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Chemistry of heavy carbene analogues R_2M (M = Si, Ge, Sn)

XVII*. Reactions of free dimethylgermylene with H-acidic compounds and donors **

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Abstract

The free germylene Me_2Ge, **1**, inserts smoothly into O–H, S–H, or N–H bonds of water, deuterium oxide, alcohols, carboxylic acids, oximes and phthalimide to yield the (mostly new) substituted organogermanium hydrides of the type X-Me_2Ge-H, **3**, **5–12**. The more acidic compounds form the more stable hydrides. Only $PhSMe_2GeH$, **11**, brings about spontaneous hydrogermylation of certain alkenes. With suitable donors **1** reversibly forms complexes $Me_2Ge \cdot D$, **15**, which are, in the case of X–H compounds, to be considered as precursors of the insertion products. These complexes are discussed as intermediates, which can add to alkenes and (stereoselectively) to alkynes.

1. Introduction

The chemistry of heavy carbene analogues R_2M, mainly silylenes, germylenes and stannylenes, has attracted considerable interest in recent years, from both mechanistic and synthetic viewpoints, see for example ref. 2. In many cases study of the germylenes R_2Ge revealed unusual modes of reaction, and also opened new routes to many organogermanium compounds. The free dimethylgermylene Me_2Ge, **1**, merits special attention because its behaviour is not influenced by severe steric or electronic effects [3]. Many addition and cycloaddition reactions have been developed [1,3] that yield many new compounds of chemical and sometimes biological interest. Compared with addition reactions, relatively few insertions of Me_2Ge, **1**, into sigma bonds have been known up to now [3].

Several olefins and alkynes, such as acrylonitrile, acrylic esters or acetylenecarboxylate, that do not react with free Me_2Ge, **1**, surprisingly give oxygen-containing adducts, when small amounts of water are present, for example as a result of water on the surface of glass flasks, or in wet silica gel. Good yields of new products could be obtained; an example of an overall reaction is shown in eqn. (1) [4]:

$$2\ H_2C{=}CHCN + 2Me_2Ge + H_2O \xrightarrow{\textbf{(1)}} (NCCH_2CH_2Me_2Ge)_2O \quad (1)$$

A number of analogous results were obtained, but only tentative hypotheses could be advanced concerning the role of the water molecule and the possible supportive influence of the glass surface or silica gel [4]. The questions were: (1) is there a form of "reactive water"; (2) is there an initial insertion of Me_2Ge, **1**, into the O–H bond, and then a hydrogermylation; or, (3) is there a decomposition of an unstable intermediate, formed by the unsaturated system and **1**, brought about by the water or a proton? Since then, our efforts have been directed towards a definite identification, or exclusion, of certain intermediates, and to examine the scope for this new type of reaction.

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* For Part XVI, see ref. 1.

** Dedicated to Professor Mikhail G. Voronkov, Irkutsk, in recognition of his extensive and valuable researches in organosilicon chemistry.

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We report now mainly on the reactions of free Me_2Ge, **1**, with water, alcohols, other proton-acidic compounds, including thiols, oximes, and carboxylic acids. We have also investigated the reactions of the products, formed by these ways, with alkenes, alkynes and dienes. The results have been used to develop a broader view on the complex formation between Me_2Ge, **1**, with donors and on the importance of such complexes in the reaction of **1**.

2. Results and discussion

2.1. Insertion into water and deuterium oxide

When Me_2Ge, **1**, is generated from its precursor, a 7-germanorbornadiene [3,5] at 70°C in anhydrous benzene, it yields only a mixture of oligogermanes **2**, probably cyclic ones (eqn. (2)).

$$n\ Me_2Ge \longrightarrow (Me_2Ge)_n \qquad (2)$$

(1) (2)

In wet benzene, however, a complex mixture of products was formed, containing $Me_2GeOGeMe_2$, Me_2GeH, and $(Me_2Ge)_n$ moieties (IR, ^1H NMR), indicating that there has been some kind of reaction between **1** and water. Our first attempts to identify a definite product failed [4]. However, one main product, the tetramethyldigermoxane, **3**, was obtained in 90% yield when the free Me_2Ge was generated in a well-stirred mixture of chloro- or bromo-benzene and water at 110°C, eqn. (3) [6*]. Generation of additional Me_2Ge yielded none of the insertion product **4**, but only the polygermane **2**, eqn. (3). Under these conditions, therefore, neither the Ge–O nor the Ge–H bond is able to undergo germylene insertion and **3** remained unchanged.

$$2\ Me_2Ge + H_2O \longrightarrow HMe_2GeOGeMe_2H \xrightarrow{(n-1)\mathbf{1}} HMe_2GeO(Me_2Ge)_nH \qquad (3)$$

(1) (3) (4)

In dry 1,2-dichlorobenzene at 70°C, we obtained only **2**. Use of increasing amounts of water led to a mixture of **2** and **3**, and in a vigorously stirred heterogeneous system containing a large excess of water, **3** was formed almost exclusively. Like other germoxanes, **3** is slowly converted into the germylester CH_3COOMe_2GeH by acetic acid even at room temperature.

With deuterium oxide D_2O, in 1,2-dichlorobenzene at 70°C a similar reaction took place but there was ready insertion of additional **1** into the product **5**, presumably into its Ge–D bond, to give **6**, eqn. (4). In general, **6** is found to be the dominant product. A large isotope effect [7] is revealed by comparison of **3** and **5**, the Ge–D bond being more reactive than the Ge–H bond, with the latter effectively inert.

$$2\ Me_2Ge + D_2O \longrightarrow DMe_2GeOGeMe_2D \xrightarrow{\mathbf{1}} DMe_2GeO(Me_2Ge)_2D \qquad (4)$$

(1) (5) (6)

This resembles the analogous, but easier, formation of the corresponding siloxane from the silylene Me_2Si and H_2O or D_2O, eqn. (5) [8] in 85% and 82% yield respectively. No isotope effect such as that implied by eqn. (4) was observed [8]. This can be attributed to the higher reactivity of Me_2Si than Me_2Ge.

$$2\ Me_2Si + H_2O(D_2O) \xrightarrow[5°C]{\text{ether}} (D)HMe_2SiOSiMe_2H(D) \qquad (5)$$

The insertion of **1** into water to give **3**, eqn. (3), is a slow reaction. This can be demonstrated by carrying out the reactions with 1,3-dienes of differing reactivities in the presence of water. The highly reactive *E*-1-Ph-2-Me-butadiene-1,3 gives the previously observed mixture of cycloadducts at 110°C in PhCl, mainly the 1,4-isomer [3,11], even in the presence of water. However *E,E*-1,4-dicyano-butadiene under the same conditions, yields 100% of the known 1,4-cycloadduct [3] in the absence of water, but only 20% in the presence of water, along with an 80% yield (based on **1**) of **2** + **3**. Under the same conditions, the even less active *E,E*-1,4-Ph_2-butadiene forms 30% of the cycloadduct of **1** in the absence of water, along with 70% of **2** [3]. In the presence of water, however, no cycloadduct is formed, and 90% of **1** is accounted for by the formation of **3**, the diene remaining unchanged. It should be kept in mind that the insertion product **3**, once formed, is stable at 110°C.

