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Germylenes and Stannylenes

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Contents

I. Introduction

Stannylenes R_2Sn, the heavy analogues of carbenes R_2C, probably belong to the first organotin compounds ever prepared, more than 140 years ago.[1] But, chemists of those days were convinced that the term "existing" in connection with a chemical compound meant that the latter could fill a bottle. Short-lived intermediates of high reactivity had not become known in those days, and, moreover, chemical or spectroscopic means for detecting and identifying them still were lacking. What one had isolated was a mixture of polymers, more or less, with the average formula $(R_2Sn)_n$, regarded as "organic compounds of divalent tin". It was not earlier than the 1960's that distinct cyclic or open-chained penta-, hexa-, or polystannanes could be evidenced out of these mixtures and specific methods for their preparation and analysis could be developed. The electronic status of their Sn atoms was shown to be $5sp^3$ like in the "organic compounds of four-valent tin", and not $5s^25p^2$ which was postulated for a stannylene. But, this was, at first, the end of the stannylene chemistry.[1]

Surprisingly, at the same time first examples of rather exotic, but kinetically stable products of a real and monomer status R_2Sn became known, first of all E. O. Fischer's dicyclopentadienyltin.[2] Here, really two lone electrons (or a lone pair thereof) could be found at the tin atom. Others followed, but in every case the central, "divalent" tin atom was highly stabilized by electronic

Wilhelm P. Neumann, born 1926 in Würzburg, Bavaria (FRG), received his Dr. rer. nat. degree in 1952 from the University of Würzburg, having studied N-heterocyclic chemistry. Studies on the first isolation and identification of neurotoxins from snake and insect venoms followed. In 1955 he joined Karl Ziegler, the later Nobel Laureate, in the Max-Planck-Institut at Mülheim-Ruhr as research associate. He applied aluminum alkyls to organic synthesis which brought him into the organotin field. From 1960 to 1968 he studied, as Privatdozent, later apl. Professor, main-group organometallic and free-radical chemistry at the University of Giessen. In 1969 he took a Chair of Organic Chemistry of the University of Dortmund, organized the new chemistry building, became head of the department, and was occupied with time-wasting and nerve-racking practices of German universities of those days. Nevertheless, organotin chemistry went on, mainly with mechanistic and free-radical points of view, including also carbon-centered radicals. After some side-ventures into organosilicon and -mercury chemistry, organogermanium chemistry grew up. His interest in reactive intermediates led him to the heavy carbene analogues, the germylenes and stannylenes. Now, reactive intermediates of group 14 are applied to organic synthesis, including the development of polymer-supported organometallic reagents. Professor Neumann is author of a monograph, a number of reviews, and chapters in handbooks and has held many Main or Plenary Lectures in national and international meetings. If he is not doing chemistry, he enjoys family life, baroque music, mountain hiking, and gliding (see the photo above).

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or steric effects, or both. Anyway, the history of the stannylenes had been reopened, and many research groups have taken part in the recent and rapid development.[3]

Germanium is a latecomer in chemistry, discovered not earlier than 1886, and its chemistry became of general interest only because of its technical importance since 1948. Soon afterward the organic chemistry of germanium also started, which is broadening up rapidly at present, not least because of biological activities of certain organogermanium compounds.[4] Among the pioneers are the Professors M. Lesbre and J. Satgé at the University of Toulouse, France.[5] One of the sources of results in germylene chemistry, too, comes from there,[6] continuing until today.

Thus, one can speak of a "modern chemistry of germylenes and stannylenes", which takes advantage, of course, of the impressive development of carbene chemistry that had taken place meanwhile, as a part of the powerful progress in mechanistic organic chemistry of the last 25 years. Therefore, germylenes and stannylenes can be regarded as heavy carbene analogues within the family R_2M, M = C, Si, Ge, Sn, Pb.

But, we are faced with all the problems and questions discussed so extensively in carbene[7] and silylene[8] chemistry, such as:

—How free are the particles, and are there real reactive intermediates, R_2M?

—Are we dealing with singlet or triplet states?

—How can we prove this, or isolate them for identification?

—Or, are we dealing with germylenoid or stannylenoid mechanisms, where a formal unit, R_2M, is transferred from an educt to a product, without appearing in the reaction coordinate as a real intermediate, R_2M, at any time?

Many potential germylene or stannylene sources have been proposed recently, and many reactions have been described as, or supposed to be, R_2M reactions, often for the sake of brevity. The confusion was—and still is—a considerable one, since very often no distinction has been (or could be) made between real R_2M reactions and germylenoid or, respectively, stannylenoid ones. Anyway, the "R_2M" concept, or the concept of "two-valent M compounds" (M = Ge, Sn) has been, and continues to be, a very useful fertilizer for new or even novel chemical reactions, mechanistic considerations, spectroscopic and other physical measurements, and a plentitude of new, interesting chemical compounds of synthetic, and sometimes biological, importance.

The present review tries to make clear where and how real chemical compounds R_2M, M = Ge, Sn, are generated or involved, how their existence is evidenced, and which reactions they undergo. To eliminate implications and complications essentially given by the kind of R, the considerations are restricted here to such compounds R_2Ge and R_2Sn, where R is bound via a σ bond and consists, whenever possible, in simple organic residues like Me, Et, Bu, or Ph. Thus, a direct contribution of R to a reaction of R_2M is nearly or fully excluded, as well as an electronic (thermodynamic) or steric (kinetic) stabilization of R_2M. Sometimes, however, this borderline will need to be crossed over for special reasons, and it will be explained in the corresponding cases.

II. Germylenes, R_2Ge

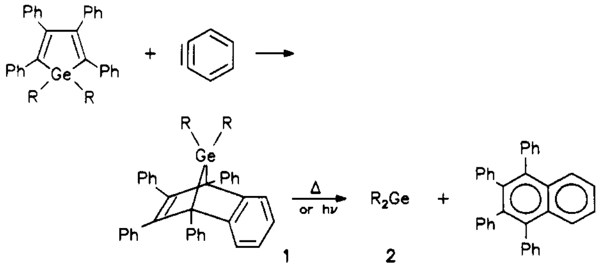
Whereas the fields of carbenes[7] and of silylenes[8] are covered by a considerable number of monographs and reviews nearly up to the present day, nothing like this exists for the germylenes. A comprehensive, very good review was written in 1972 by J. Satgé et al.[6] on "Divalent Germanium Species as Starting Materials and Intermediates in Organogermanium Chemistry". Ample material is collected and screened in that review, in part certainly concerned with free germylenes or at least germylenoids, and in part, however, certainly not. It was too early to differentiate between "divalent germanium species" and carbene-analogue germylenes, R_2Ge. Also, several brief overviews and reviews on special aspects are available and cover parts of the literature up to 1982.[3b,9,10] Thus, at least 10 years of animated research in germylene chemistry have to be covered by the present review, a period of fundamental manifestations in this field.

The chemistry of germanium dihalides, $GeHal_2$, is not comprehensively included here in order to keep this review within the given scope: Ge dihalides sometimes behave as germylenes (then certain reactions will be reported), and sometimes they do not and behave more or less as halogen atoms bound to Ge in a given mechanism. As a warning it should be mentioned that, for example $GeCl_2$ inserts smoothly into the nonactivated C–Hal bonds of butyl or cyclohexyl chlorides,[6] real germylenes like Me_2Ge do not, see below. For the same reasons, the chemistry of $Ge(OR)_2$, $Ge(SR)_2$, $Ge(NR_2)_2$, $Ge(PR_2)_2$, Ge(pseudo-halide)$_2$, and the like would exceed the limit of this review. However, some examples, for comparison, will refer to them.

A. Generation of Free Germylenes from Precursors

1. 7,7-Dialkyl- or 7,7-Diaryl-7-germanorbornadienes

The most used sources for free germylenes R_2Ge are at present the 7,7-disubstituted-7-germabenzonorbornadienes (1).[11,12,13] They are best prepared, after some difficulties,[6] from the corresponding tetraphenyl germoles and dehydrobenzene (eq 1) and are stable, pure, colorless, crystalline compounds. R in R_2Ge 2 often is Me, but also can be Et,[13] Bu, Ph,[14] and 4-MePh (this sometimes is convenient, because the 4-Me group can be used by ^1H NMR as a tracer in order to follow what happens[15]). Me groups in the benzo ring enhance the thermal stability of 1, if desired, which allows reasonable decay rates from 70 up to 180 °C. Tetraphenyl naphthalene, the side product, is generally inert in the reaction mixture and can easily be separated.



(1)

The cycloreversion (eq 1) is strictly first order and can easily be followed by ^1H NMR. This is important

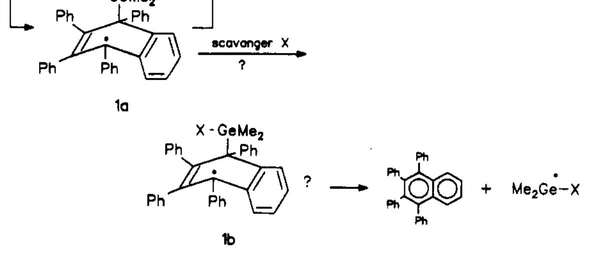
TABLE I. UV Spectroscopy of Germylenes RR′Ge

RR′Ge[a]	UV_{max}, nm	source	irradiation	condition	ref(s)
R = R′ = Me	430[b]	4	Hg, high pressure (450 W)	3-MP matrix, 77 K	31
	420	1	Hg, low pressure (254 nm)	3-MP matrix, 77 K	13,45
	380	1	flash photolysis	20 °C, heptane, benzene	46
	420	$Me_2Ge(SePh)_2$	Hg, low pressure	Ar matrix, 21 K	26
	420	$Me_2Ge(SePh_2)$	XeCl excimer laser (308 nm)	20 °C, cyclohexane	26
	405	$Me_2Ge(N_3)_2$	Hg, low pressure (254 nm)	Ar matrix, 26 K	25
	425	$PhMe_2GeSiMe_3$	flash photolysis (248 nm)	20 °C, cyclohexane	49b
R = R′ = Et	440	1	Hg, low pressure (254 nm)	3-MP matrix, 77 K	13,45
	425	$Et_2Ge(SePh)_2$	Hg, low pressure (254 nm)	3-MP matrix, 77 K	47
R = R′ = Pr	425	$Pr_2Ge(SePh)_2$	Hg, low pressure (254 nm)	3-MP matrix, 77 K	47
R = R′ = Bu	425	$Bu_2Ge(SePh)_2$	Hg, low pressure (254 nm)	3-MP matrix, 77 K	47
	440	1	Hg, low pressure (254 nm)	3-MP matrix, 77 K	13
R = Ph; R′ = Me	440	1	Hg, low pressure (254 nm)	3-MP matrix, 77 K	13
R = R′ = Ph	466	1, 3	Hg, low pressure (254 nm)	3-MP matrix, 77 K	13,45
	445	3	laser flash photolysis (266 nm)	20 °C, cyclohexane	22
R = R′ = Tol	471	3	Hg, low pressure (254 nm)	3-MP matrix, 77 K	13
R = R′ = Xy	543[c]	3	Hg, low pressure (254 nm)	3-MP matrix, 77 K	13
R = R′ = Ar	544[c]	3	Hg, low pressure (254 nm)	3-MP matrix, 77 K	13
R = R′ = Mes	550[c]	3	Hg, low pressure (254 nm)	3-MP matrix, 77 K	13,24,25
R = R′ = Ar′	558[c]	3	Hg, low pressure (254 nm)	3-MP matrix, 77 K	13,24
R = Mes, R′ = tBu	508[c]	3	Hg, low pressure (254 nm)	3-MP matrix, 77 K	13,45

