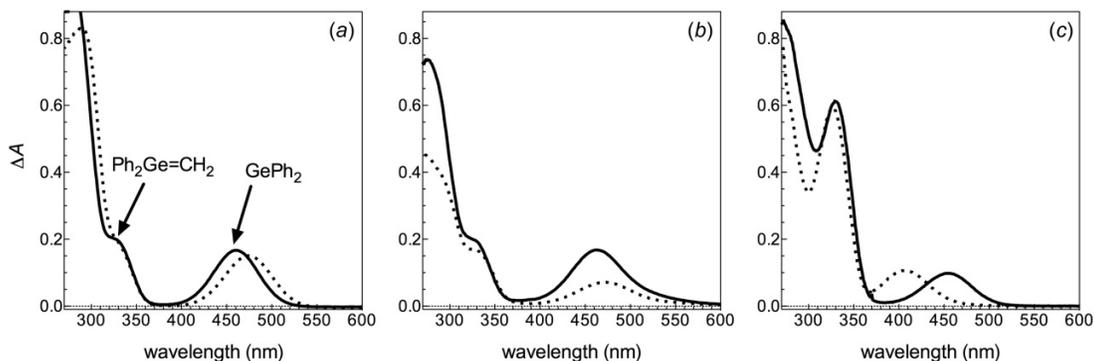
GePh₂ in detectable amounts owing (presumably) to rapid reaction with DMB in the solvent cage.⁶⁵



As expected, photolysis of a solution of **17** in 3-MP (glass transition temperature ≈ 77 K⁶⁶) at 78 K afforded two distinct transient products that were detectable by low-temperature UV-vis spectroscopy, one exhibiting $\lambda_{\text{max}} = 460$ nm and a second exhibiting a shoulder absorption centred at 326 nm, on the edge of an intense band centred below 300 nm (see Fig. 4a). The absorption at 326 nm is assigned to germene **18**,^{64,67} whereas the 460 nm absorption band is assigned to GePh₂. The latter spectrum agrees well with those obtained in low-temperature experiments using other precursors, such as the known disilylgermane **19**^{26,68}

and disilyldigermene **20**.⁶⁹ The solution was then warmed in 1 K increments and a spectrum was recorded at each temperature. At ca. 82 K the 460 nm absorption band began to decrease in intensity slightly and shift to longer wavelengths, ending up finally at $\lambda_{\text{max}} = 474$ nm; the spectrum recorded at 87 K is shown as the broken line in Fig. 4a. The spectrum also shows a slight red-shift of the band below 300 nm, which is also due (at least partly) to GePh₂. The red-shift of the spectrum upon warming the solution between 78 and 82 K is consistent with geometrical relaxation of the solute, formed in a nonequilibrium geometry during the photochemical reaction that produces it.^{70,71} Warming the solution further caused an accelerated reduction in the intensity of the (474 nm) band and a slight blue-shift (to $\lambda_{\text{max}} = 470$ nm), until it had all but disappeared entirely by the time the temperature reached 91 K, and the remaining spectrum consisted mainly of that owing to **18**. The latter disappeared upon further warming of the solution, presumably because of dimerization.^{67,72}

Fig. 4. (a) UV-vis spectra from photolysis of a deoxygenated 3-methylpentane solution containing **17** at 78 K (solid line); the same solution after warming to ca. 87 K is shown as the broken line. (b) As in (a) except the solution contained 0.15 mol/L CCl₄. (c) As in (a) except the solution contained 0.15 mol/L CDCl₃.



The procedure was repeated with a solution of **17** in 3-MP containing 0.15 mol/L CCl₄, the results of which are shown in Fig. 4b. In this case, warming the solution from 78 to 87 K resulted in a similar red-shift of the 460 nm band to what was observed in the absence of the halocarbon, but it was accompanied by a much more rapid decrease in intensity. This is consistent with reaction of GePh₂ with the halocarbon substrate; the spectrum showed no evidence for a detectable product of the reaction.

Finally, the procedure was repeated again with a solution of **17** in 3-MP containing 0.15 mol/L CDCl₃. This experiment afforded considerably different results than were observed in the others (see Fig. 4c); the 326 nm band at the end of the photolysis period was considerably more intense relative to the long wavelength band, and the latter was centered at slightly shorter wavelengths ($\lambda_{\text{max}} = 453$ nm). More importantly, warming the solution resulted in a blue-shift of the long wavelength band to 405 nm and a concomitant reduction in the intensity of the absorption below 300 nm; the intensity of the 326 nm band remained unaffected. Warming the solution past 88 K led to a gradual decrease in the intensity of the 405 nm absorption band until it eventually disappeared. This is again consistent with a halocarbon-induced reaction of GePh₂, but to yield a new transient product. Similar results were obtained (for the 450–460 nm band owing to GePh₂) using **20** as the GePh₂ precursor.