In view of these facts and of the very rapid polymerization of **1** to give **2** (eqn. (2)) if no other reagent is present (the rate constant k is in the range 10^8–10^9 $M^{-1}\ s^{-1}$ [3]), it can be assumed that an intermediate is formed between the free germylene **1** and its insertion product **3**. This is discussed later in Section 2.7.

2.2. Insertions into O–H bonds of alcohols, carboxylic acids, and oximes

The reaction of Me_2Ge with H_2O and D_2O, which we also observed during earlier investigations [3,4],

* Reference number with asterisk indicates a note in the list of references.

prompted us to investigate which other species containing O–H bonds could undergo insertion of the free germylene **1**.

When we generated **1** in the presence of a 25-fold excess of methanol or benzyl alcohol, ^{1}H NMR signals indicating the presence of **7** in the reaction mixture were observed [9], but disappeared during work-up. It is known that products of the type **7**, obtained by other methods, decompose in the presence of an excess of alcohol or base [10–13*]. When we used silica gel, just a threefold excess of MeOH was sufficient to obtain **7** (R = Me) quantitatively, and no polygermane **2** was formed, eqn. (6). For R = Me_2CH and PhOH, again **7b** and **7d**, were formed quantitatively whereas $PhCH_2OH$ yielded 40% of **2**.

$$Me_2Ge + ROH \xrightarrow[70°C]{SiO_2} ROMe_2GeH \qquad (6)$$

(1) **(7a–d)**

(R = Me (**a**), $CHMe_2$ (**b**), CH_2Ph (**c**), Ph (**d**))

Compounds **7a–c** are stable only in solution, even gentle evaporation of the solvent resulted in complete decomposition [11], eqn. (7), in a reaction resembling the well-known α-elimination leading to carbenes (or carbenoids) [10,11,14].

$$Me_2GeH(OR) \xrightarrow[-ROH]{} [Me_2Ge] \longrightarrow \underset{(1)}{} \; 1/n(Me_2Ge)_n \qquad (7)$$

(2)

Only the phenol derivative **7d** is stable. In this case, reaction (6) occurs even without the presence of silica gel; this may be associated with the higher reactivity of the phenolic O–H bond ($pK_a = 9.95$) compared with, *e.g.* the EtO–H bond ($pK_a \approx 17$).

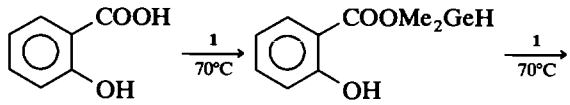
Subsequently, we obtained stable products from the insertion into the more acidic O–H bonds of carboxylic acids, (eqn. (8)). With R = cyclohexyl ($pK_a \approx 5.0$), **8a** was isolated, and underwent α-elimination analogous to that in eqn. (7) only at about 100°C. The product **8b** derived from PhCOOH ($pK_a = 4.22$), could be distilled at 95°C without decomposition.

$$Me_2Ge + RCOOH \longrightarrow RCOOMe_2GeH \qquad (8)$$

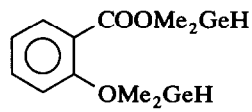
(1) **(8a,b)**

(R = Cyclohexyl (**a**), Ph (**b**))

Again, the more acidic O–H bond gives the more stable insertion product. A further instructive example is provided by the reaction with salicylic acid, eqn. (9). Insertion of one equivalent of **1** into the carboxylic group ($pK_a = 4.2$) yields exclusively **8c**, whereas use of an excess of **1** leads also to insertion into the phenolic group, ($pK_a = 9.95$), to give **8d**.



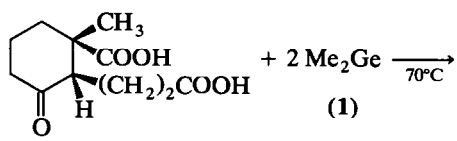
(8c)

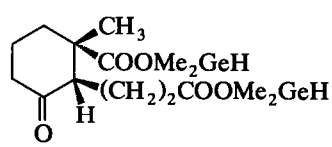


(9)

(8d)

This type of insertion to give acyloxygermanium hydrides seems to be widely applicable and is of potential interest as a route to biologically active germanium compounds [15]. This is demonstrated by the reaction of a ketodicarbonic acid, which is important in the synthesis of vitamin D_3 [16], which gives **8e**, as shown in eqn. (10).





(10)

(8e)

To examine the behaviour of a rather different type of species containing an acidic O–H bond, we generated **1** in the presence of acetophenone oxime, and observed a smooth insertion to give **9**, eqn. (11), which was unequivocally identified spectroscopically.

$$PhMeC{=}NOH + Me_2Ge \xrightarrow[70°C]{} PhMeC{=}NOMe_2GeH \qquad (11)$$

(1) **(9)**

2.3. Insertions into S–H bonds of H_2S and thiols

If the conventional cycloreversion to generate **1** is carried out at 70°C in dry chlorobenzene saturated with a steady stream of H_2S, only polygermanes **2** are formed. If, however, an equimolar amount of 18-crown-6 is present, polygermanes are no longer detected; **1** is completely converted by H_2S into tetramethyldigermathiane **10** and a small amount of **3**, as a result of the presence of some water that could not be removed from the 18-crown-6, eqn. (12). The germathiane was readily isolated, and found to be identical to a sample prepared by a different method [17].

$$Me_2Ge + H_2S \xrightarrow[70°C]{\text{18-crown-6}}$$

(1)

$$HMe_2GeSGeMe_2H + HMe_2GeOGeMe_2H \quad (12)$$

(10) (3)

We conclude that the low concentration of H_2S allows no insertion of the short-lived **1**, so that the very rapid polymerization of the latter to give **2** predominates. The influence of 18-crown-6, which is a very strong electron donor, can be understood in terms of the reversible formation of an intermediate complex $Me_2Ge \cdot$ 18-crown-6 (Section 2.7), which increases the average lifetime of **1**, and permits the insertion into the S–H bond.

The more acidic S–H bond of thiophenol ($pK_a = 6.5$) easily inserts Me_2Ge **1** (eqn. (13)) as was expected from experience with acidic O–H bonds. The phenylthiogermanium hydride **11** was isolated and identified. No **2** was detected, indicating that the normally rapid polymerization of **1** does not take place [18*].

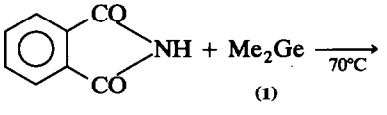
$$PhSH + Me_2Ge \xrightarrow[70°C]{} PhSMe_2GeH \quad (13)$$

(1) (11)

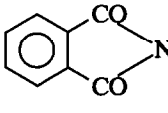
2.4. Insertions into N–H bonds

Even in the presence of 18-crown-6 we could not detect any insertion of **1** into the N–H ($pK_\alpha \approx 35$) bonds of ammonia. As usual, small amounts of **3** were formed, but almost all of **1** was converted into **2**.