[a] Tol = 4-methylphenyl; Mes = 2,4,6-trimethylphenyl; Xy = 2,6-dimethylphenyl; Ar = 2,6-diethylphenyl, Ar′ = 2,4,6-triisopropylphenyl. [b] The authors did not exclude other transients like the digermene. [c] For discussion of these high values see ref 13.

for the decision whether, in the presence of a potential reagent for 2, a reaction of 2 really takes place (then the rate of disappearance of 2 is not influenced by the reagent, and the rate of appearance of any products including polygermanes has to be in accordance with the disappearance of 2) or whether there is a direct attack of the reagent to 1 (then, no germylene reaction should be discussed, but any other presumable mechanisms can be).

The cycloreversion of 1 (R = Me), for example, has the same rate in benzene or in Ph_2O and is not influenced by the strong germylene scavengers (see below) CCl_4, CCl_3Br, or tBuC≡CCN; $k = 0.18–2.94\ h^{-1}$ in the range 58-80 °C;[16] $E_A = 28.1 \pm 1.0$ kcal/mol (0.05-0.21 M solutions). Consistent results have been found in the presence of excess styrene or 2,3-dimethylbutadiene.[17a] For 1, in CCl_4 at 70 °C, $t_{1/2} = 0.7$ h. This is enlarged by Me groups in the benzo ring, e.g. to 120 h by having 4 Me groups. Without any reasonable doubt, Me_2Ge 2 is generated from 1, can be trapped and identified by spectroscopy, and is identical with Me_2Ge generated from other sources (see Table I). But, are the two Ge-C bonds ruptured in a synchronized or at least concerted way, which would be (but not necessarily must be) a thermal, symmetry-allowed cheletropic reaction? Or, is there a biradical **1a** as an intermediate, see eq 1a, as stressed in the case of carbene formation starting from norbornadienes?[17b] Kinetic data[16,17a] do not exclude one of these hypotheses. In fact, the influences of substituents at the basic ring of 1 at first have been discussed in favor of **1a**.[11] However, these arguments are likewise valid for a concerted mechanism[12] (see eqs 1 and 1a).



(1a)

There are plenty of stereospecific additions to unsaturated systems, well to be understood via a free germylene R_2Ge (see section C.3.c) but hardly via a germyl radical **1a**. Also the insertion reactions with, for example, CCl_4 and their CIDNP effects (see eq 16) are in accordance with a free singlet Me_2Ge following Kaptein's rules and rule out a free radical like **1a**.[51]

Nevertheless the discussion, whether there might be a biradical **1a** between 1 and 2 or not, continues.[17a,17c,46] Irradiation of 1 generated weak CIDNP (^1H NMR) effects. A decrease of the two MeGe singlets is interpreted in terms of intermediate formation of **1a** and an equilibrium 1 ⇌ **1a**.[17c] An unspecific enhanced absorption in the complex ^1H NMR aryl-H region is assigned to CIDNP signals of Ph_4-naphthalene and therefore, the intermediate existence of **1a**.[17c] In other CIDNP experiments, no effects backing these assumptions have been seen.[51,75] A photoinduced equilibrium, 1 ⇌ **1a**, without germylene formation has been concluded from matrix experiments at 77 K (see section B.1).[46]

Whatever the precursor of the many insertion or addition products (see sections C.2 and C.3), a germylene 2 or a biradical **1a**, might be, it unavoidably must be long-lived enough for bimolecular, diffusion-controlled reactions, and it must not be sterically crowded. If it were **1a**, it also would be trapped by strong and specific germyl radical scavengers, one of the strongest being tBu-Br and form Ge-Br compounds and tBu radicals. But, no products like isobutene and isobutane and X-Me_2Ge-Br can be detected (see eq 1a). Moreover, styrene gives, without or in the presence of equimolar amounts of tBu-Br, thermally the cycloadducts as shown in eq 21.[82] The rate of decrease of 1 remains first order and identical with the spontaneous thermolysis of 1; the rate of cycloadduct formation and the yield of the latter, also, are not influenced by the presence of tBu-Br.[82]

The same is the case photolytically with other scavengers like excess CCl_4 or 2,3-dimethylbutadiene.[17a]

By the way, it is hard to understand that a germyl radical like **1a**, when scavenged by any reagent X, being then a tetra-covalent Ge compound, X–Me_2Ge–CRPhAr (**1b**), should split the Ge–C bond (see eq 1a). Moreover, it would have to do this so rapidly that the new germyl radical $XMe_2Ge^{\bullet}$ could neither be detected nor traced by chemical, spectroscopic, or kinetic means, in spite of the numerous attempts to do so.

The same cycloadducts to 1,3-dienes as with **1** (see section C.3.c) have been found in very similar ratios when starting from a completely different germylene precursor, Ph–Me_2Ge–$SiMe_3$.[49b]

Also the carbon-centered benzyl radical moiety of **1a** should reasonably be evidenced if such a radical exists. But, neither trapping experiments with strong radical scavengers like R_3SnH or styrene nor detection of any other consecutive products nor ESR signals (**1a** should be considerably long-lived) have been successful.[82]

These facts are not in accordance with a free radical like **1a**, but they are in accordance with a free germylene **2** as reacting species, at least for the thermolysis reactions of **1** described in this review (for photolysis of **1**, see also section B.1).

The application of **1** comprises not only many new syntheses of organogermanium compounds or mechanistic studies, but also spectroscopic investigations of transient particles **2**; see below.

2. R_2GeX_2

The general idea here is to have equal, fairly electroneutral and/or easily recombining leaving groups in order to disfavor intermediates like anions or cations.

Probably one of the first germylene sources was the yellow, air-sensitive germyl mercurial, which was split thermally or by long-waved irradiation[6,18,19,20,21] (eq 2).

$$n\ Ph_2GeH_2 + n\ Et_2Hg \xrightarrow[-2n\ EtH]{exoth.} (-Ph_2Ge-Hg-)_n \xrightarrow[h\nu]{\Delta\ or} n\ Ph_2Ge + n\ Hg \qquad (2)$$

In those days (1963) any hope of investigating the chemistry of free germylenes more exactly had been too presumptious because of lack of spectroscopic or other physical means. Thus, one enjoyed the isolation and identification of the spontaneous oligomerization products, e.g. $(Ph_2Ge)_4$, of the assumed germylenes (eq 2). Anyway, this had been the early modest beginning of germylene chemistry in the present author's laboratory.

Diaryl bissilylgermanium compounds **3** have been established to generate **2** upon UV irradiation (eq 3) with a 266-nm laser flash[22] or a low-pressure mercury lamp. This source has been used both for spectroscopic and chemical experiments, apparently since 1985.[23] One driving force is the formation of the Si–Si bond, more stable than the Ge–Si bonds that split[13,24] (eq 3).

$$\underset{3}{Ar_2Ge(SiMe_3)_2} \xrightarrow{h\nu} \underset{2}{Ar_2Ge} + Me_3Si-SiMe_3 \qquad (3)$$

Ar = e.g. Ph, 4–Me–Ph, 2,6–Me_2–Ph, 2,6–Et_2–Ph, Mesityl, 2,4,6–iPr_3–Ph

The aryl residues are necessary for the energy absorption of the molecule. At least $Me_2Ge(SiMe_3)_2$ remained inert toward the light of a low-pressure mercury lamp.[25] This drawback is not given with $Me_2Ge(SePh)_2$, which is split by a 308-nm laser to give Me_2Ge.[26]

An elegant photochemical generation of Me_2Ge has been established by photolysis of the well-known[27] azide (eq 4).[25,28]

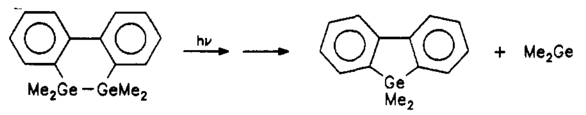
$$Me_2Ge(N_3)_2 \xrightarrow[-3\ N_2]{h\nu} Me_2Ge \qquad (4)$$

The leaving groups are stable N_2 molecules. But, care has to be taken so that no intermediate germanimines or nitrides remain (see, for example, ref 29a). This has been achieved.

3. Strained Cyclogermanes, Oligogermanes, and Others[29b]

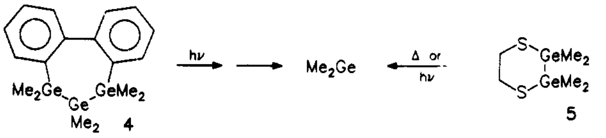
In principle, this section is not different from the foregoing one. But, the particles leaving from the R_2Ge moiety are not as stable as above, and ring strain may be utilized in addition. So, a number of useful applications or proposals can be found here.

The thermal or photolytical splitting of Ge–Ge bonds can form germylenes as consecutive products of germyl or digermyl radicals. Thus, a primary Ge–Ge splitting is assumed to lead to Me_2Ge extrusion,[30] as shown by UV spectroscopy (eq 5).



(5)

The analogue cyclic trigermane **4** showed a similar behavior, and a diradical intermediate is assumed since the existence of Me_2Ge follows from UV and trapping experiments[31] (eq 6). More generally, cyclic di(or oligo)germanes such as **5** seem to be able to extrude R_2Ge, as is concluded from the isolation of two products of **5**, one of them having lost a Me_2Ge unit, the other being an insertion product of Me_2Ge into the Ge–Ge bond of **5**, and other trapping products.[32]



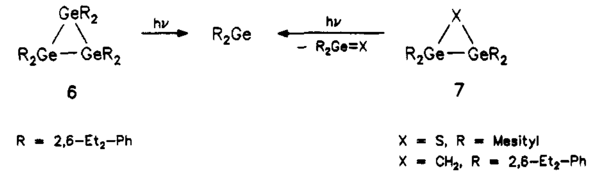
(6)

These are given facts even though it is surprising that no consequent efforts have been made to use the well-known cyclogermanes like $(Me_2Ge)_n$ or $(Ph_2Ge)_n$ as germylene sources.