Taken together, the results of these experiments indicate that GePh₂ reacts with both CCl₄ and CDCl₃ at 82–90 K, but only with CDCl₃ does a transient product build up in high enough concentrations to be detected. We tentatively assign the species formed in the reaction with CDCl₃ under these conditions to the GePh₂-CDCl₃ Lewis acid–base complex.

Discussion

Reaction of CCl₄ with diarylgermylenes

The product studies are complicated somewhat by side reactions owing to the accompanying formation of H(D)Cl and the high reactivity of the diene co-product (DMB)

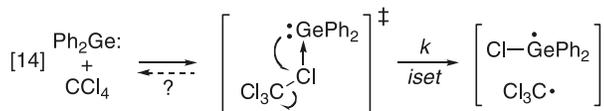
toward radical reactions, but they nevertheless show conclusively that the reaction of GePh₂ with CCl₄ in hydrocarbon solvents proceeds mainly by initial Cl-atom abstraction, producing the corresponding germanium dichloride (**10**) as the major product along with minor amounts of the formal C–Cl insertion product, **12**. The behaviour is thus closely analogous to that exhibited by GeMe₂, which was studied by several groups using both thermal and photochemical methods and a variety of different precursors,^{40,73–75} most of them considerably less prone to the radical side reactions that complicate the product mixtures in the present study. The formation of **11** is particularly difficult to account for completely, as it is clear that it is formed via a number of mechanisms. Roughly 50% of the compound is formed as the deuterated isotopomer, which must be derived ultimately from radical reactions involving the relatively strong C–D bonds associated with the solvent. Of the various radical species that we can anticipate being formed under the conditions of our experiments, only chlorine atoms possess sufficient potency to abstract deuterium from C₆D₁₂.⁷⁶ Some of the **11-d** that is formed could then arise from reaction of GePh₂ with DCl. The most obvious route to chlorine atoms is via photolysis of CCl₄,^{61,77} yet the conditions of our steady-state experiments were such that only ca. 0.7% of the excitation light could be absorbed by the substrate at an initial concentration of 0.1 mol/L. The quantum yield for GePh₂ formation from **6a** is 0.55,¹⁰ so it seems unlikely that all of the **11-d** is formed in this way unless the quantum yield for CCl₄ photolysis is significantly greater than the value of ~0.2 reported for the process in the gas phase.⁵² It is similarly difficult to account completely for the formation of protiated **11**; its formation from the Ph₂GeCl radical via radical disproportionation processes and (perhaps) via H abstraction from an allylic hydrogen in the precursor, which is thermodynamically plausible based on predicted bond dissociation energies,^{76,78} is a possibility at low conversions. We thus conclude that the cage-escape:recombination ratio of the (singlet)⁷³ [Ph₂GeCl + CCl₃] radical pair formed in the primary reaction of GePh₂ with CCl₄ in hydrocarbon solvents is on the order of about 10:1, assuming that roughly half of the **11** that is formed is derived from Ph₂GeCl radical reactions.

The present results also demonstrate that the presence of nonreactive Lewis bases such as THF or NEt₃, either as the solvent or in low concentration in hexanes, shifts the product

distribution in favor of the formal C–Cl insertion product, **12**. This too is consistent with early studies of GeMe₂; Egorov et al.⁴⁰ obtained high yields of the formal C–Cl insertion product from the reaction of GeMe₂ with CCl₄ in the presence of triphenylphosphine. It thus seems likely that the detailed mechanisms of the reactions of this halocarbon with GePh₂ and GeMe₂ are quite similar. Our reported rate constants for the reaction of GeMe₂ with CCl₄ in hexanes ($k = (9 \pm 1) \times 10^7 \text{ (mol/L)}^{-1} \text{ s}^{-1}$)^{11,79} and THF ($k = (3.3 \pm 0.3) \times 10^7 \text{ (mol/L)}^{-1} \text{ s}^{-1}$)³⁰ are both 7–8 times larger than the corresponding values reported here for GePh₂, differences that are typical of those observed for the reactions of most (common) substrates with these two transient germynes in solution.^{11,20,21,30}

The various kinetic and spectroscopic data reported in the present work provide a potentially much more detailed picture of the mechanism of the reaction than has been possible in previous studies with GeMe₂. A Hammett plot of the rate constants for the reactions of the substituted derivatives in hexanes (Fig. 5a) shows a modest correlation, affording a reaction constant of $\rho = -0.4 \pm 0.1$. This indicates there is significant charge donation from germanium to the substrate in the rate-determining step for the reaction. The Arrhenius parameters for the reaction of the parent diarylgermylene (**8a**) in hexanes ($E_a = -0.7 \pm 0.7 \text{ kcal/mol}$; $\log(A/(\text{mol/L})^{-1} \text{ s}^{-1}) = 6.5 \pm 0.5$; $\Delta S^\ddagger = -31 \pm 3 \text{ cal K}^{-1} \text{ mol}^{-1}$ at 35 °C) indicate the reaction to be entirely entropically controlled, with no enthalpic barrier. Interestingly, these features are broadly similar to those exhibited by the reaction of (singlet) chlorophenylcarbene with CCl₄, which was studied in detail by Platz and co-workers³⁸ in the early 1990s.