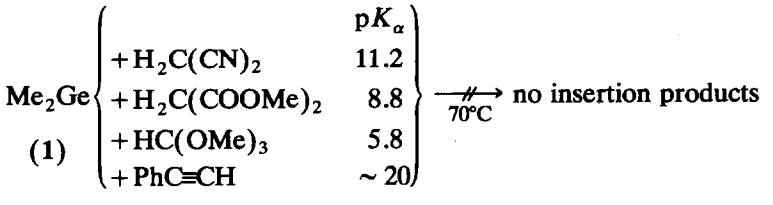
With the acidic N–H bond of phthalimide ($pK_a = 9.8$), however, we observed formation of the insertion product **12**, eqn. (14). This was identified unequivocally in the reaction solution by spectroscopic means, but was rather unstable, and decomposed when we tried to isolate it.



(1)



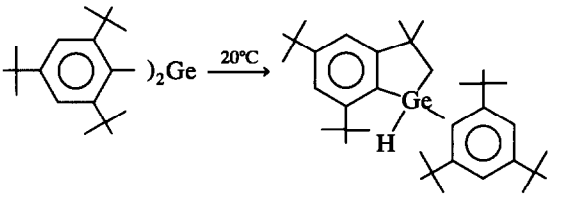
(12) (14)



Scheme 1.

2.5. Attempted insertions into acidic C–H bonds

An intramolecular insertion of a germylene into a C–H bond has been described previously [3,19]. Much of the strain in this germylene (which is kinetically stable at low temperatures), is relieved by insertion into a non-acidic C–H bond at 20°C, eqn. (15).



(15)

We were not able to find any other examples involving acidic C–H bonds (see Scheme 1). In no case was an insertion observed. Brönsted acidity, which played an important role in the behaviour of O–H, S–H, or N–H bonds as reported above, is evidently not the only feature of importance for an insertion of **1**. As is seen in Scheme 1, even malonic ester ($pK_a = 8.8$) and methyl orthoformate ($pK_a = 5.8$), do not react with **1**. π-electrons of phenylacetylene also do not lead to activation of the C–H bond. No insertion of a germylene into vinylic C–H bonds has ever been observed [3].

We conclude that the insertion of **1** into an H–C bond (X = C, N, O, S) occurs only if X is a strong donor containing free electron pairs, as for X = N, O, or S, and the acidity is of secondary importance [20*,21]. Pre-complexation of **1** to X is indicated, where X is the donor, and Me_2Ge **1** is the acceptor. This is discussed in Section 2.7.

2.6. The new germanium hydrides $RXMe_2GeH$ in hydrogermylation

One of the reasons for the present investigation was to address the question of whether insertion products of **1** into O–H, S–H, or N–H bonds could be actual intermediates in the surprising additions to unsaturated systems, as exemplified in eqn. (1) [4] in the Introduction.

Thus, we exposed the hydrides $RXMe_2GeH$, prepared as described in Sections 1–4, to olefins, 1,3-dienes and alkynes under the conditions that led to

reactions such as those in eqns. (1), (18) or (19) at 70°C or 110°C (Scheme 2).

The features of the facts presented in Scheme 2 are as follows: Hydrogermylations do not take place with the new germanium hydrides under the conditions used, except that $PhSMe_2GeH$ gives the adducts **18a–c**. One of the questions raised in the introduction in connection with reactions of the type shown in eqn. (1) was: Is there an actual initial insertion of Me_2Ge **1** into an O–H bond, and then a hydrogermylation by $ROMe_2GeH$? The answer is no. Thus the germylene follows other routes to the products observed with alkenes and alkynes in the presence of water, ROH, or RCOOH [3,4,22] as discussed below.

2.7. *Complexation of germylenes by donor molecules*

In all cycloadditions investigated so far, Me_2Ge **1** clearly behaved as a nucleophile, interacting by means of its HOMO, containing the singlet electron pair, with the LUMO of the diene [3,23]. On the other hand, it can also be expected to react as an electrophile, using its empty p-orbital; reactions of other germylenes with azides, for example, are viewed in this way [3,21,24]. (Interactions of germylenes with donors were discussed some years ago by J. Satgé *et al.* [10].) Strong spectroscopic evidence for this concept was obtained by W. Ando *et al.* by matrix techniques [25]. The long-wave absorptions of five typical germylenes are, in general,

$$O(Me_2GeH)_2 \left\{ \begin{matrix} +XHC{=}CHY \\ +XHC{=}CHY \\ +XHC{=}CHY \end{matrix} \right\} \xrightarrow[4\ h,\ 70°C]{} \text{no products}$$

(3)

(X, Y = H, CN; H, COOMe; 2 × COOMe [a])

$$\left.\begin{matrix} Me_2CHOMe_2GeH \\ MeOMe_2GeH \\ PhCH_2OMe_2GeH \end{matrix}\right\} + H_2C{=}CHCN \xrightarrow[10\ h,\ 70°C]{} \text{no products}$$

$$\left.\begin{matrix} PhOMe_2GeH \\ PhOMe_2GeH \\ PhMeC{=}NOMe_2GeH \end{matrix}\right\} + H_2C{=}CHCN \begin{cases} \xrightarrow[10\ h,\ 70°C]{} \text{no products} \\ \xrightarrow[4\ h,\ 70°C]{AIBN} \text{slow decomposition} \\ \xrightarrow[4\ h,\ 70°C]{} \text{no products} \end{cases}$$

$$PhSMe_2GeH + XHC{=}CHY \xrightarrow[4\ h,\ 70°C]{} PhSMe_2GeCHXCH_2Y$$

(18a–c)

(X, Y = H, CN (**a**); H, COOMe (**b**); 2 × COOMe (**c**))

$$\mathbf{3} + Ph{-}\!\!\diagup\!\!\diagdown{-}Ph \xrightarrow[70°C]{} \text{no cycloaddition [b]}$$

$$PhCOOMe_2GeH + \left\{ \begin{matrix} NC{-}\!\!\diagup\!\!\diagdown{-}CN \\ MeOOC{-}\!\!\diagup\!\!\diagdown{-}COOMe \\ Ph{-}\!\!\diagup\!\!\diagdown{-}Ph \\ \begin{matrix} Ph \\ \diagdown \\ Me{-}\!\!\diagup \end{matrix} \end{matrix} \right\} \xrightarrow[70°C\ \text{or}\ 100°C]{PhH\ \text{or}\ PhCl} \text{no cycloaddition [b]}$$

$$ROMe_2GeH + R'C{\equiv}CH \xrightarrow[4\ h,\ 7°C]{} \text{no products}$$

(R = Ph, PhCO, $C_6H_{11}CO$; R′ = Ph,COOMe)

[a] In the presence of water, **1** gives products of the type shown in eqn. (1) [3,4].

[b] On its own **1** undergoes cheletropic 1,4-cycloadditions to these 1,3-dienes [3,5].

Scheme 2.