It seems, more generally, that polygermyl radicals can split off germylenes via a monoelectronic α elimination.[33] Trapping experiments with Me_2S_2 and 2,3-dimethylbutadiene are rendering this reasonable, but definite proof of the existence of free **2** would be welcome. Free-radical mechanisms also are feasible here. Both the photolytical extrusion of **2** and the formation of germyl radicals are well established in the case of open-chained phenyltrigermanes.[34]

$$R'-R_2Ge-R_2Ge^{\bullet} \longrightarrow R'-R_2Ge^{\bullet} + \underset{2}{R_2Ge}$$

R_2Ge is trapped after photolysis of the cyclotrigermane **6**.[23] Whether its extrusion occurs via a synchronous cycloreversion or after a primary splitting of a Ge–Ge bond (see above) is becoming experimentally undistinguishable if one reaction follows the other very rapidly. The same situation seems to be given for the splitting of a digermirane 7[35,36] (eq 7). Also for the



(7)

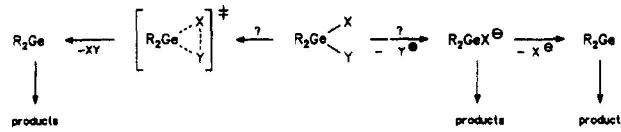
thermolysis or photolysis of 6, R = mesityl, the generation of a germylene could be concluded.[14,37] Analogously, without mechanistic anticipation, a transient 1,1-dimethyl-2-phenylgermirane in the gas phase is concluded to form styrene (which is evidenced) and Me_2Ge.[38]

There is a number of additional α elimination starting from di- or oligogermanes. This type is well established in the stannylene or, respectively, stannylenoid chemistry (see section III). A clear case seems to be the hydrogen shift in 8[39] (eq 8). Whether the subsequent

$$\underset{\mathbf{8}}{Me_3GeMe_2Ge{-}H} \xrightarrow{250\,^{\circ}C} Me_2Ge \xleftarrow{-\,\mathbf{8}} Me_3Ge(Me_2Ge)_2{-}H \qquad (8)$$

trapping occurs via the Ge–H (as claimed) or the Ge–Ge bond is not finally established.

Care should be taken, when one or both of the leaving groups have a strong tendency to form ions. Then, often a stepwise mechanism is more likely (as in the corresponding carbene case) (eq 9) and good evidence for the details should be presented before concluding a free germylene. The products might be the same in



(9)

all cases, e.g. with 1,3-dienes. Both Y^+ or R_2GeX^-, and R_2Ge as well, can give the formal 1,4-cycloadducts and, moreover, free radicals, too (which may emerge from SET processes). The same may come out with certain "insertion products", which might be in fact the consequence of a S_H2 reaction, etc. (see sections C.2 and C.3).

Whenever Na, Li, Na/K alloy,[40] or, for example, germyllithium derivatives are involved in a "germylene formation" details of the mechanism should also be checked carefully. Thus, Me_2GeCl_2 + 2Li gives, with styrene, products which are different from those which a real, free germylene Me_2Ge yields (see section C.3.a). Considerations like this may be needed also for the amine-assisted (Et_3N, pyridine) α dehydrohalogenation of $R_2GeHHal$[41] reported to form 2. In some cases of this kind, the participation of germyl anions is clearly assumed.[42] In others where, at room temperature or even above, the formation of rather stable complexes $R_2Ge{\cdot}OR_2$, $R_2Ge{\cdot}NR_3$, or $R_2Ge{\cdot}PR_3$ had been thought to be involved, new interpretation of the observed facts seems unavoidable, (see section C.4).

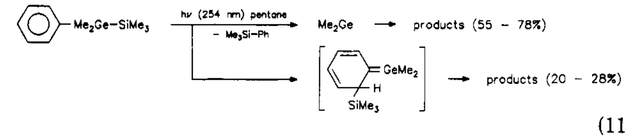
A borderline group of reactions is given by the formal 1,2-shifts of halides in di- or oligogermanes like 9 and 10[43] (eq 10). Similar reactions are quite common in the stannane chemistry (see section III).

$$\underset{\mathbf{9}}{Et_3GeEt_2GeCl} \xrightarrow[-\,Et_3GeCl]{\text{first order}} Et_2Ge \xrightarrow{\mathbf{9}} Et_3GeEt_2GeEt_2GeCl$$

$$\underset{\mathbf{10}}{R_2GeCl{-}GeClR_2} \xrightarrow[-\,R_2GeCl_2]{\Delta\text{ or }h\nu} R_2Ge \longrightarrow \text{products} \qquad (10)$$

R = Ph, Mes

A surprising 1,2-shift of a phenyl group from Ge to Si, starting from $Ph{-}Me_2Ge{-}SiMe_3$ and by means of short-wave UV irradiation, opens a new germylene source. Free Me_2Ge 2 is evidenced by time-resolved laser flash spectroscopy (see Table I). But, a minor byproduct also is generated (see eq 11).[49b]



(11)

The recommendations or warnings given in this section are, of course, restricted to mechanistic investigations or discussions. The application of the corresponding reactions for synthetic purposes might be, nevertheless, of considerable value.

B. Isolation and Identification of Free Germylenes

From the beginning of any germylene chemistry, there has been no doubt that the latter certainly are highly reactive, short-lived species, at least those within the scope of this review like Me_2Ge or Ph_2Ge. Therefore, like in the carbene[7] and silylene chemistry,[8] the question was obvious whether they really do exist, and if so, what is their shape, are they singlets or triplets, what are their spectroscopic properties, and what is their specific reactivity? This has been a challenge for all kinds of chemists. After tedious work in many laboratories, after long and often fruitless attempts or even misinterpretations of findings, clear answers can be given now: they exist, and here are their properties.

1. Matrix Spectroscopy and Trapping

Meanwhile, a restricted number of kinetically stable germylenes became known (see section C.1). But, these are more or less "disturbed" by steric and/or electronic effects. It is of interest to look for, e.g., Me_2Ge or Ph_2Ge or the like.

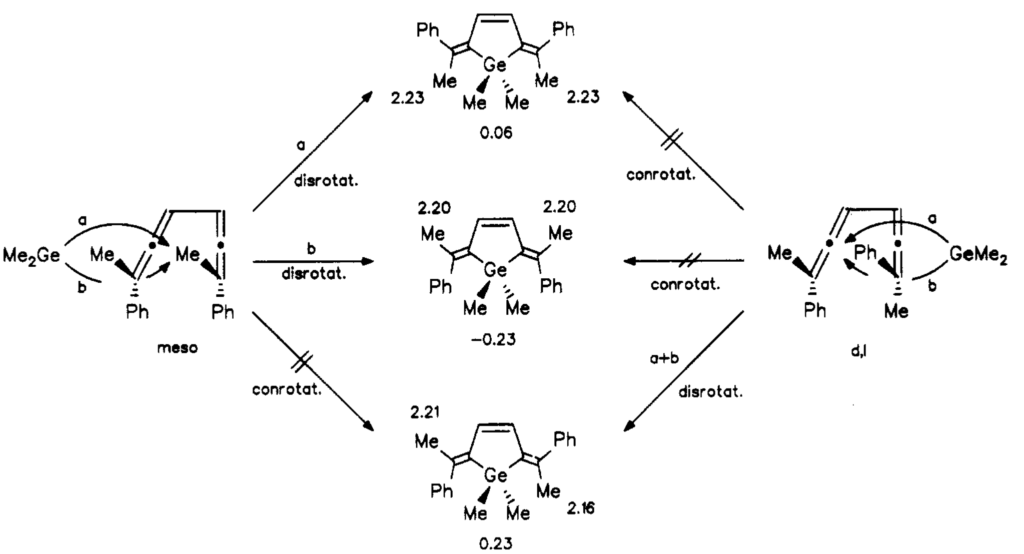
Apparently the first attempt to isolate Me_2Ge in matrix, starting from 1 ended up with the identification of the first unhindered digermene, $Me_2Ge{=}GeMe_2$.[44] Nearly simultaneously, the first isolation of Me_2Ge (hydrocarbon matrix, at 77 K) and its UV investigation has been published,[31] starting from 4 (eq 6). Others followed, starting from 3[13,22-24,45] (Ar_2Ge) (eq 3), 1[45] (eq 1), $Me_2Ge(SePh)_2$[26] or $Me_2Ge(N_3)_2$[25] (eq 4).

A complete and unequivocal assignment of IR and UV/vis spectra of Me_2Ge in hydrocarbon matrix at 77 K has been done in the last reference, combined with clear insertion and addition trapping experiments in matrix, and also at room temperature a free Me_2Ge has been made quite likely emerging from the diazide.

A complete list of the IR vibrations of Me_2Ge also has been observed and assigned.[25] The C–Ge stretches have been found at 527 (vs) and 541 cm^{-1} (w).

Table I will give an overview on the available UV/vis spectroscopic data of short-lived R_2Ge. Finally, the existence, identity, and spectroscopic data of free ger-

SCHEME I



mylenes R_2Ge, R = alkyl or aryl, have been evidenced satisfactorily. Nevertheless, some UFO's (unidentified factual objects) are still crawling through the landscape of photolytic germylene generation. Thus, it has been claimed that the absorption at 420 nm is due to the biradical **1a** being in a rapid and reversible equilibrium with **1** in hydrocarbon glasses when irradiated, because the equilibrium does not generate Me_2Ge at 77 K (several Me_2Ge scavengers remained inactive), but does so only upon heating of the matrix to 143 K. At 20 °C in heptane, however, Me_2Ge is formed directly from **1** under flash photolysis, absorbing at 380 nm (the 420 nm intermediate is not observed, then), and being trapped by scavengers as to be expected, or it polymerizes, $k = 3500\ s^{-1}$.[46] Besides, a broad absorption around 460 nm has been registered, $k_{decay} = 500\ s^{-1}$ at 20 °C, which is tentatively assigned to the corresponding germabenzonorcaradiene being in a photochemical equilibrium with **1**.[46] But, other (photo) excited states emerging from **1** cannot be excluded more generally. It also should be kept in mind that in photolytic germylene chemistry, too, a primary, sterically uniform product can be scrambled or isomerized photochemically afterward, as in eq 28.[12] Evidently there is, generally, a need for unequivocal chemical or molecular spectroscopic identification of a reactive intermediate detected by, e.g., time-resolved spectroscopy. It seems that the story of photolysis of **1** not yet has come to its end.