The negative Hammett ρ value and the observed temperature dependence are consistent with a mechanism involving the initial reversible formation of a weakly bound germylene–halocarbon Lewis acid–base complex, which undergoes rate-controlling dissociative inner-sphere electron transfer (“iset”) from germanium to the halocarbon moiety to afford the [Ph₂GeCl + CCl₃] radical pair (eq. [14]). It should be noted that our data do not demand a discrete reactive complex as a steady-state intermediate in the reaction; it is merely suggested by our detection of the corresponding GePh₂–CDCl₃ complex in the low-temperature UV–vis experiments (vide infra). The data for CCl₄ are equally compatible with a single step concerted mechanism.⁸⁰ The reaction must involve a surface crossing with the (excited) open-shell singlet state of the germylene as it proceeds, as Platz and co-workers³⁸ indicated in their study of the reaction of PhCCl with CCl₄; this, presumably, is where the free energy barrier to the process is located.

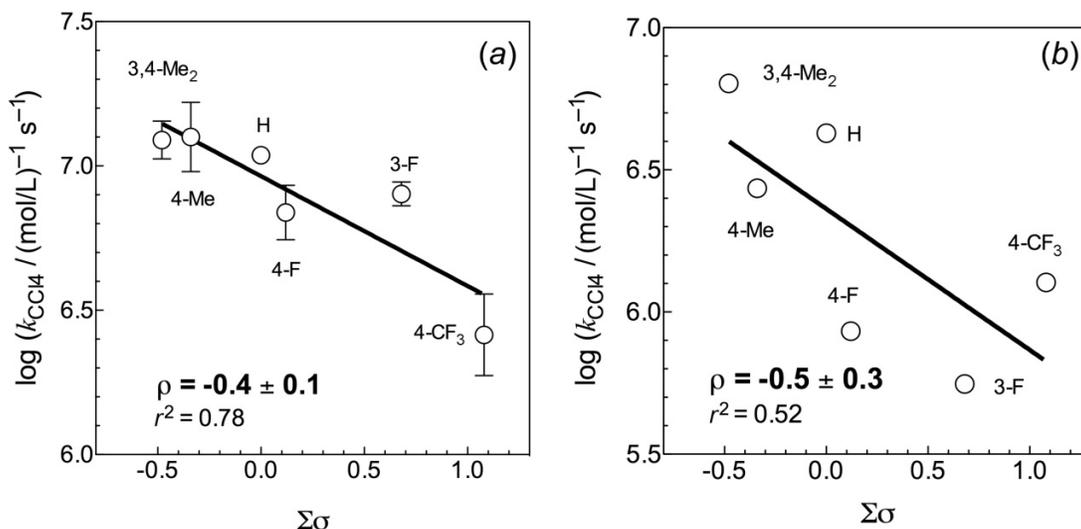


Ando et al.²⁶ reported the spectroscopic detection of the complexes of various germynes (including GePh₂) with chlorohexane and chlorobenzene in hydrocarbon glasses at 77 K, prompting the later proposal by Neumann¹⁶ for their involvement in the reactions of GeMe₂ with halocarbons; computational evidence for the intermediacy of analogous

complexes in the reactions of some stable silylenes with CCl₄ has been reported by Su and co-workers.^{81–83} If a reactive complex is involved as a discrete intermediate in the reaction of GePh₂ with CCl₄, we are unable to detect it even at 80–90 K, so the free energy barrier for its further transformation must be relatively small. The low-temperature experiments with CDCl₃ as substrate are consistent with the formation of a complex in this case, judging from the similarity of the spectrum to those of the complexes of GePh₂ with the chlorocarbons reported by Ando et al.²⁶ The rate constant for reaction of GePh₂ with CHCl₃ in hexanes at 25 °C is at least 50 times smaller than that with CCl₄,²⁰ consistent with a significantly higher barrier for the second step of the reaction with CHCl₃, whose C–Cl bond is ca. 5 kcal/mol stronger than that in CCl₄⁷⁶ and which is less easily reduced.⁸⁴ As a result, the GePh₂–CHCl₃ complex is detectable at low temperatures, whereas the putative GePh₂–CCl₄ complex (assuming it exists at all) is not. We were also unable to detect the product radical (Ph₂GeCl) in our laser photolysis experiments, which is an interesting point of difference between GePh₂ and its silicon homolog, SiPh₂. In the latter case, the primary reaction with CCl₄ produces a second intermediate that was assigned to the SiPh₂Cl radical on the basis of its UV spectrum and the fact that its lifetime decreases with increasing CCl₄ concentration.²² The reason for the difference is likely due to the fact that the primary Cl-abstraction step is roughly two orders of magnitude faster for the silylene than the germylene, but there is a much smaller difference in the rate constants for Cl abstraction by the Ph₂GeCl and Ph₂SiCl radicals.^{85–87}