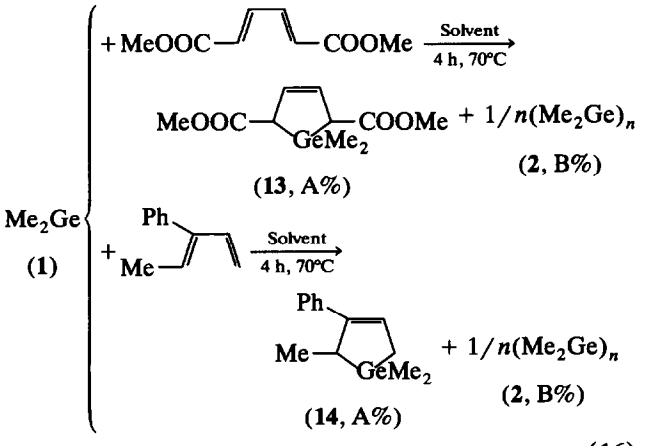
TABLE 1

R_2Ge,R = matrix–solvent	λ_{max} in matrix at 77 K [25], nm					Yields of cycloadducts **13** and **14** (A%) with **1** *vs.* polygermane **2** (B%) from eqn. (16) at 343 K			
	Me	Ph	Mesityl	2,6-$Et_2C_6H_3$	2,4,6-$^iPr_3C_6H_2$	Me, **13**, A	**2**, B	Me, **14**, A	**2**, B
Free 3-Me-pentane	420	466	550	544	558	–	–	–	–
Free Benzene	–	–	–	–	–	80	20	76	24
Free Cyclohexane	–	–	–	–	–	–	–	77	23
PhCl	392	403	538	532	553	–	–	76	24
1,4-$Cl_2C_6H_4$	–	–	–	–	–	71	29	–	–
Cyclohexyl-Cl	341	374	495	508	544	66	34	57	43
Dioxane : Benzene 1 : 10	–	–	–	–	–	–	–	74	–
Dioxane : Benzene 1 : 1	–	–	–	–	–	–	–	60	–
Dioxane pure	–	–	–	–	–	–	–	37	63
2-MeTHF	–	325	360	369	376	33	67	–	–
H_4-Thiophene	–	332	352	359	366	–	–	–	–
$HC(CH_2CH_2)_3N$	–	334	349	356	363	–	–	–	–
Me_2S	–	326	348	357	357	–	–	–	–
EtOH [a]	–	320	333	332	–	–	–	–	–
Bu_3P	–	–	306	314	334	–	–	–	–
Ph_3P (in benzene)	–	–	–	–	–	< 30	> 70	–	–
18-Crown-6 (in benzene)	–	–	–	–	–	–	–	0	100 [b]

[a] Insertion into the H–O bond does not happen at this low temperature.
[b] Including 50% **3** caused by moisture in 18-crown-6.

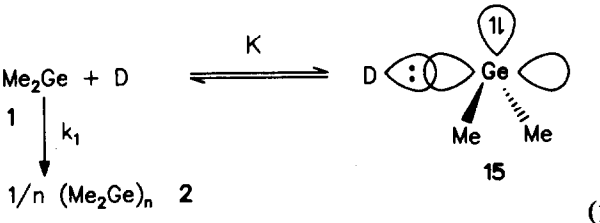
markedly shifted to shorter wavelengths with increasing strength of the donor with which it can interact (Table 1).

The well-known cycloaddition of free Me_2Ge **1** to 1,3-dienes [3] is inhibited by donors in essentially the same sequence as we have now observed. The quantitative results from two test systems, eqn. (16), shown in Table 1, imply that strong donor interaction lowers the reactivity of Me_2Ge toward the diene; the formation of polygermanes **2**, which involves practically no activation energy [3], is thus favoured.



(16)

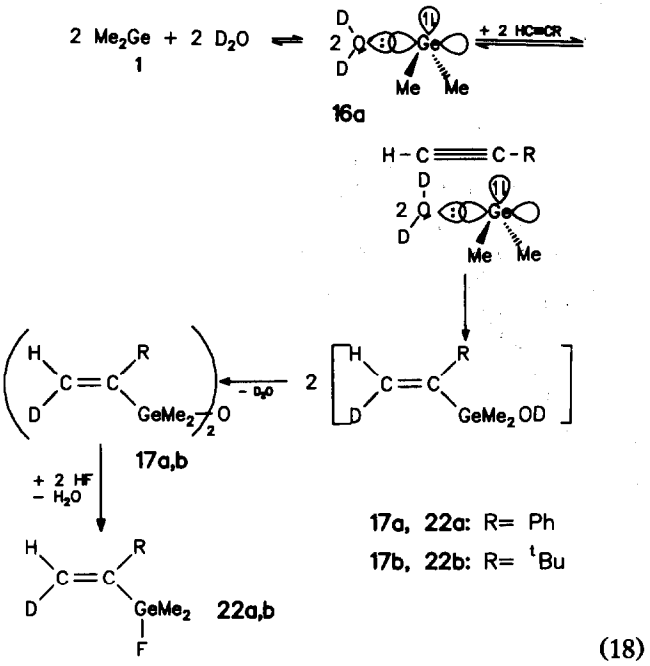
Considering together the spectroscopic data [25] and the dependence of the chemical influence of solvents on their donor strength implies a complexation of the free germylene with donors (see eqn. (17)). The lifetime of **15** and the equilibrium constant K depend on the strength of the donor. From Table 1, it can be seen for example, that the chlorine in cyclohexyl chloride is a stronger donor than that in chlorobenzene as would be expected.



(17)

The very rapid polymerization of **1** to give **2**, step k_1 in eqn. (17), should be increasingly slowed down as the donor strength of D is increased. Thus the adducts, **15**, must be considered to be real intermediates in the reactions of **1** in the presence of donors. As outlined in Sections 2.1 and 2.2, the insertions of **1** into O–H bonds are not very fast, and so, active reagents, such as certain 1,3-dienes, can successfully compete with the insertion. (It has been shown in Section 2.6 that the final insertion products are inert toward alkenes and 1,3-dienes.) Thus, donor complexes **15** of **1** with H_2O, ROH, RCOOH *etc.* must also be considered as real reaction intermediates.