2. Chemical Techniques

Thermal cycloaddition of Me_2Ge to adequately substituted 1,3-dienes points strongly to a concerted 1,4-addition following the Woodward–Hoffmann rules, a chelotropic [4 + 2]-pericyclic reaction, hence also to a singlet state of free Me_2Ge. Starting from **1** and the meso or, respectively, *d*/*l* diallenes given below at 70 °C, exclusively those isomers to be expected from a synchronous addition[12,48] have been detected (accuracy 98%) (see eq 12). The cross-check is a convincing one (see Scheme I (the figures given correspond to the *identification of the isomeric germacyclopent-3-enes by* ^1H NMR)). Exclusively the isomers following from the disrotatory ring closure allowed by the supposed mechanism could be detected.

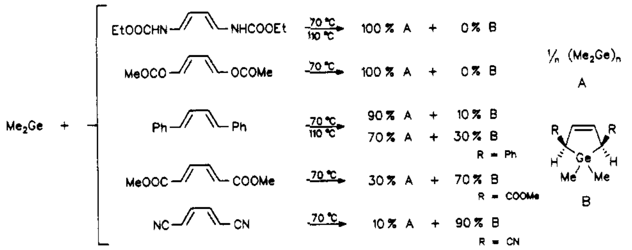
Intermediate biradicals or zwitterions are strictly to be excluded during reactions with these diallenes, because they would not allow stereospecificity. Other intermediates could not be detected. The results are backed by a number of additional examples of 1,4-disubstituted dienes[12,48] (see section C.3.c).

Consistent results have been obtained in the gas phase with 2,4-hexadienes, where the pure *E,E* diene yielded 98% of the anti isomer.[49a] Here, too, the cross-check gives the unequivocal proof.

Precisely, this stereospecifity could, theoretically, also be reached by a sequence of two consecutive steps, each of them being stereospecific, e.g. a concerted 1,2-addition followed by a concerted 1,2–1,4-rearrangement. (This principal problem—exclusion of any intermediate—is given, however, in many chemical reactions).

In fact, 1,2-additions of R_2Ge to alkenes, and 1,3-dienes also are possible (see section C.3.a–c). From a time-resolved kinetic study with short-wave irradiation (248 nm) it has been concluded for a number of 1,3-dienes that really a 1,2-addition happens first. Its unstable products rearrange to the final 1,4-adducts in a (presumably) sigmatropic way, or to other products.[49b] It seems that the role of photoactivated educts or intermediates is not discussed so far. It would be desirable to differentiate photochemical reactions from the thermal ones described above and below, which are much less influenced by energetic or kinetic complications in principle.

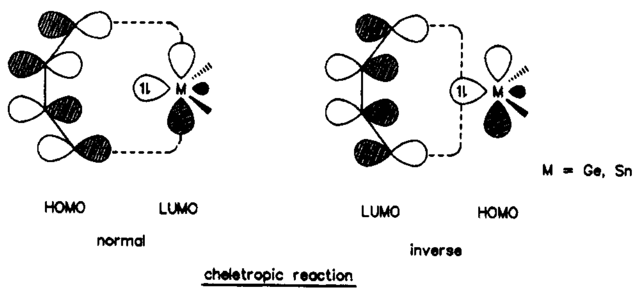
Free Me_2Ge acts in these chelotropic reactions as a donor (nucleophile): electron-poor dienes react more rapidly than electron-rich ones[50] (see eq 12).



(12)

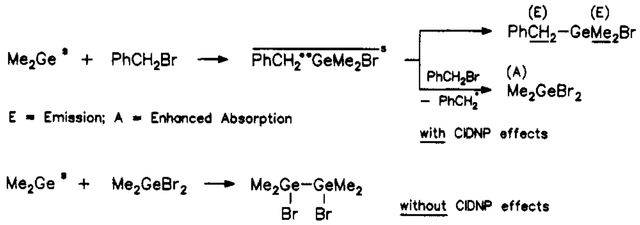
In the transition state, therefore, an interaction of the HOMO of Me_2Ge (the paired electrons) with the

SCHEME II



LUMO of the diene follows, (see Scheme II).

During insertion of free Me_2Ge, generated both photochemically or thermally from 1, into the C-Br bond of benzyl bromide, ^1H NMR–CIDNP signals have been observed. Their pattern is in accordance only with a caged singlet radical pair[51] (see eq 13). Conforming CIDNP evidence has been gained from insertion of Me_2Ge into the C–Br bond of Cl_3CBr and the C–Cl bonds of benzyl chloride and CCl_4. The insertion here is in fact a radical abstraction–recombination procedure (see section C.2). Following the CIDNP rules, a singlet state of the germylene has to be concluded in any of these cases.



(13)

3. *Quantum Chemical Considerations and Calculations*

In accordance with the chemical facts detected later (see section B.2), singlet ground states $4s^2$, $4p^2$, for H_2Ge, F_2Ge, and Me_2Ge have been predicted for "the organic derivatives which are practically unexplored" (in 1980).[52] Following from ab initio valence-only calculations, the singlet–triplet gaps are (SCF) 10, 64, and 14 kcal/mol, or, by the more adequate extended CI method 19 kcal/mol for $^1A_1$–$^3B_1$ in the case of Me_2Ge. That means, they are not much higher than for silylenes. The bond lengths and angles have been calculated for singlet Me_2Ge (SCF): C–Ge = 2.02 Å, $\angle$C–Ge–C = 98°. The dipole moment was calculated to be 0.97 D, the ionization potential 8.12 eV, the IR frequencies $\nu_1 = 560$, $\nu_2 = 288$, and $\nu_3 = 497$ cm^{-1} [52] (For measured IR values, see B.1). Other ab initio calculations gave for H_2Ge with double-ζ quality in the valence region for $^1A_1$ and $^3B_1$ states a singlet–triplet separation of ~25 kcal/mol. This value has later been lowered to 19 kcal/mol.[53] For the singlet $^1A_1$ ground state, this method resulted in the case of H_2Ge a bond length of -1.571 ± 0.005 Å and an angle H–Ge–H of $93.0 \pm 0.5°$. For the $^3B_1$ state of H_2Ge, a H–Ge bond length of 1.516 ± 0.005 Å and an angle H–Ge–H of $119.0 \pm 0.5°$ have been calculated.[54] With the more strained Lappert's germylene,[55,56] $Ge[CH(SiMe_3)_2]_2$, $\angle$ C–Ge–C = 107° and C–Ge = 2.04 Å have been measured by gas electron diffraction, and ab initio MO calculations for Me_2Ge have also been reported by the same group. In another laboratory, the Austin Model 1 (AM 1) has been parametrized for germanium and shown to be superior to MNDO here, especially in geometries, but apparently results neither for Me_2Ge nor its reactions are available so far.[57] This would be desirable. However, for $GeCl_2$ a synchronous 1,4-cycloaddition seems more probable than for $SiCl_2$, as older MO treatments suggest.[58] Thus, a synchronous or better concerted mechanism is at least not disfavored at present. For the (even bigger and weaker) stannylenes, a synchronous 1,4-cycloaddition with a symmetrical transition state has been calculated to be favorable (see section III.B.3).

Optimized SCF calculations gave a stability of $HGeCH_3$ toward isomerization $HGeCH_3 \rightleftharpoons H_2Ge{=}CH_2$ of 15 kcal/mol.[59] Other ab initio calculations have shown qualitatively the same results.[60]

C. Reactions of Germylenes

1. *Oligo- and Polymerization, Influence of Bulky Substituents*[29b]

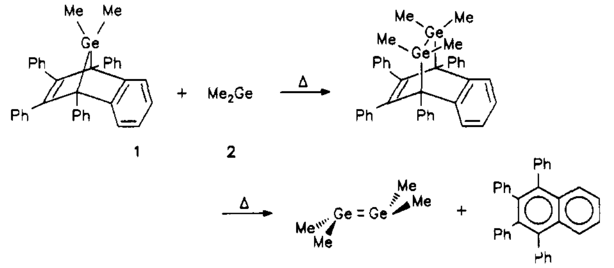
Uncomplicated germylenes polymerize very rapidly apparently without noticeable activation energy, that means controlled only by the diffusion rate $k \sim 10^9$ M^{-1} s^{-1}.[8] Lastly, polygermanes $(R_2Ge)_n$ are formed. In most cases the structure of the latter has not been determined unfortunately. Presumably high contents of cyclogermanes should be formed, n = 4,5,6... In a few cases this has been confirmed.[6] It is reasonable to assume a dimerization at first $2R_2Ge \rightarrow R_2Ge{=}GeR_2$. At least, this dimer exhibits a certain stability in the matrix, when prepared by an independent way.[61] Also for R = Ph this has been shown.[22] Moreover, certain digermyl products, e.g. during addition experiments of free Me_2Ge with alkynes,[62,63] can best be explained by this intermediate digermene (see section C.3.b). Then, probably an addition of R_2Ge to the digermene takes place. This is backed by the case of R = mesityl, where it is established.[23] Further insertion, or a dimerization of the digermene could give the cyclotetragermane, and so on. Considerable research work remains to be done here.

Bulkier residues reduce the polymerization rate. Ph has no measurable effect, but tBu has. 2,6-Et_2-Ph is sufficiently bulky to stop the polymerization at the dimer $R_2Ge{=}GeR_2$.[23] Very bulky residues can lead to a monomer–dimer equilibrium $2R_2Ge \rightleftharpoons R_2Ge{=}GeR_2$, R = e.g. $CH(SiMe_3)_2$[56] or $R_2 = [N(tBu)]_2SiMe_2$.[64] These dimers give rise to an interesting, individual chemistry,[23,56,61,65] giving, e.g., Diels–Alder additions, but do not belong to the scope of this review.[29b]

Consequently, even more steric hindrance renders a germylene kinetically stable. R = 2,4,6-tBu_3-Ph is sufficient; this germylene has been isolated in solid state and is stable at -10 °C.[66]

2. *Insertion into σ Bonds*

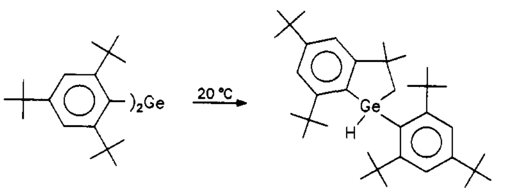
For an insertion of R_2Ge into C–C bonds apparently no examples are known. Going down the group 14, the bonds become more ready to insert R_2Ge. The strained C–Ge bonds in 7, 7-dialkyl-7-germanorbornadienes 1 compete, if present in maximum concentration, i.e. in the melt or even in the tempered crystal just below the melting point, successfully with the polymerization of free Me_2Ge,[67] forming the (substituted) digermabicyclooctadienes. This is a clear-cut case, moreover since the structure of the latter is fully evidenced,[68] in addition, by the thermal cycloreversion (140–200 °C) forming $Me_2Ge{=}GeMe_2$ (see eq 14).[67] For the C–Sn bond, only examples with $GeCl_2$ and EtGeCl are reported for allyl and $Cl_3C{-}SnR_3$,[69] but a more general reactivity of C–Sn bonds may be anticipated.