The reaction in THF, where the germylene exists essentially exclusively as the Lewis acid–base complex with the solvent, proceeds with a rate constant that is only ca. 3 times smaller than that of the free germylene in hexanes and produces a substantially higher yield of the formal C–Cl insertion product, **12**. While it is clear that some portion of the reaction continues to follow the free radical pathway, it appears to be a relatively minor component. We thus conclude that a different mechanism operates (either in whole or in part) in the presence of the nonreactive complexing agent compared with that in pure hexanes. The product distribution is quite similar in hexanes containing 0.05 mol/L THF and the reaction is similarly well-behaved, so it is clear that bulk solvent properties have nothing to do with the effect of the O donor on the product distribution. More dramatically, C–Cl insertion is essentially the exclusive reaction pathway (**10:12** ≈ 1:60) in hexanes containing 3 mmol/L NEt₃, which binds much more strongly to GePh₂ than does THF;^{20,21} the presence of the amine would have the added benefit of soaking up any H(D)Cl that is formed, thus eliminating the formation of **11**. This all suggests that in the presence of O or N donors, the formation of the C–Cl insertion product proceeds via nucleophilic attack of the substrate by germanium in the germylene–donor complex. The Hammett plot of the rate constants for reaction of the substituted derivatives in THF solution (Fig. 5b) exhibits a significantly greater degree of scatter compared with that observed in hexanes, but is nevertheless broadly consistent with the germylene–O-donor complex playing the role of nucleophile in the reaction. The temperature dependence for the reaction of the parent (**8a**) leads to activation parameters of

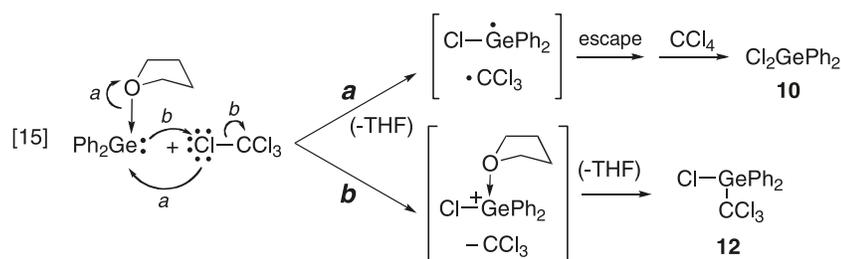
Fig. 5. Hammett plots of the rate constants for the reaction of CCl_4 with (a) free **8a–8f** in hexanes and (b) **8a–8f**–THF complexes in THF, at 25 °C.



$E_a = +5.9 \pm 0.4$ kcal/mol and $\log(A/(\text{mol/L})^{-1}\text{s}^{-1}) = 10.9 \pm 0.3$, the latter corresponding to an overall entropy of activation of $\Delta S^\ddagger = -11.6 \pm 1.3$ cal K^{-1} mol^{-1} at 35 °C.

The results suggest that the **8a**–THF complex reacts with CCl_4 via two competing mechanisms, as depicted in eq. [15]. We propose that the formation of **10** (along with perhaps a small fraction of the total amount of **12** that is produced) is due to Cl-atom abstraction as it is in hexanes, the only difference being that the coordinated THF moiety is liberated (presumably) at some stage during the formation of the resulting radical pair. We suggest that the formation of **12** arises mainly via nucleophilic attack of the germanium lone pair in the complex at a chlorine atom in the substrate, to yield a contact ion pair that rapidly annihilates to form

the product. The process requires prior coordination with the Lewis base, both to impart nucleophilic character at germanium and stabilize the formation of the ion pair. This pathway would be expected to be enhanced relative to the other in the presence of a stronger Lewis base, as indeed we observe. The latter mechanism, as opposed to one involving nucleophilic attack at carbon in the substrate, is consistent with the roughly 200-fold lower reactivity of the GePh_2 –THF complex with CHCl_3 ($k_{\text{CHCl}_3} \approx 2.4 \times 10^4$ $(\text{mol/L})^{-1}$ s^{-1}) compared with CCl_4 under similar conditions. An electron-transfer mechanism might also be consistent with the observed results, provided the transfer of chlorine in the contact radical ion pair occurs largely as an atom transfer rather than ion transfer.