This conclusion provides a satisfactory interpretation of the surprising *syn*-additions of an H (or D) atom and a germyl moiety to alkynes, that we have clearly demonstrated, but we cannot yet satisfactorily account for the exclusive stereoselectivity in the formation of the products **17a,b** **22a,b** and **19** respectively

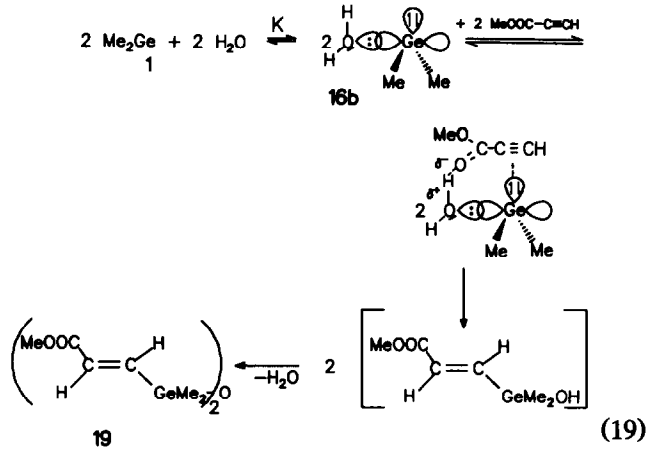


(18)

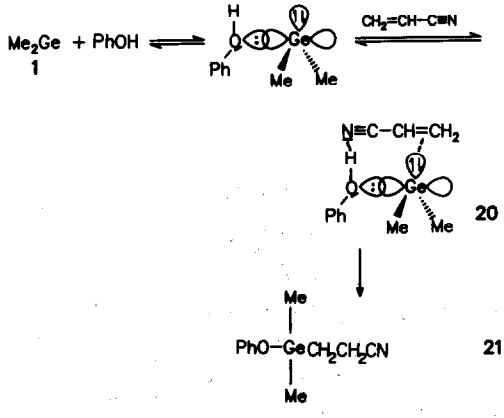
[4,26], (eqns. (18) and (19)). What is certain is that without water or D_2O present, either other or no products are formed.

In the light of the above reasoning, we conclude that complexes of **1** with D_2O **16a** or H_2O **16b**, rapidly formed as in eqn. (17), are real intermediates. They ultimately stereoselectively form, perhaps *via* a transient germirene, the vinyl compounds **17** or **19** respectively. The intermediates, **17a,b**, were in addition identified by their reaction with HF [26], eqn. (18).

The complete, but inverse regioselectivity depicted in eqns. (18) and (19) may be understood in terms of interaction with the carbonyl group as shown in eqn.



(19)



(20)

(19), but further investigation of this point is in progress, including HMO as well as experimental methods.

In extension of our previous mechanistic proposals [3,4], we now regard complexes of type **15** as the intermediates **20** in the additions of **1** to alkenes such as acrylonitrile or acrylic esters. Transient generation of germirane from **20** must also be considered. Ultimately, stable adducts, for example **21**, in eqn. (20), are formed.

3. Experimental details

For general experimental and analytical details see ref. 1. The precursor for **1**, the 7,7-dimethyl-7-germanorbornadiene [3,5], is denoted below by **A**, and 1,2,3,4-tetraphenyl-naphthalene by TPN.

3.1. 1,1,3,3,-Tetramethyldigermoxane, 3

To a solution of **A** (1.1 g, 2.0 mmol) in 20 ml of chlorobenzene was added 10 ml of water. The well-stirred mixture was heated for 40 min at 110°C then allowed to cool to room temperature. The yield of **3** was shown by ^1H NMR spectroscopy to be 90%. Volatiles were evaporated off at 0.001 torr, but attempts to fractionate the products resulted only in a concentration of **3** in chlorobenzene; b.p. 114–119°C/760 torr. The analytical data are in accordance with literature values [6]. Similar results were obtained when bromobenzene was used instead of chlorobenzene. When a solution of **A** (0.05 g, 0.1 mmol) and wet 18-crown-6 (0.35 g, 1.0 mmol) in 1 ml of benzene was stirred for 4 h at 70°C, **3** was formed in 50% yield. The volatiles were evaporated off, and **A** (0.05 g, 0.01 mmol) is added. Thermolysis (4 h, 70°C) yielded 100% of **2**, **3** remained unchanged.

A (0.05 g, 0.1 mmol) was dissolved in 1 ml 1,2-dichlorobenzene and water (0.5 ml) was added. After stirring for 4 h at 70°C, 80% of **3** was formed. When a water-

saturated solution of 1,2-dichlorobenzene was used, **2** was formed quantitatively.

3.2. 1,3-Dideutero-1,1,3,3-tetramethyldigermoxane, 5 and 1-deutero-3-(deuterodimethylgermyl)-1,1,3,3-tetramethyldigermoxane, 6

To a solution of **A** (2.0 g, 3.7 mmol) in 25 ml 1,2-dichlorobenzene were added 8 ml D_2O. The well-stirred mixture was heated for 4 h at 70°C then allowed to cool to room temperature. The ratio of **2** to (**5** + **6**) was shown to be 1:1 (^{1}H NMR). The mixture of **5**, **6** and 1,2-dichlorobenzene was evaporated at 0.001 torr. ^{1}H NMR (*o*-$C_6H_4Cl_2$, 60 MHz): δ −0.01 (s, $GeCH_3$ (**5** + **6**)). IR (KBr): (GeD) 2030(s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (relative intensity) **5**: 224 (17, $M^+ - D$), 209 (48, $M^+ - D\text{-}Me$), 119 (100, Me_3Ge^+), 106 (22, Me_2GeD^+), 89 (33, $MeGe^+$); **6**: 328 (24, M^+), 313 (17, $M^+ - Me$), 224 (100, $M^+ - MeGeD$), 119 (87, Me_3Ge^+), 106 (58, Me_2GeD^+) 89 (60, $MeGe^+$).

3.3. Reaction of A in the presence of a 1,3-diene and water

Heating of a mixture of **A** (0.05 g, 0.1 mmol), *E*-1-Ph-2-Me-butadiene-1,3 (0.04 g, 0.3 mmol), H_2O (0.50 ml, 28 mmol) and chlorobenzene (1 ml) at 110°C for 40 min gave (like the analogous procedure in the absence of water) to the known mixture [3,11] of germacyclopentene (40%) and -pentane (less than 20%).

The analogous reaction of *E,E*-1,4-dicyano-butadiene-1,3 (0.03 g, 0.3 mmol) (amounts of **A**, H_2O and chlorobenzene as above) yielded 100% of the 1,4-cycloadduct in the absence of water, and 20% in its presence (80% of **2**).

The analogous reaction of *E,E*-1,4-Ph_2-butadiene (0.2 g, 0.1 mmol) yielded 90% of **3**, the diene remaining unchanged.

3.4. Methoxydimethylgermane, 7a

In an NMR tube, a mixture of **A** (50 mg, 0.093 mmol), SiO_2 (25 mg) and methanol (10 μl, 0.28 mmol) was heated with 1 ml of C_6D_6 for 4 h at 70°C. ^{1}H NMR: δ 0.24, (d, 6H, ^3J(HH) = 2.3 Hz, $GeCH_3$), 3.30 (s, 3H, CH_3), 5.20 (spt, 1H, ^3J(HH) = 2.3 Hz, GeH). IR (benzene): (Ge–H) 2048(m) cm^{-1}.

3.5. Isopropoxydimethylgermane, 7b

This was prepared from **A** (50 mg, 0.093 mmol), SiO_2 (25 mg) and isopropanol (20 μl, 0.28 mmol) in 1 ml of benzene, as described for **7a**. ^{1}H NMR: δ 0.20 (d, ^3J(HH) = 2.3 Hz, $GeCH_3$). IR (chlorobenzene): (Ge–H) 2048(m) cm^{-1}.