(14)

No mechanistic implications have been proposed for these reactions so far.

C–H bonds are generally stable toward germylenes.[40] But, strain release may overcome this barrier,[66] as demonstrated by the example in eq 15, apparently being the only so far.



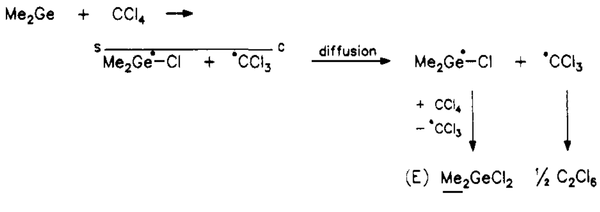
(15)

For Si–H (in $PhMe_2Si{-}H$), a nucleophilic attack of free Me_2Ge (from 1) has been found, passing a plausible pentacoordinate transition state or intermediate.[70] Insertions into Ge–H[39] and Sn–H bonds are commonly assumed and reasonable, but not evidenced in detail (in our case,[39] e.g., also a Ge–Ge bond could take up the germylene, in principle).

H–O bonds do insert, apparently after forming a complex with the germylene (see section C.4). A product with water seems rather unstable and could only be evidenced in matrix.[13,71a] A consecutive product of $Me_2Ge(H)OH$ could be obtained, $(HMe_2Ge)_2O$[71b] (see also section C.4). With alcohols ROH, R = e.g. Et, products have been isolated (see section C.4). $Et_2Ge(H)OMe$[72] has also been found, starting, however, not from a free germylene, but from $Et_2Ge{\cdot}NEt_3$. With Lappert's bulky germylene, a ready reaction with MeOH or EtOH takes place, and the product of the latter is characterized by single-crystal X-ray analysis as $R_2Ge(H)OEt$, R = $CH(SiMe_3)_2$.[73] More acidic OH groups seem to behave generally in an equal manner, e.g. in oximes,[74] where, with free Me_2Ge, $Me_2Ge(H){-}O{-}N{=}CRR'$ has been found with an excess of the oxime (see section C.4). Also acidic N–H moieties can insert free Me_2Ge, phthalimide thus forms $1,2\text{-}C_6H_4(CO)_2NMe_2GeH$.[74]

Now, we should return to the other carbon–heteroatom bonds. The best investigated are the carbon–halogen bonds. Free Me_2Ge inserts into the C–Br bond of benzyl bromide via a two-step, radical abstraction–recombination process, as has been shown by CIDNP measurements (eq 13).[51,75]

An identical mechanism involving a caged singlet radical pair is given when starting from $Cl_3C{-}Cl$, $Cl_3C{-}Br$, $PhCH_2{-}I$ and $PhCH_2{-}Cl$ (see, e.g., eq 16).[51]



(16)

(E) = Emission of the ¹H-NMR signal

No indications for a radical pathway or for any intermediate could be found with $H_2C{=}CHCH_2{-}X$, $PhCH{=}CH{-}X$ (X = Cl, Br), and $H_3CC(Br){=}CHCH_3$. The insertion products into the C–Hal bond are formed here, as it seems, by a one-step (synchronous) mechanism. The same concerted type is exhibited by the C–Cl or C–Br bonds of a number of alkynyl and propargyl halides, both under thermal and photolytical conditions.[16] The former give (see eq 17) the corresponding germyl alkynes. The latter halides give, in addition, in part or almost exclusively the rearranged products, allenyl germyl halides (see eq 18). Allenyl bromides yield, consequently, quantitatively the allene products $R_2C{=}C{=}CHMe_2GeBr$[16] (eq 19).

$$\mathrm{Ph{-}C{\equiv}C{-}Hal} \xrightarrow[\text{or } h\nu]{1,\ \Delta} \mathrm{Ph{-}C{\equiv}C{-}Me_2Ge{-}Hal} \qquad (17)$$

Hal = Cl, Br

$$\mathrm{HC{\equiv}C{-}CH_2{-}X} \xrightarrow[\text{or } h\nu]{1,\ \Delta} \mathrm{HC{\equiv}C{-}CH_2{-}Me_2Ge{-}X} + \mathrm{H_2C{=}C{=}CH{-}Me_2Ge{-}X}$$

X = Cl, Br, SCN

$$\mathrm{HC{\equiv}C{-}CRMe{-}Hal} \xrightarrow[\text{or } h\nu]{1,\ \Delta} \mathrm{RMeC{=}C{=}CH{-}Me_2Ge{-}Hal} \qquad (18)$$

Hal = Cl, R = H, Me; Hal = Br, R = H, Me

$$\mathrm{R_2C{=}C{=}CHBr} \xrightarrow[\text{or } h\nu]{1,\ \Delta} \mathrm{R_2C{=}C{=}CH{-}Me_2Ge{-}Br} \qquad (19)$$

R = H,Me

In all the cases of insertions into C–Hal bonds, a donor–acceptor complex may precede any of the mechanisms mentioned, where the halogen electrons interact with the vacant p orbital of the germylene (see section C.4). Such a complex has been evidenced by matrix UV spectroscopy[13] in the case of allyl chloride and gives insertion of the germylene upon annealing. Thus the insertion in this case is at least a two-step procedure: (1) donor complex formation, (2) insertion. With benzyl halides, it may be a three-step procedure: (1) donor complex formation, (2) radical abstraction, (3) radical recombination.

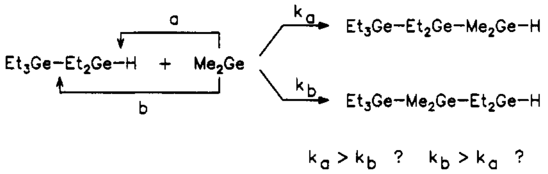
Here, again, it should be pointed to the fact, that results with $GeHal_2$ or RGeHal cannot be related generally to the behavior of R_2Ge. For example, simple alkyl chlorides like $CHCl_3$, CH_2Cl_2, CH_3Cl, higher alkyl, or cyclohexyl chlorides do not react with free Me_2Ge,[51] but they do so with $GeCl_2$, etc.[6] It seems that a dissociation energy of more than about 70 kcal/mol for the C–Hal bond involved cannot be overcome by a free germylene like Me_2Ge.[51] Anyway, it is clear now, that even in the case of free Me_2Ge at least two mechanisms are established, see above.

For C–O and C–S bonds, the insertion of R_2Ge moieties, starting from $Et_2Ge{\cdot}NEt_3$ or $PhMeGe{\cdot}NEt_3$ (see, however, section C.4, concerning the nature of the latter) is described in the case of the strained bonds of various oxiranes and thiiranes, giving ring expansion to the corresponding oxa- and thiagermacyclobutanes, whereas the C–N bond of N-substituted aziridines remained inert.[72] Allyl thioethers insert free R_2Ge into the allyl–S bond[13] (see eq 45).

C–Hg bonds, e.g. in Et_2Hg or Bu_2Hg, inserted PhGeCl moieties forming the C–Ge–Hg group whose Ge–Hg part continues to insert.

More generally, insertions into the Ge–Hg bond have been observed, e.g. with $(Ph_3Ge)_2Hg$.[76] It seems that a broader variety of Ge–X bonds (X = O, S, N, P) inserts moieties PhGeHal,[77] but this not necessarily allows a conclusion to the behavior of R_2Ge in the sense of this review. The same may be considered for the analogous insertions into the Ge–O bond of oxagermacycloalkanes which are found to be stereospecific, and a concerted mechanism is concluded.[78] Anyway, the strained Ge–S bonds in germathiiranes do insert free R_2Ge[79] (see eq 37).

Ge–Ge bonds certainly insert free germylenes (and also, it seems, germylenoids), forming tri-, oligo-, and, lastly, polygermanes.[32,39,51,80,81] The same is the case for insertions into Ge–H groups. The decision, whether the latter or Ge–Ge bonds are more reactive,[39] can only be answered in the future, when a digermyl hydride and a germylene with a different kind of R are used (see e.g. eq 20).



(20)

For the competition between Ge–Ge and Ge–Cl bonds, the same question is still open: the products $Cl(Me_2Ge)_nCl$, $n = 2,3...$[51] can arise by Me_2Ge insertion into the Ge–Cl ($n = 2$), but also into the Ge–Ge bond as well ($n = 3,...$).

Insertions of Me_2Ge into the Sn–Hal bond give a 60% yield in the case of tBu_2SnCl_2 and about 90% with Me_2SnCl_2 and Me_3SnCl.[12] In the latter case, ^1H CIDNP results have been reported in the insertion product.[17c,46] However, no escape products like Me_2GeCl_2 or Me_6Sn_2 have been observed, which have to be expected here. A final clarification is needed.

3. Addition to Unsaturated Systems

This section offers, like the foregoing one dealing with insertions, ample insight into the mechanistic behavior of germylenes. But, moreover, the additions of germylenes to unsaturated systems have opened, and still open, entirely new fields of synthetic interest and plenty of new or novel organogermanium compounds, whose importance for further syntheses or biological aspects just started to be investigated.

Again, it should be kept in mind that the polymerization of, e.g., Me_2Ge is without noticed activation energy and only controlled by diffusion, $k \approx 10^9\ M^{-1}\ s^{-1}$.[8] Thus, any addition has to be very rapid to have a chance to compete successfully, i.e. to give a product not being $(Me_2Ge)_n$. In the future, a retarding of this polymerization by intermediate complexing of R_2Ge (see section C.4) may be helpful for syntheses.

a. Alkenes. Simple alkenes like 1-octene, cyclohexene, 2-butene, 4,4-dimethylpentene, or 3-phenylpropene seem not to react with free germylenes. But, styrene and α-substituted styrenes do. With styrene, exclusively a 1:1 mixture of the syn/anti isomers of 3,4-diphenyl-1,1-dimethyl-1-germacyclopentanes has been obtained. Two moles of the olefin reacted with one germylene. No traces of 2,5-substituted or other isomers have been detected.[82] In an earlier attempt, styrene was reacted with Me_2GeCl_2 and Li in order to generate the germylene **2**.[83] Repetition of the experiments and determination of the structure gave evidence for a syn/anti mixture of mainly 2,5-diphenylgermacyclopentanes.[82] This result should be a warning with respect to real intermediates and mechanisms, when discussing germylenes (see section B.2).