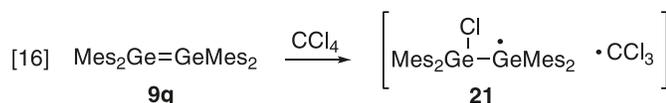


Reaction of CCl_4 with tetraaryldigermenes

The reaction of CCl_4 with tetramesityldigermene (**9g**) affords the corresponding 1,2-dichlorodigermene (**15**) as a major product, allowing the conclusion that Cl-atom abstraction to yield the 2-chlorodigermeryl radical (**21**; eq. [16]) is a dominant mode of reaction of the Ge–Ge bond in this compound with CCl_4 . The reaction produces a number of unidentified additional products, some of them presumably derived from side reactions resulting from the accompanying formation of the CCl_3 radical. This supports our inference that the primary reaction of the other tetraaryldigermenes (**9a–9f**) with

CCl_4 is Cl-atom abstraction, as Mochida et al.⁴³ found to be the case for Ge_2Me_4 . It is interesting to note that the reactions of **9g** with CCl_4 and CHCl_3 ⁴⁵ (which affords the 1,2-dichloride in only trace amounts; vide supra) exhibit similar differences in product distribution as Kira et al.⁴² reported for the reactions of these two halocarbons with the less sterically hindered (**1a** and **1b**) of the three tetraaryldisilene derivatives they studied. The more sterically hindered derivative (**1c**) afforded the corresponding 1,2-dichlorides in both cases; it did as well with CH_2Cl_2 as substrate, whereas **1a** afforded only the formal cage recombination product.

They interpreted these differences in terms of steric effects on the cage-escape–recombination ratio of the initially formed radical pairs, but the possibility that the formal recombination product (when it is observed) might be formed at least in part via an entirely different mechanism cannot be discounted. In any event, it is certainly clear that with all the disilenes they studied, the reaction with CCl_4 proceeds to a very large extent via initial Cl-atom abstraction. This is also true for Ge_2Me_4 ,⁴³ and probably as well for **9g** and the other less-hindered systems that we have characterized kinetically in the present work. It is also clear from the results of Kira et al.⁴² that CHCl_3 can react the same way, and does so exclusively when the Si=Si bond is severely sterically hindered. It is also clear from their results that CHCl_3 is a characteristically much less reactive substrate than CCl_4 toward Si=Si bonds. This is true as well for the Ge=Ge bonds in Ge_2Me_4 ,⁴³ Ge_2Mes_4 (vide supra), and Ge_2Ph_4 .²⁰ The difference in absolute rate constant is on the order of 1000 or more for both disilene **1c**⁴² and Ge_2Me_4 .⁴³ Kira et al.⁴² reported activation parameters of $\Delta H^\ddagger = +7.0 \pm 0.1$ kcal/mol and $\Delta S^\ddagger = -43.9 \pm 0.1$ cal $\text{K}^{-1} \text{mol}^{-1}$ for Cl abstraction from CHCl_3 by **1c**, but unfortunately did not study the temperature dependence of the corresponding reaction with CCl_4 .



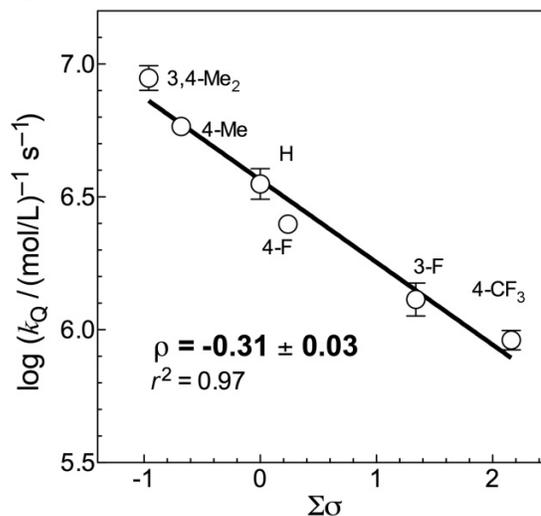
The Arrhenius plot of the absolute rate constants for reaction of **9a** with CCl_4 in hexanes (Fig. 3b) affords activation parameters of $E_a = +4.3 \pm 0.8$ kcal/mol and $\log(A/(\text{mol/L})^{-1} \text{s}^{-1}) = 9.6 \pm 0.6$, corresponding to an enthalpy and entropy of activation of $\Delta H^\ddagger = +3.7 \pm 0.8$ kcal/mol and $\Delta S^\ddagger = -16.7 \pm 1.3$ cal $\text{K}^{-1} \text{mol}^{-1}$ at 35 °C, respectively, which we tentatively ascribe to those characterizing the Cl-abstraction process from this substrate by the Ge=Ge bond in Ge_2Ph_4 . Su⁴⁶ reported a calculated value of $\Delta E^\ddagger = +0.6$ kcal/mol at the B3LYP/6–311G(d,p) level of theory for the Cl-abstraction reaction of Ge_2Me_4 with CCl_4 , which is the only direct comparison possible with the results of earlier studies on related systems.