3.6. Benzyloxydimethylgermane, 7c

This was similarly prepared from **A** (50 mg, 0.093 mmol), SiO_2 (25 mg) and benzyl alcohol (30 μl, 0.28 mmol) in 1 ml of benzene. ^{1}H NMR: δ = 0.13 (d, 6H, ^3J(HH) = 4.0 Hz, $GeCH_3$), 4.63 (s, 2H, CH_2). IR (benzene): (Ge–H) 2042(m) cm^{-1}.

3.7. Dimethylphenoxygermane, 7d

Phenol (1.0 g, 11 mmol) was added to a solution of **A** (2.0 g, 3.7 mmol) in 25 ml of benzene and the mixture was stirred for 4 h at 70°C then allowed to cool to room temperature. The solution was evaporated to dryness (15 torr) and the residue dissolved in $CDCl_3$. ^{1}H NMR ($CDCl_3$): δ 0.75 (d, 6H, ^3J(HH) = 2.5 Hz, $GeCH_3$), 5.98 (spt, 1H, ^3J(HH) = 2.5 Hz, GeH), 6.9–7.2 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ −0.52 (C_p, $GeCH_3$), 120.67, 125,33, 134.97, (C_t, Ph), 155.28 (C_q, Ph). GC-MS (EI, 70 eV): *m/z* 198 (88, M^+), 183 (75, $M^+ - Me$), 167 (59, $M^+ - Me_2H$), 105 (71, Me_2GeH^+), 94 (100, $PhOH^+$), 89 (40, $MeGe^+$), 77 (61, Ph^+). IR (CCl_4): (Ge–H) 2064(s) cm^{-1}.

3.8. Cyclohexanecarboxylic acid dimethylgermyl ester, 8a

Cyclohexylcarboxylic acid (0.12 g, 0.93 mmol) was added to a solution of **A** (0.50 g, 0.93 mmol) in 10 ml of benzene. The mixture was stirred for 4 h at 70°C, then filtered and evaporated to dryness (15 torr). The residue was treated with 10 ml of cold pentane [5] and the residue of TPN was filtered off and washed with 5 ml of cold pentane. The pentane filtrate was concentrated to yield **8a** as a colourless oil (180 mg, 85%). ^{1}H NMR (C_6D_6): δ 0.63 (d, 6H, ^3J(HH) = 2.3 Hz, $GeCH_3$), 1.0–1.8 (m, 11H, Cyclohexyl-H), 5.8 (spt, 1H, ^3J(HH) = 2.3 Hz, GeH). ^{13}C NMR (C_6D_6): δ −0.01 (C_p, $GeCH_3$), 25.54, 26.00, 29.05 (C_s, Cyclohexyl-CH_2), 43.16 (C_t, Cyclohexyl-CH), 182.60 (C_q, C = O). IR (KBr): (Ge–H) 2120(s) cm^{-1}.

3.9. Benzoic acid dimethylgermyl ester, 8b

This was prepared from **A** (2.0 g, 3.7 mmol) and benzoic acid (0.90 g, 7.4 mmol) in 20 ml of benzene, as described for **8a**. Kugelrohr distillation (95°C/0.1 torr) yielded **8b** as a colourless oil (0.90 g, 60%). ^{1}H NMR ($CDCl_3$): δ 0.81 (d, 6H, ^3J(HH) = 2.5 Hz, $GeCH_3$), 5.93 (spt, 1H, ^3J(HH) = 2.5 Hz, GeH), 7.23–7.60 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 0.00 (C_p, $GeCH_3$), 128.36, 130.19, 132.76 (C_t, Ph), 131.63 (C_q, Ph), 169.79 (C_q, C = O). IR (KBr): (C=O) 1680(s), (Ge–H) 2100(s) cm^{-1}. MS (EI, 70 eV): *m/z* 226 (26, M^+), 211 (24, $M^+ - Me$), 196 (5, $M^+ - 2\,Me$), 122 (77, $M^+ - Me_2Ge$), 105 (100, $PhCO^+$), 89 (8, $MeGe^+$).

3.10. o-Hydroxybenzoic acid dimethylgermyl ester, 8c

This was prepared from **A** (0.50 mg, 0.93 mmol) and salicyclic acid (130 mg, 0.93 mmol) in 10 ml benzene, analogously to **8a**. Viscous colourless oil (74%, 160 mg). ^{1}H NMR (C_6D_6): δ 0.25 (d, 6H, ^3J(HH) = 2.5 Hz,

$GeCH_3$), 5.70 (spt, 1H, ^3J(HH) = 2.5 Hz, GeH), 6.9–7.4 (m, 4H, Ph), 5.4 (s, 1H, OH). ^{13}C NMR (C_6D_6): δ −0.74 (C_p, $GeCH_3$), 127.65, 127.97, 131.25, 132.55 (C_t, Ph), 138.92, 140.80 (C_q, Ph), 162.57 (C_q, C=O). IR (KBr): (Ge–H) 2095(s) cm^{-1}. MS (EI, 70 eV): *m/z* 226 (11, $M^+ - 15$), 135 (23, $M^+ - GeMe_2H$), 119 (65, $GeMe_3$), 105 (100, $GeMe_2$), 89 (10, GeMe).

3.11. o-(Dimethylgermanoxy)benzoic acid dimethylgermyl ester, 8d

This was prepared analogously to **8c** with 1.0 g **A** (1.9 mmol). Viscous, colourless oil (206 mg, 65%). ^{1}H NMR (C_6D_6): δ 0.25 (d, 6H, ^3J(HH) = 2.5 Hz, $GeCH_3$), 0.31 (d, 6H ^3J(HH) = 2.4 Hz, $GeCH_3$), 5.7 (2 x spt, 2H, GeH), 6.9–7.3 (m, 4H, Ph). ^{13}C-NMR (C_6D_6): δ −0.65 (C_p, $GeCH_3$), −0.26 (C_p, $GeCH_3$), 127.55, 127.89, 131.7, 133.02 (C_t, Ph), 139.61, 141.2 (C_q, Ph), 164.20 (C_q, C=O). IR (KBr): (Ge–H) 2090(s), (GeH) 2105(s) cm^{-1}. An MS analysis was not possible because of complex thermolysis of **8d** at the very high temperature required.