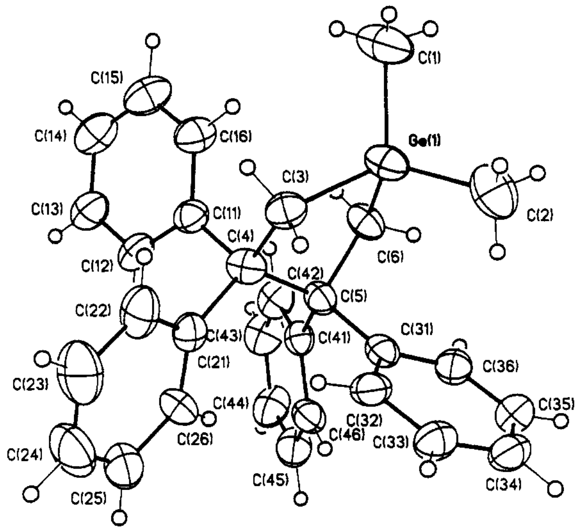
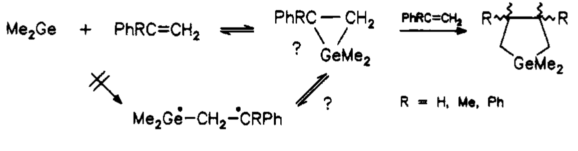


Figure 1.

Other styrenes $PhC(R){=}CH_2$ (R = Me, Ph) gave analogous cyclogermanes with $3,4\text{-}Ph_2\text{-}3,4\text{-}R_2$ substitution patterns. To establish the structure definitely, an X-ray analysis with R = Ph (Figure 1) has been carried out.[84] The five-membered ring is very strained due to the pressure by the four Ph groups, the C(4)–C(5) bond being one of the longest known so far, 1.626 Å, ∠ C(3)–Ge–C(6) = 90.3°. Styrenes of the type $PhCH{=}CHR$, R = e.g. Me, did not react. A free terminal CH_2 group is essential, therefore.

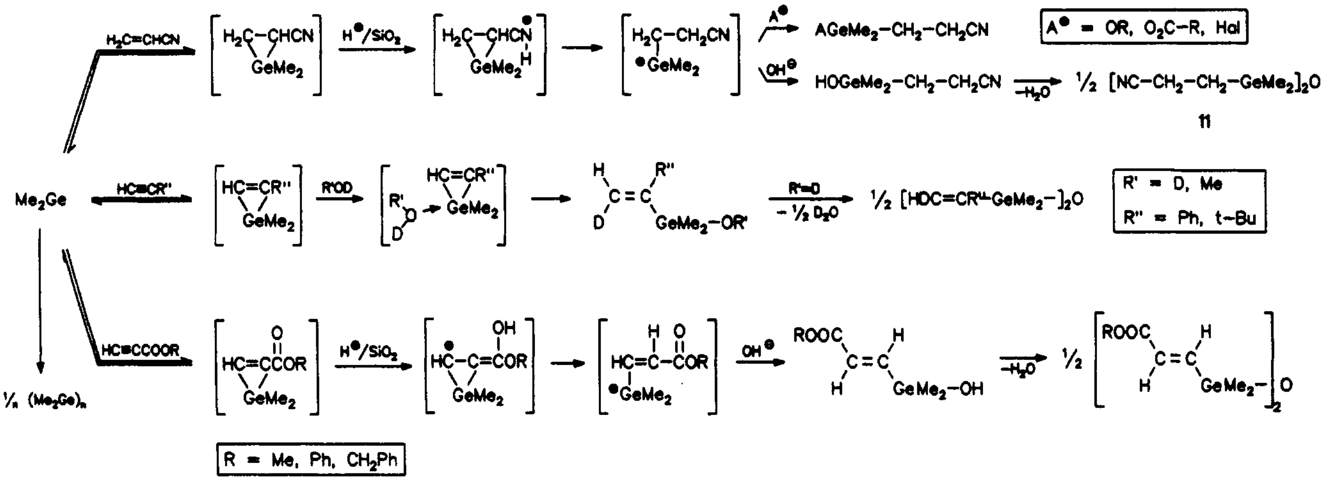
A 1:1 intermediate, a 2-phenylgermirane, has been assumed, but could not be evidenced.[82] The same germirane had been made quite probable in another, earlier context.[38] In the present connection, neither the mechanism of the 1,2-addition of free Me_2Ge to styrene, nor that of the following 1,2-insertion of the second mole of styrene, could be cleared (see eq 21).



(21)

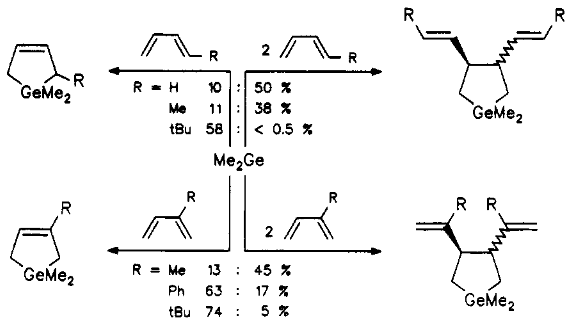
The use of *E*-2-deuteriostyrene yielded a mixture of cis/trans 2,5-dideuterio-3,4-diphenylgermacyclopentanes, and acyclic diradical intermediates have been concluded.[17a] On the other hand, no ESR signal could be observed, and strong radical scavengers both for carbon and Ge radicals (tBuBr) remained without any effect, no polystyrene was found, and the structure of both pure *E*- and *Z*-stilbenes remained unaffected.[82]

SCHEME III



Therefore, at least no free, diffusing radicals can be involved (see eq 21). Lastly a regiospecific but not stereospecific mechanism is in operation here.

Other conjugated olefinic systems gave also surprising reactions. Thirteen different 1,3-dienes, butadiene, and its 4-substituted derivatives showed that products of a 1,4-cycloaddition of free Me_2Ge are favored in the case of electron-deficient dienes (see section C.3.c). But, in several cases 1,2-addition also followed (concerning 1,2-addition, see also ref 49b) by an 1,2-insertion of a second diene, like with styrenes, see above, was obtained. Syn/anti mixtures of the corresponding 3,4-divinylgermacyclopentanes have been identified[85] (see eq 22).

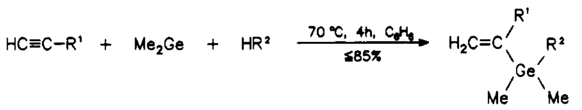


(22)

With acrylonitrile and free Me_2Ge 2, no product had been obtained, surprisingly at first. Thorough inspection revealed a side product whose origin, finally, could coordinate with unexpected traces of water diffusing out of the glass material of the dried and preheated flask. Stoichiometric amounts of H_2O, mediated by ground glass powder or silica gel, led to nearly quantitative yields of 11 (see Scheme III). A reversible formation of a germirane whose splitting yields lastly the germoxane 11 can be assumed. This mechanism is supported by the use of D_2O or $H_2{}^{18}O$ instead of H_2O.[74,86] The detailed impact of the H_2O molecules remains to be clarified (see also section C.4). Replacement of water by ROH or RCOOH gave the corresponding (alkoxygermyl)- or (acyloxygermyl)propionitriles (see Scheme III). Acrylic esters and methyl vinyl ketone behaved likewise, and only the olefinic group reacted.[86]

b. Alkynes and Phosphaalkynes. The C≡C group gives, with free germylenes, a puzzling variety of quite different types of products, or nothing at all. It is reasonable to assume the formation of a germirene in the first step, but has never been clearly be evidenced so far, unfortunately. In the presence of acid protons, however (in water, alcohols, or carbonic acids), a strictly regiospecific splitting occurs, rationalized in Scheme III.[86]

A variety of new 2- and 1,2-substituted-vinylgermyl acylates, alkoxides, and halides are formed in high yield and regioselectivity (eq 23).[87]

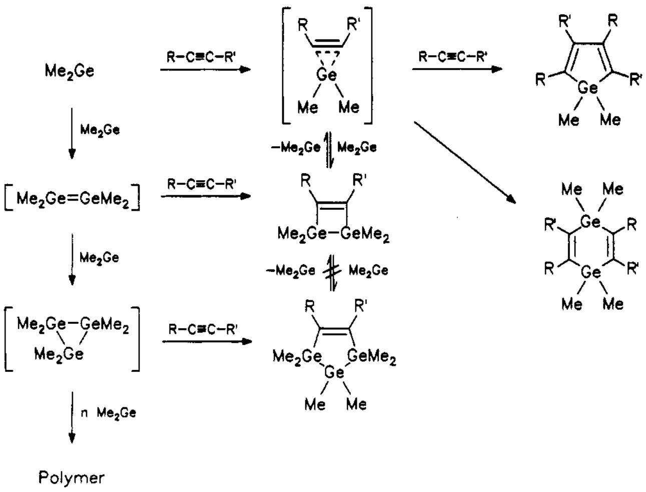


(23)

	a	b	c	d	e	f	g
R^1	Ph	t-Bu	Ph	t-Bu	CMe_2OAc	Ph	t-Bu
R^2	O_2CPh	O_2CPh	O_2CMe	O_2CMe	O_2CMe	O_2CCF_3	O_2CCF_3
	h	i	j	k	l	m	n
R^1	Ph	t-Bu	CMe_2OAc	Ph	t-Bu	Ph	t-Bu
R^2	OPh	OPh	OPh	OMe	OMe	F	F
	o	p	q	r	s	t	
R^1	Ph	t-Bu	Bu	Ph	t-Bu	Ph	
R^2	Cl	Cl	Cl	Br	Br	I	

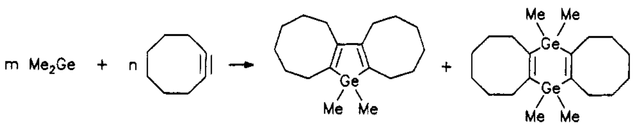
Without protic agents, the assumed germirene can insert a second alkyne molecule (R = Ph, R′ = H) or is stable enough to attend for dimerization (R = Ph, R′ = H; R = Bu, R′ = H; R = R′ = CH_2OMe; R = tBu or Bu, R′ = CN). There is a competition by the very rapid oligomerization of 2 (see section C.1) which often is successful. So, photolytically generated Me_2Ge is quenched by tBuC≡CCN with $k = 5 \times 10^8\ M^{-1}\ s^{-1}$, by $MeOCH_2C{\equiv}CCH_2OMe$ with $k = 2.8 \times 10^8\ M^{-1}\ s^{-1}$.[95] With certain alkynes, R = R′ = CF_3, e.g., the digermene is scavenged forming the 1,2-digerma-3-cyclobutene, whereas 1,2,3-trigerma-4-cyclopentenes apparently are generated by the cyclotrigermane (see Scheme IV).[62,63,89] The digermacyclobutene formation is made reasonable, since it has been shown[37,89] that an unequivocal digermene $R_2Ge{=}GeR_2$ (R = 2,6-Et_2-Ph) adds smoothly to PhC≡CH. Two other 1,2-digerma-3-cyclobutenes have been found, one of them by cycloaddition of $Me_2Ge{=}GeMe_2$ to the thiacycloheptyne mentioned below.[90,91] On the other hand, Me_2Ge insertion into strained C–Ge or Ge–Ge bonds (see section C.2) cannot be excluded at present to be responsible for the ring

SCHEME IV



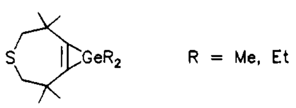
enlargements in Scheme IV.