The Hammett plot of the rate constants for the reactions of **9a** and the five substituted derivatives (Fig. 6) reveals an excellent correlation with substituent constants and affords a reaction constant of $\rho = -0.31 \pm 0.03$. The value is indicative of significant charge donation from the Ge=Ge bond in **9** to the substrate in the transition state for the Cl-atom abstraction and is again broadly consistent with the results of Kira et al.⁴² for disilene **1c**. They observed a good two-parameter correlation between the rates of reaction of disilene **1c** with a series of substituted benzyl chlorides and polar (Hammett σ_p) and spin delocalization (σ_{JJ}) substituent constants; the polar reaction constant was $\rho = +0.9$, which reflects the effects of substituent polarity from the opposite frame of reference to that probed in the present study.

Conclusions

The reaction of GePh_2 with CCl_4 in hydrocarbon solvents proceeds exclusively via Cl-atom abstraction, as is known

Fig. 6. Hammett plot of the rate constants for the reactions of tetraaryldigermenes **9a–9f** with CCl_4 in hexanes at 25 °C.



also to be the case for GeMe_2 based on the results of early studies of the simpler germylene derivative using both thermal and photochemical methods for its generation. The present study affords considerably greater information in regards to the detailed mechanism of the process. The temperature dependence of the rate constant indicates the reaction is entropically controlled and possesses little or no enthalpic barrier, consistent with a two-step mechanism involving a reversibly formed intermediate whose collapse to the primary products is rate-controlling. It is well-established that GePh_2 (and other transient germylenes) form detectable Lewis acid–base complexes with other, less reactive halocarbons, and the present work extends the list of such substrates to include chloroform. We thus envisage the reaction with CCl_4 to begin with such an interaction, which allows the Cl-atom transfer to occur via a dissociative inner-sphere electron transfer process; if a discrete Lewis acid–base complex is involved, it is a steady-state intermediate that is undetectable even at very low temperatures. Reactivity is enhanced modestly by electron-donor substituents on the germylene, which supports the proposed mechanism. So too does the sizeable reduction in rate constants exhibited by the reactions of GePh_2 with CHCl_3 and other less easily reduced halocarbons.

A second mechanism comes into play in the presence of “spectator” donors such as THF (either as solvent or a catalyst) and NEt_3 , which lead to increased yields of the formal C–Cl insertion product at the expense of radical-derived products, to an extent that depends on donor basicity. The reaction of GePh_2 with CCl_4 in THF solution exhibits activation parameters of $E_a = +5.9 \pm 0.4$ kcal/mol and $\Delta S^\ddagger = -11.6 \pm 1.3$ cal $\text{K}^{-1} \text{mol}^{-1}$ at 35 °C, the interpretation of which is complicated by the fact that competing reaction channels are operative and product studies have not been carried out over the full temperature range probed in the kinetic experiments. The rate constants for reaction of the substituted derivatives in this solvent correlate poorly with Hammett substituent constants, but show a trend toward higher reactivity with the more electron-rich derivatives in the series; this too may be a reflection of the competing reaction

channels that may operate. Nevertheless, a mechanism involving nucleophilic attack at the chlorine of the substrate by the germylene lone pair in the germylene–donor complex, to yield a contact ion pair that rapidly annihilates to form the observed product, is consistent with the data and explains the higher yield of formal C–Cl insertion product that is obtained.

The reaction of CCl_4 with the corresponding tetraaryldigermenes also proceeds via Cl-atom abstraction in hexanes solution, affording the corresponding 1,2-dichlorodigermene as the main product. Activation parameters of $E_a = +4.3 \pm 0.8$ kcal/mol and $\Delta S^\ddagger = -16.7 \pm 1.3$ cal K^{-1} mol^{-1} have been determined for the reaction of Ge_2Ph_4 , which are consistent with theoretical estimates for Ge_2Me_4 and the results of earlier studies of the corresponding reactions with sterically stabilized tetrasilyldisilenes. The process involves significant charge donation from the Ge=Ge bond to the substrate in the transition state for the rate-determining step, as revealed by an excellent correlation of the rate constants for reaction of the substituted tetraaryldigermenes with Hammett substituent constants.

Carbon tetrachloride represents an extreme in the reactions of transient germylenes, silylenes, and their corresponding dimers with halocarbon substrates, reacting exclusively by Cl-atom abstraction. This behaviour is shared by benzyl chloride, which possesses a C–Cl bond of similar strength to that in CCl_4 . Interestingly, allyl chloride undergoes exclusive C–Cl insertion with GeMe_2 in spite of a similar C–Cl bond strength to those in CCl_4 and benzyl chloride.¹⁶ This and other reactions of transient silylenes and germylenes are the subject of continued study in our laboratory.