3.12. 2'(R),3'(S)-3-[3'-carboxylic acid dimethylgermyl ester-3'-methyl-cyclohexane-1'-one-2'-yl]-propanoic acid dimethylgermyl ester, 8e

This was prepared from **A** (0.5 g, 0.9 mmol) and the ketodicarbonic acid (107 mg, 0.47 mmol) as described for **8a**. Viscous, colourless oil (175 mg, 86%). ^{1}H NMR (C_6D_6): δ 0.55 (d, 6H, ^3J(HH) = 2.5 Hz, $GeCH_3$), 0.62 (d, 6H, ^3J(HH) = 2.5 Hz, $GeCH_3$), 0.90 (s, 3H, CH_3), 1.60–2.25 (m, 7H, Cyclohexyl-H), 5.8 (2 x spt, 2H, ^3J(HH) = 2,5 Hz, GeH). ^{13}C NMR (C_6D_6): δ 0.20 (C_p, $GeCH_3$), 0.25 (C_p, $GeCH_3$), 16.45 (C_q, CH_3), 21.46, 22.82 (C_s, Cyclohexyl-C), 34.53 (C_s, CH_2), 36.65 (C_s, Cyclohexyl-C), 41.13 (C_s, CH_2CO_2), 51.66 (C_q, C-CH_3), 55.30 (C_t), 175.16 (C_q, C=O), 177.60 (Cq, C=O), 210.43 (C_q, C=O). IR (KBr): (Ge–H) 2110(s), (Ge–H) 2120(s) cm^{-1}. MS (EI, 70 eV): *m/z* 434 (3, M^+), 419 (11, $M^+ - Me$), 375 (6, 419-$CO)_2$), 287 (60, M^+-CO_2GeMe_2H), 137 (59, $M^+ - 2CO_2$-2GeMeH), 119 (25, $GeMe_3$), 105 (100, $GeMe_2$), 89 (26, GeMe).

3.13. Acetophenonoximatodimethylgermane, 9

A solution of **A** (1.0 g, 1.9 mmol) and acetophenone oxime (0.90 g, 6.7 mmol) in 20 ml of benzene was stirred for 4 h at 70°C then allowed to cool to room temperature. The volatiles were evaporated off under reduced pressure (15 torr), and Kugelrohr distillation of the residue gave a fraction of 1.1 g (90°C/0.02 torr) that contained 30 mol % of **9**. (^{1}H NMR) along with acetophenone oxime. ^{1}H NMR ($CDCl_3$): δ 0.54 (d, 6H, ^3J(HH) = 2.5 Hz, $GeCH_3$), 2.16 (s, 3H, CH_3), 5.71 (spt, 1H, ^3J(HH) = 2.5 Hz, GeH). ^{13}C NMR ($CDCl_3$): δ −0.93 (C_p, $GeCH_3$), 11.93 (C_p, CH_3), 126.10, 128.11, 129.03 (C_t, Ph), 139.77 (C_q, Ph), 156.74 (C_q, C=N). IR (CCl_4): (Ge–H) 2068(s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (relative intensity) 238 (20, $M^+ - H$), 118 (100, $M^+ - OGeMe_2H$), 105 (44, $GeMeO^+$), 77 (70, Ph^+).

3.14. 1,1,3,3-Tetramethyldigermathiane, 10

A steady stream of H_2S was passed through a solution of **A** (0.5 g, 1.0 mmol) and 18-crown-6 (0.30 g, 1.0 mmol) in 5 ml of benzene for 4 h at 70°C. Compounds **3** and **10** were formed in 25% and 75% yield. The volatiles were evaporated off (20°C/0.001 torr) and condensed in a cooling trap. The distillate was fractionated at 20°C/15 torr yielding 65% (0.15 g, 0.6 mmol) of **10**. The analytical data are in accordance with those in the literature [17]. Attempts to prepare **10** analogously from **A** (0.5 g, 1 mmol) and H_2S in 5 ml chlorobenzene resulted in quantitative formation of **2**.

3.15. Reaction with gaseous ammonia

A steady stream of NH_3 was passed through a solution of **A** (0.5 g, 1 mmol) and 18-crown-6 (0.3 g, 1 mmol) in 5 ml of benzene or 1,2-dichlorobenzene for 4 h at 70°C (0.5 h at 160°C). Compound **2** was formed quantitatively in both cases.

3.16. Dimethyl-thiophenolato-germane, 11

A solution of **A** (1.0 g, 1.9 mmol) and thiophenol (0.5 ml, 4.8 mmol) in 20 ml of benzene was stirred for 4 h at 70°C then allowed to cool to room temperature. The volatiles were evaporated at reduced pressure (15 torr), and Kugelrohr distillation of the residue yielded **11** (0.21 g, 52%) as a colourless oil; b.p. 130°C/15 torr. Anal. Found: C, 44.5; H, 6.1. $C_8H_{12}GeS$ calc.: C, 45.16; H, 5.64%. ^{1}H NMR ($CDCl_3$): δ 0.54 (d, 6H, ^3J(HH) = 2.9 Hz, $GeCH_3$), 5.08 (spt, 1H, ^1J(HH) = 2.9 Hz, GeH), 7.2–7.4 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): −0.69 (C_p, $GeCH_3$); 126.41, 128.73, 134.23 (C_t, Ph), 133.51 (C_q, Ph). IR (KBr): (Ge–H) 2054(s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (relative intensity) 213 (71, $M^+ - H$), 199 (13, $M^+ - Me$), 183 (75, $M^+ - C_2H_7$), 121 (58, $MeGeS^+$), 105 (100% Me_2GeH), 77 (62, Ph^+).

3.17. Dimethyl-phthalimido-germane, 12

Attempts similar to those used for **11** were used to isolate **12** prepared from **A** (1.0 g, 1.9 mmol) and phthalimide (0.60 g, 4.1 mmol) in 20 ml of benzene and resulted in complete decomposition. NMR spectra of the crude reaction solution show the formation of about 60% of **12**. ^{1}H NMR: δ 0.48 (d, 6H, ^3J(HH) = 2.9 Hz, $GeCH_3$), δ = 5.40 (spt, 1H, ^3J(HH) = 2.9 Hz, GeH). IR (benzene): (Ge–H) 2010(s) cm^{-1}.

3.18. Bis-[Z-(β-deuterostyryl-α-dimethylgermanium)]oxid, 17a

To a solution of **A** (1.0 g, 1.9 mmol) in 5 ml of benzene was added phenylacetylene (0.2 g, 1.9 mmol) and D_2O (35 μl, 2.0 mmol). The mixture was stirred for 4 h at 70°C then allowed to cool to room temperature. The organic layer was separated from D_2O, dried over $MgSO_4$ and evaporated to dryness. The residue was washed to leave behind the TPN, as described for the preparation of **8a**, and the filtrate was concentrated. Distillation (140°C, 0.01 torr) yielded **17a** as a colourless oil (0.32 g, 79%). ^1H NMR ($CDCl_3$): δ 0.45 (s, 6H, $GeCH_3$), 5.97 (s, 1H, HC=), 7.25 (m, 5H, Ph). GC/MS: *m/z* (relative intensity) 430 (7, M^+), 415 (8, $M^+ - Me$), 326 (32, $M^+ - PhC_2HD$), 192 (100, $GeC_8H_6O^+$), 119 (61, $GeMe_3^+$), 105 (86, $GeMeO^+$), 104 (21, PhC_2HD^+), 89 (12, $GeMe^+$).