Whereas internal alkynes, R = R′ = unsubstituted alkyl, are inert toward **2** (perhaps better: react too slowly to compete with the rapid polymerization of **2**), the strained cyclooctyne gives 2:1 and 2:2 products as well (eq 24).[63]



(24)

For several years germirenes have been sought after. The only one which has been clearly identified is **12**.

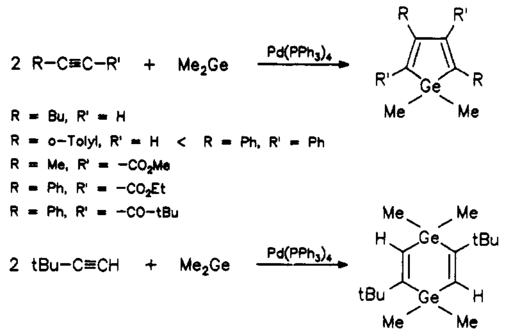


12

Its kinetic stability is deduced from the shielding by the four Me groups, preventing dimerization or the other consecutive reactions described above. It has been prepared from the corresponding thiacycloheptyne and **1** and has been explained at first by a germylene addition.[92] A recent observation of the authors, however, revealed that the formation of **12** proceeds much faster than it would correspond to the thermal, spontaneous generation of free Me_2Ge out of **1**.[93] In fact, an attack of the thiacycloalkyne to **1** takes place, therefore, and not a germylene reaction. Anyway, the existence of germirenes, when stabilized kinetically, thus is evidenced, also by X-ray analysis.[94]

Certain alkyne reactions with germylenes can be catalyzed by Pd complexes. For example, acetylene reacts with R_2Ge (R = Me,[62] Bu,[96] generated from **1**) to the corresponding 1,2,3-trigermacyclopent-4-enes. In the presence of Pd, acetylene forms a 2:1 cycloadduct, a germole, with R_2Ge (R = Bu, from **1**, R = mesityl, from the cyclotrigermane, see sections A.1 and A.3).[96] A number of substituted alkynes formed, analogously, a variety of substituted germoles or other cycloadducts with Me_2Ge[62] (see eqs 25 and 26) only by means of Pd catalysis.

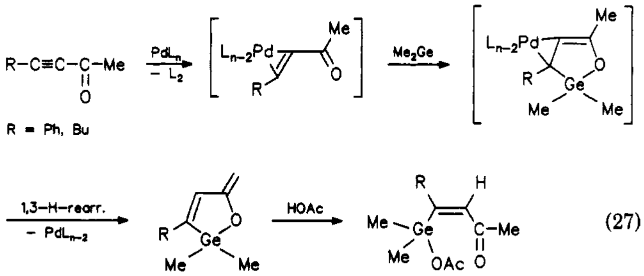
Acylalkynes formed oxagermacycloalkenes, presumably via the procedure shown in eq 27. Subsequent treatment with acetic acid leads to the vinylgermyl



(25)

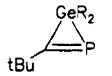
(26)

acetates indicated (see eq 27).[62]



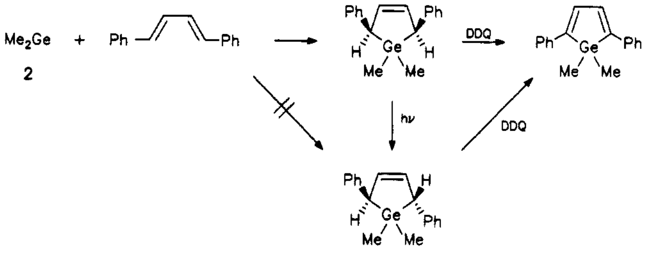
(27)

A first phosphagermirene **13** has been obtained from the phosphaalkyne tBuC≡P with R_2Ge, R = $CH(SiMe_3)_2$.[97]



13

c. Conjugated Dienes. 1,4-Cycloaddition of free germylenes is preferred by conjugated dienes.[85] A concerted mechanism takes place, the germylene acting as a nucleophile[60] (see section B.2). With adequate, pure stereoisomers of 1,4-disubstituted dienes, a disrotatory ring closure of the [4 + 2] chelotropic type has been observed exclusively.[12] This type of reaction and its stereospecificity has been used extensively to clarify where and when a free germylene is acting (see section B.2 and eq 28 as an example).



(28)

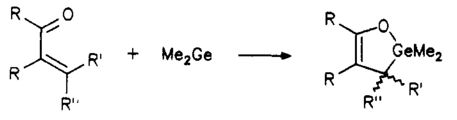
As shown here, only the energetically less favored syn isomer arises, but it can be converted afterward photolytically into the more stable anti isomer. The dehydration of the cycloadducts to germoles can be effected, e.g., by DDQ.[12] A high reactivity is exhibited by 1,2-bis(methylene)cyclohexane, but even more reactive is 1,2-bis(methylene)cyclopentane.[85] 2,3-Bis(methylene)norbornane and -bornene also give 1,4-cycloadditions, but also an addition of the germylene to one methylene carbon atom of two molecules, whereas the corresponding ring C atoms recombine, giving rather sophisticated polynuclear compounds with a germacyclopentane ring, preserving the remaining exocyclic methylene groups.[85] The latter case is the only and rapid reaction of 1,2-bis(methylene)cyclobutane. 1,4-Addition is more favored for a conjugated diene, when it is electron deficient, has a relatively high s-cis content (although maybe, absolutely low), and a C-1–C-4 distance of around 3.10 Å.[85] Many additional 1,4-cycloadditions are given in the literature cited, using also 2- and 2,3-substituted dienes. But, a proof for the involvement of a free germylene can only be provided by 1,4-disubstituted dienes (and not, for example, by the often-used 2,3-dimethylbutadiene[41,98]) as mentioned in section B.2.

Also for $GeCl_2$ 1,4-cycloadditions to 1,3-dienes have been described,[99] the like for the diaminogermylene R_2Ge, $R_2 = (NtBu)_2SiMe_2$, but in bad yield, besides a product of polymerization.[100a] This points against germylene mechanisms. With diallenes, however, clear germylene reactions could be achieved, equaling those in Scheme I.[100b] For GeI_2, similarly, clear evidence for a germylene-type behavior has been found.[12]

In any of the 1,4-adducts described in this section, a germacyclopentane or -cyclopentene ring is formed. Because of the close relationship of these rings to the germoles, and the increasing interest in the latter,[101,102] also an additional synthetic interest in the rings presented here may be anticipated.

d. Conjugated Hetero-Dienes. The versatile reactions of dienes with germylenes prompted, of course, in recent time a search into five-membered germacycloalkenes with additional heteroatoms.

Cyclic or acyclic vinyl ketones give good yields of cycloadducts with free Me_2Ge, yielding germanium-enolates, the 1-oxa-2-germacyclopent-4-ene derivatives (eq 29).[103]



(29)

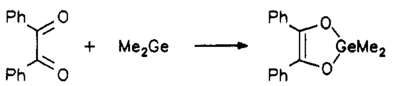
R, R =	R', R'' =
Me, Me	H, Ph
$(CH_2)_3$	H, Me
$(CH_2)_4$	$(CH_2)_4$

This reaction is, as it follows from the good yields, considerably fast. Me_2Ge, generated photolytically from 1, is quenched, e.g.; by PhCH=CH—C(Ph)=O with $k \approx 2.5 \times 10^9$ M^{-1} s^{-1}.[95]

Later on, crotonaldehyde, acrylic acid methyl ester, acrylic acid dimethylamide, and methyl vinyl ketone have been reacted the same way with the bulky diaminogermylene, $Ge[N(SiMe_3)_2]_2$.[104]

These Ge–enolates are, of course, of interest for further syntheses, beginning with hydrolysis forming γ-ketogermanes, or reactions with an electrophile like an aldehyde.

Nonenolizable α-diketones and 1,2-quinones produced 1,3-dioxa-2-germacyclopent-4-enes in acceptable to quantitative yields (e.g. eq 30).[43,103] With enolizable

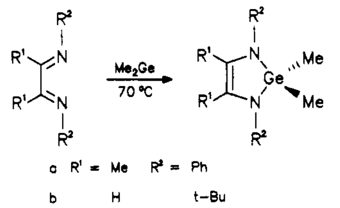


(30)

ketones, mainly insertion of the free Me_2Ge into the O–H bond of their enols has been found. tBuCOCOtBu did not react, apparently because of the complete absence of the s-cis conformer. This is in contrast to the behavior of Me_2Si, which forms 1,3-dioxa-2-silacyclopent-4-ene, probably via an 1,2-addition followed by a rearrangement.[105]

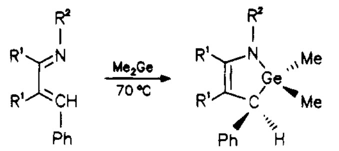
About the mechanism in eqs 29 and 30, nothing is certain except the involvement of a free germylene (from thermolysis of 1 whose rate is not accelerated). No intermediates could be detected. A 1,4-addition mechanism seems, however, acceptable.