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker AV200 or AV600 spectrometers in CDCl_3 , CD_3CN , C_6D_6 , C_6D_{12} , or $\text{THF}-d_8$ (Cambridge Isotope Laboratories). High-resolution mass spectra were recorded on a Micromass TofSpec 2E mass spectrometer using electron impact or chemical ionization (NH_3 reagent gas). MALDI mass spectra were recorded on a WatersMicromass MALDI MicroMX mass spectrometer operating in reflectron mode (matrix: α -cyano-4-hydroxycinnamic acid). GC–MS analysis of product mixtures was performed using a Varian Saturn 2200 GC–MS–MS system equipped with a VF-5ms capillary column (30 m \times 0.25 mm; 0.25 μm ; Varian, Inc.) using electron impact or chemical ionization (MeOH reagent gas); an asterisk by an m/z value indicates it is the most intense peak of a Ge isotopomeric cluster. X-ray crystallographic analysis was performed in the McMaster Analytical X-Ray (MAX) Diffraction Facility on a single crystal (grown from slow evaporation of hexanes), mounted and cooled to -100°C on a SMART APEX II diffractometer with a 3 kW sealed tube Mo generator.

All synthetic preparations were carried out in flame-dried glassware under an atmosphere of dry nitrogen. The germa-cyclopentenes **6a–6f**,^{10,27,30,48} hexamesitylcyclotrigermene (**7g**),⁸⁸ 1,2-dichloro-1,1,2,2-tetramesityldigermene (**15**),⁵⁹ 1,1-diphenyl-1-germacyclobutane (**17**),⁶⁷ and diphenylgermanium dichloride (**10**)⁸⁹ were prepared as previously described.

Trichloro(trichloromethyl)germane ($\text{Cl}_3\text{GeCCl}_3$) was prepared following the method of Nefedov and co-workers.⁵⁵ GeCl_2 -dioxane (10.3 g, 44 mmol) was dissolved in CCl_4 (150 mL) and refluxed for 4 h under nitrogen. The reaction mixture was stirred under vacuum (~ 0.1 mm Hg; 1 mm Hg = 133.3224 Pa) at ambient temperature until the solvent had been removed, yielding the crude product as a pale yellow solid. While still under vacuum, the flask was gently warmed with a water bath (ca. 40 – 50°C) and the product, a white solid (8.68 g, 29 mmol, 66%), sublimed onto a cold-finger cooled to $-(30$ – $40)^\circ\text{C}$ using dry ice–isopropanol. The melting point was measured in a sealed tube (mp 104 – 106°C ; lit.⁵⁵ mp 106 – 107°C). MS (m/z (I)): 297.7* (3) [M^+], 260.8* (80) [$\text{M} - \text{Cl}$]⁺, 178.8* (28) [$\text{M} - \text{CCl}_3$]⁺, 159.9* (18), 116.9 (100).

Chloro(trichloromethyl)diphenylgermane (**17**): A two-neck 250 mL round bottom flask, fitted with a dropping funnel and a condenser, was charged with $\text{Cl}_3\text{GeCCl}_3$ (0.80 g, 2.7 mmol) and anhyd ether (20 mL). The dropping funnel was charged with freshly prepared PhMgBr (10.8 mmol, 4 equiv) in ether (50 mL). The Grignard reagent was added dropwise over 40 min, causing the formation of white insoluble salts. After the addition was complete, the mixture was allowed to stir for 2 h at room temperature. The solvent was removed under vacuum and the residue was washed with pentane (5 \times 20 mL). The combined washes were filtered and the solvent removed under vacuum to yield a yellow oil (0.66 g). The product was isolated from the crude reaction mixture by Kugelrohr distillation as a colourless oil (0.10 g, 0.3 mmol, 11%), distilling at 110 – 120°C ($P = 0.05$ mm Hg). IR (cm^{-1} , intensity): 3075 (m), 3055 (m), 1960 (w), 1885 (w), 1816 (w), 1585 (w), 1485 (s), 1434 (s), 1092 (s), 998 (s). ^1H NMR (C_6D_{12}): 7.34–7.42 (m, 6H), 7.79–7.87 (m, 4H). ^1H NMR (CD_3CN): 7.55–7.59 (m, 4H, *ortho*), 7.61–7.67 (m, 2H, *para*), 7.87–7.91 (m, 4H, *meta*). ^{13}C NMR (CD_3CN): 92.05 (CCl_3), 130.19 (*ortho*), 130.69 (*ipso*), 133.09 (*para*), 135.38 (*meta*). Note: the ^{13}C shift of CCl_3 is consistent with literature data for this group on Ge.^{40,90,91} GC–MS (Saturn, CI) m/z : 344.7* (20) ($\text{M} - \text{Cl}$)⁺, 299.2* (44), 201.3 (100), 161.1 (30), 159.2 (50). GC–MS (Saturn, EI) m/z : 263.2* (100) ($\text{M} - \text{CCl}_3$)⁺. MS (Micromass, CI) (m/z , intensity): 306.9* (7), 280.0* (4), 263.0* (18), 151.0* (8), 108.9* (9), 94.1 (24), 93.1 (28), 78.0 (100). HRMS calcd for $\text{C}_{12}\text{H}_{10}^{74}\text{GeCl}$ ($\text{M} - \text{CCl}_3$)⁺: 262.9683; found: 262.9621.