3.19. Bis-[Z-(2-deutero-1-tert-butylethenyl-1-dimethylgermanium)]oxide, 17b

This was prepared from **A** (1.0 g, 1.9 mmol), neohexyne (1.0 g, 12.2 mmol) and D_2O (35 μl, 2.0 mmol) as described for **17a**. Distillation (160°C, 0.01 torr) yielded **17b** as a colourless oil (0.32 g, 86%). ^1H NMR (CCl_4): δ 0.32 (s, 6H, $GeCH_3$), 1.02 (s, 9H, ^tBu), 5.43 (s, 1H, HC=). GC/MS: *m/z* (relative intensity) 390 (2, M^+), 375 (71, $M^+ - Me$), 306 (29, $M^+ - C_6H_{10}D$), 223 (73, $C_4H_{13}OGe_2^+$), 207 (100, $Ge_2Me_3O^+$), 188 (14, $GeC_8H_{16}D^+$), 173 (9, $C_7H_{13}DGe^+$), 119 (89, $GeMe_3^+$), 105 (20, $GeMeO^+$), 89 (10, $GeMe^+$), 84 (95, $C_6H_{10}D^+$).

3.20. (2-Cyanoethyl)(dimethyl)(thiphenolato)germane, 18a

A solution of **A** (1.0 g, 1.9 mmol), acrylonitrile (0.40 ml, 6.1 mmol) and thiophenol (0.50 ml, 4.9 mmol) in 20 ml of benzene was stirred for 4 h at 70°C then allowed to cool to room temperature. The volatiles were evaporateds off under reduced pressure (15 torr). As described for **8a**, the residue was washed with cold pentane to remove the TPN and the pentane solution was concentrated. Kugelrohr distillation of the residue yielded **18a** (0.41 g, 80%) as a colourless oil; b.p. 150°C/0.02 torr. Anal. Found: C, 49.5; H, 5.5; N 5.2 $C_{11}H_{15}GeNS$ calc.: C, 49.68, H, 5.65, N, 5.27%. ^1H NMR ($CDCl_3$): δ 0.48 (s, 6H, $GeCH_3$), 1.24 (t, 2H, $^3J(HH) = 8.3$ Hz, $GeCH_2$), 2.40 (t, 2H, $^3J(HH) = 8.3$ Hz, CH_2CN), 7.2 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ −0.26 (C_p, $GeCH_3$), 12.44 (C_s, $GeCH_2$), 13.84 (C_s, CH_2CN), 120.17 (C_q, CN), 126.74, 128.64, 136.61 (C_t, Ph), 131.59 (C_q, Ph). GC-MS (EI, 70 eV): *m/z* (relative intensity) 267 (66, M^+), 213 (100, $M^+ - C_3H_4N$), 158 (43, $M^+ - SPh$), 109 (73, SPh^+).

3.21. (2-Methoxycarbonylethyl)(dimethyl)(thiophenolato)germane, 18b

This was prepared from **A** (1.0 g, 1.9 mmol), acrylic acid methylester (0.55 ml, 6.1 mmol) and thiophenol (0.5 ml, 4.9 mmol) in 20 ml of benzene as described for **18a**. Kugelrohr distillation yielded **18b** (0.38 g, 67%) as a colourless oil; b.p. 120°C/0.02 torr. ^1H NMR ($CDCl_3$): δ 0.40 (s, 6H, $GeCH_3$), 1.21 (t, 2H, $^3J(HH) = 8.1$ Hz, $GeCH_2$), 2.40 (t, 2H, $^3J(HH) = 8.1$ Hz, CH_2CO_2), 3.59 (s, 3H, OCH_3), 7.3 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ −0.14 (C_p, $GeCH_3$), 13.35 (C_s, $GeCH_2$) 28.95 (C_s, CH_2CO), 51.43 (C_p, OCH_3), 126.34, 128.44, 134.66 (C_t, Ph), 132.69 (C_q, Ph), 174.18 (C_q, CO). GC-MS (EI, 70 eV): *m/z* (relative intensity) 269 (4, $M^+ - OMe$), 191 (100, $M^+ - SPh$), 105 (19, $GeMeO^+$), 77 (10, Ph^+).

3.22. (1,2-Di-methoxycarbonylethyl)(dimethyl)(thiophenolato)germane, 18c

This was prepared from **A** ((1.0 g, 1.9 mmol), fumaric acid dimethylester (0.80 g, 5.5 mmol) and thiophenol (0.50 ml, 4.9 mmol) in 20 ml of benzene as described for **18a**. Kugelrohr distillation yielded **18c** (0.46 g, 70%) as a colourless oil; b.p. 130°C/0.01 torr. Anal. Found: C, 46.0; H, 5.6. $C_{14}H_{20}GeO_4S$ calc.: C, 47.1; H, 5.6%. ^1H NMR ($CDCl_3$): δ 0.45, 0.47 (each s, 6H, $GeCH_3$), 2.8 (m, 3H, CH_2, CH), 3.61, 3.64 (each s, 6H, OCH_3), 7.2–7.3 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ −0.91, −0.06 (C_p, $GeCH_3$), 31.30 (C_s, CH_2-CH) 34.00 (C_t, CH_2-CH), 51.47, 51.79 (C_p, OCH_3), 127.01, 128.72, 135.09 (C_t, Ph), 131.24 (C_q, Ph), 172.85, 173.71 (C_q, CO). GC-MS (EI, 70 eV): *m/z* (relative intensity) 249 (100, $M^+ - SPh$), 135 (14, $GeMe_3O^+$), 105 (15, $GeMeO^+$).

3.23. Z-(β-Deutero-α-(dimethylfluoro)germylstyrene), 22a

This was prepared from **17a** (0.32 g, 0.7 mmol) and HF (4 ml, HF/H_2O (40%)) in 10 ml of diethyl ether at 0°C. The mixture was stirred for 2 h at room temperature, then the organic layer was dried over $MgSO_4$ and evaporated to dryness to leave a colourless, viscous oil (0.38 g, 93%). ^1H NMR ($CDCl_3$): δ 0.69 (d, 6H, $^3J(HF) = 6.9$ Hz, $GeCH_3$), 6.08 (d, 1H, $^4J(HF) = 4.3$ Hz, HC=), 7.34 (m, 5H, Ph). GC/MS: *m/z* (relative intensity) 227 (6, M^+), 208 (17, $M^+ - F$), 123 (5, $GeMe_2F^+$), 104 (100, $GeMe_2^+$), 89 (4, $GeMe^+$), 77 (95, Ph^+).

3.24. Z-[1-Tert-butyl-1-(dimethylfluorogermyl)-2-deutero-ethene], 22b

This was prepared from **17b** (0.32 g, 0.82 mmol) and HF (4 ml HF/H_2O (40%)) as described for **22a**. Colourless oil (310 mg, 92%). ^1H NMR ($CDCl_3$): δ

0.43 (d, 6H, $^3J(HF) = 7.0$ Hz, $GeCH_3$), 0.93 (s, 9H, ^tBu), 5.50 (d, 1H, $^4J(HF) = 4.0$ Hz, HC=). GC/MS (EI, 70 eV): m/z (relative intensity) 207 (7, M^+), 192 (25, $M^+ - Me$), 187 (4, $M^+ - HF$), 172 (19, $M^+ - CH_3$-HF), 143 (2, $GeC_5H_7D^+$), 123 (23, $GeMe_2F^+$), 84 (20, $C_6H_{10}D^+$).

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