Attempts to crystallize the compound were unsuccessful; however, slow evaporation of a hexane solution in contact with atmospheric moisture led to the formation of colourless crystals of trichloromethyldiphenylgermanol (**14**) (mp 65.6 – 67.7°C). IR (cm^{-1} , intensity): 3375 (br, m), 1961 (w), 1882 (w), 1810 (w), 1481 (m), 1431 (s), 999 (s). ^1H NMR (CD_3CN): 7.50–7.54 (m, 4H, *ortho*), 7.56–7.60 (m, 2H, *para*), 7.82–7.87 (m, 4H, *meta*).

Chlorodiphenylgermane (**11**) was prepared following the method of Kunai and co-workers.⁹² The product was isolated from the crude reaction mixture as a colourless oil by Kugelrohr distillation ($T = 100^\circ\text{C}$, $P = 0.2$ mm Hg). IR (cm^{-1}): 3071 (m), 3052 (m), 3008 (br, w), 2076 (br, s), 1484 (m), 1433 (s), 1334 (w), 1305 (w), 1095 (s), 1027 (w), 998 (w), 855 (br, w). ^1H NMR δ : 6.56 (s, H), 7.46–7.54 (m, 6H, *ortho/para*), 7.63–7.73 (m, 4H, *meta*). ^{13}C NMR δ :

128.9 (*meta*), 130.8 (*para*), 133.8 (*ortho*), 135.3 (*ipso*). MS *m/z* (I): 263.0* (15), 227.0* (13), 185.9* (100), 151.0* (48), 108.9* (49), 79.1* (60). HRMS C₁₂H₁₀⁷⁴GeCl (M – H) calcd: 262.9683; found: 262.9675.

Steady-state photolysis experiments were carried out using a Rayonet photochemical reactor (Southern New England Ultraviolet Co.) equipped with a merry-go-round and 2 × RPR2537 (254 nm) lamps. For those monitored by NMR spectroscopy, aliquots (ca. 0.7 mL) of solutions in C₆D₁₂ or THF-*d*₈ containing Si₂Me₆ (ca. 2 mmol/L) as an internal integration standard were placed in quartz NMR tubes, sealed with a septum, and deoxygenated with a fine stream of dry argon for ca. 10 min prior to the experiment. Reaction products were identified by spiking the mixture with authentic samples as well as by GC–MS analysis at the end of the experiment.

For those monitored by GC–MS only, solutions of the compounds and CCl₄ were prepared in dry cyclohexane or THF (5 mL) containing dodecane (1 mmol/L) as the internal integration standard. If applicable, THF or NEt₃ (Sigma-Aldrich, refluxed over and distilled from KOH) was added as well. The solution was transferred to a quartz NMR tube, sealed with a rubber septum, and deoxygenated with a stream of dry argon for 5 min. Aliquots were removed at regular intervals and analyzed by GC–MS, repurging the sample with argon after each aliquot was taken.

Nanosecond laser flash photolysis experiments were carried out using the pulses from a Lambda-Physik Compex 120 excimer laser, filled with F₂–Kr–Ne (248 nm; ca. 25 ns; 100 ± 5 mJ) and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.¹⁰ 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 mm × 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 thermostatted 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 constants 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.^{20,27} 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.⁹³

Low-temperature UV–vis spectrophotometry employed a 2 cm × 1 cm × 1 cm cuvette constructed from quartz tubing (Vitrocom, Inc.) and an Oxford Optistat liquid nitrogen cryostat equipped with an Oxford ITC601 temperature controller. Solutions of **6a** (ca. 0.001 mol/L; A_{254 nm} ~ 0.8) in 3-methylpentane (Sigma-Aldrich spectrophotometric grade) were deoxygenated with argon, sealed in the cuvette with a rubber septum, and placed in the cryostat, which was then cooled to 78 K. The entire assembly was placed in a Rayonet photochemical reactor equipped with twelve RPR-2537 lamps to irradiate the sample, with UV–vis spectra being obtained before and during the photolysis procedure at selected time intervals. The cryostat was then warmed in 1 K increments and a spectrum recorded after ca. 5 min equilibration at the new temperature. The spectra shown in Fig. 4 are difference spectra, obtained by subtracting the UV spectrum obtained prior to photolysis from those obtained after irradiation and subsequent warming.

Supplementary data

Supplementary data (concentration vs time plots and representative NMR spectra from steady-state photolysis experiments and kinetic data determined in laser flash photolysis experiments) for this article are available on the journal Web site (canjchem.nrc.ca). CCDC 788625 contains the X-ray data (for **14**) in CIF format for this manuscript. These data can be obtained, free of charge, via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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