1-Aza- and 1,3-diaza-2-germacyclopent-4-enes became accessible by cycloaddition of free Me_2Ge to several (di)azabutadienes (eqs 31 and 32).[106]



(31)

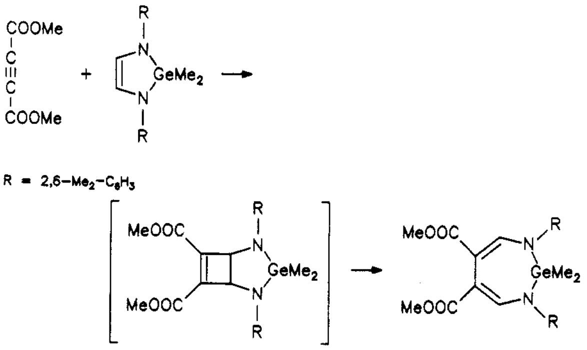
	R¹ =	R² =
a	Me	Ph
b	H	t-Bu
c	H	cyclo-C_6H_{11}
d	H	p-Me-C_6H_4
e	H	2,6-Me_2-C_6H_3



(32)

	R¹ =	R² =
a	Me	Ph
b	H	Ph
c	H	p-EtOOC-C_6H_4
d	H	p-MeO-C_6H_4
e	H	NH-C_6H_5

The products can, since they are also enamines or enediamines, be used for further syntheses. For example, the last mentioned diaza derivative e in eq 31 gives, via its double bond of high electron density, a smooth [2 + 2] cycloaddition with acetylenedicarboxylic acid dimethyl ester, forming at 20 °C finally the new (substituted) heterocycle 1,3-diaza-2-germa cyclohepta-4,6-diene[106] (see eq 33).

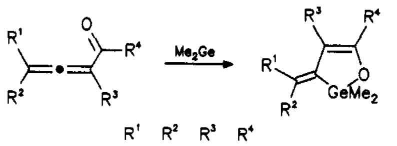


R = 2,6-Me_2-C_6H_3

(33)

e. Cumulated Systems like Allenes, Ketenes, Thioketenes, and Azides. The allene system C=C=C reacts—if it does so—exclusively with one of its strained double bonds (in contrast, normal alkenes like 1-octene do not react, see section C.3.a). An assumed 1:1 intermediate dimerizes or inserts a second allene, but it is hard so far to obtain uniform, pure compounds.[95,107] Anyway, electron-deficient allenes are easier engaged with germylenes (eq 34).[107]

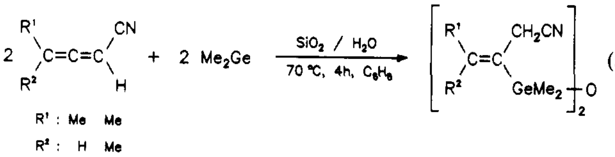
A completely regioselective synthesis of substituted vinyl germyl derivatives can be achieved when starting from allenes and free Me_2Ge. With water, the supposed



(34)

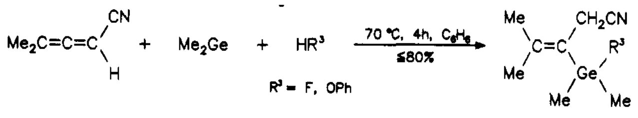
R¹	R²	R³	R⁴
H	H	H	Me
Bu	H	H	Me
H	H	Me	Ph
H	H	Bu	Ph
$(CH_2)_5$		Bu	Ph

unstable intermediate is stabilized, giving the germoxane (eq 35).[87]



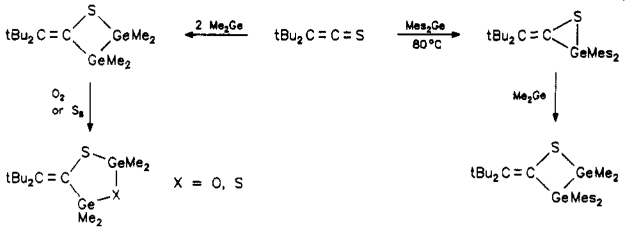
(35)

Other protic agents like HF or PhOH provide the halides or aroxides (eq 36)[87] where R^3Me_2GeH can be excluded as reactive intermediate.



(36)

Apparently no certain information has become known on reactions of germylenes with ketenes. Sterically hindered thioketenes, however, give with germylenes which are likewise sterically hindered (Mes_2Ge from the cyclotrigermane) an addition across the C=S bond, forming the stable alkylidene thiagermirane (eq 37).[79]

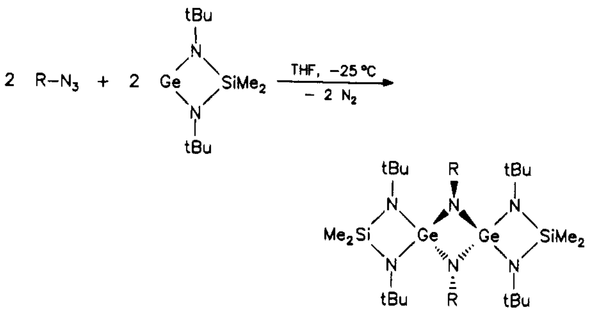


(37)

This thiagermirane is able to insert the small-sized Me_2Ge into the strained Ge–S bond, forming the alkylidene thiadigermetane (see eq 37). By starting with Me_2Ge (from 1), addition and insertion seem to follow each other immediately. Anyway, the thiadigermetane is obtained at once. Its structure is evidenced by X-ray crystallography, the Ge–Ge bond in this case still is reactive enough to insert O or S.[108]

Azides such as PhN_3 do not react with free Me_2Ge at 70 °C. The reason for this might be seen either in the very rapid polymerization of the latter, or, more probably, in its low Lewis acidity.[109] The kinetically stable diaminogermylene $Ge(NtBu)_2SiMe_2$, having a higher Lewis acidity,[64] reacts smoothly with phenyl and a number of acyl azides, $ArCON_3$. The dispirodigermatricyclodecane is formed (eq 38) presumably via the (not identified) germanimine which dimerizes or attacks another azide molecule via a 1,3-dipolar cycloaddition, giving the germa tetrazoline derivative (Scheme V).[109,110]

Germanimines have been postulated or evidenced earlier in many cases.[6,113] Another one is obtained from a diaminogermylene (eq 39).[111]

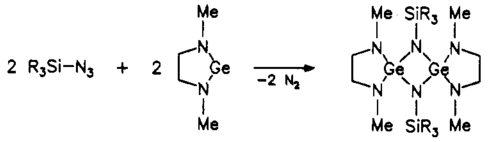


(38)

$$R_3Si{-}N_3 + Ge(NR'_2)_2 \xrightarrow[-N_2]{} R_3Si{-}N{=}Ge(NR'_2)_2 \qquad (39)$$

R = Et, OtBu, R' = $SiMe_3$

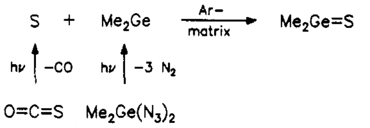
Silyl azides also gave rise to hexaazadigermadispirododecanes, well established by X-ray analysis (eq 40).[111]



(40)

The question still is open whether these reactions with azides can really be regarded as typical germylene reactions. More probably, the N–Ge–N unit acts as a Lewis acid here.[64,112]

f. Sulfur Atoms, Ketones, Thioketones, and Others. Certainly, germylenes will be oxidized by oxygen and other reagents, forming germanones, $R_2Ge{=}O$.[113] But, only consecutive products have been observed so far.[113] In the analogous case of sulfur, a sophisticated method has led to the matrix isolation of $Me_2Ge{=}S$, having a highly polar, true double bond, as established by IR (eq 41).[28] In other cases, the germanthione has been concluded from its consecutive products,[113] e.g. in the case of the crowded $(2,4,6\text{-}tBu_3Ph)_2Ge$.[66]

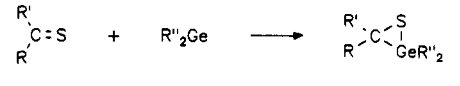


(41)

Results of unequivocal germylene 1,2-additions to carbonyl groups are apparently not known so far. A borderline case might be the first attack during the "redox copolymerization" of the diaminogermylene $Ge[N(SiMe_3)_2]_2$ with *p*-benzoquinone (eq 42).[114]

(42)

Good evidence, however, is available for germylene additions to thioketones. With a very crowded thioketone and a bulky germylene, X-ray crystallography gave clear evidence for the thiagermirane (eq 43).[115]

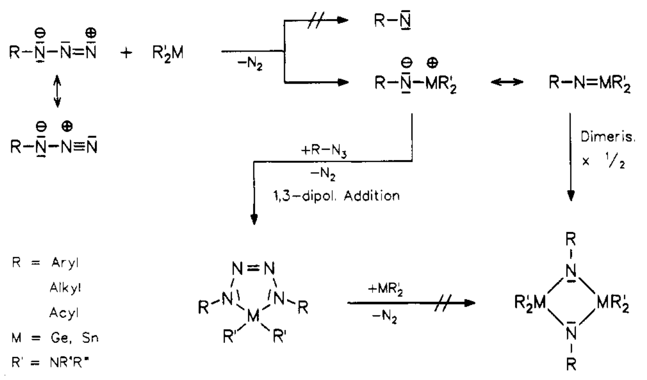


(43)

R = spiroadamantane, R' = spiro-1,1,3,3-Me_4-2-indanyl, R'' = Mesityl

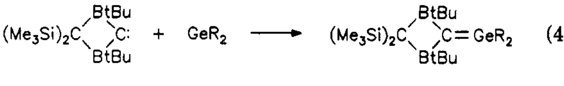
The same thioketone gave, with the smaller Me_2Ge, only a transient thiagermirane splitting off an intermediate $Me_2Ge{=}S$ which adds to another molecule of the thiagermirane forming 1,3-dithia-2,4-digermolanes.[115] An analogous five-membered consecutive product also followed from the reaction of adamantanethione with Me_2Ge, (from 1 at 70 °C) besides other

SCHEME V



cyclic derivatives.[116] Stronger crowding stabilized the thiagermirane also in this case. It has been isolated in crystalline form by addition of Mes_2Ge to adamantanethione. An analogous product could be scavenged by EtOH after the reaction of the less bulky Ph_2Ge (thermally generated from 1, R = Ph).[14]

Germenes $R_2Ge{=}CR_2$ have been derived from the interaction of germylenes with generated carbenes. Oligomers are formed spontaneously, and addition or cycloaddition products are formed as well.[117] A stable germene (germaethene) was obtained by this method and has been established by X-ray crystal analysis (eq 44).[118]



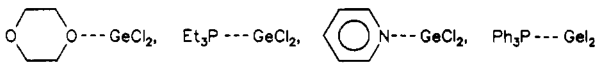
$$(Me_3Si)_2C\genfrac{}{}{0pt}{}{BtBu}{BtBu}C: + GeR_2 \longrightarrow (Me_3Si)_2C\genfrac{}{}{0pt}{}{BtBu}{BtBu}C{=}GeR_2 \quad (44)$$

R, R = $N(SiMe_3)_2$; R_2 = $(NtBu)_2SiMe_2$

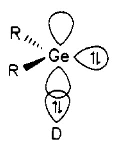
It should be made clear that this section can contain only the present, incomplete view on the possibilities given for germylenes here, as it follows from the scattered examples available.

4. Complexation by Donors

It has long since been known that germanium dihalides form rather strong complexes with donors, mostly stable at room temperature, e.g.[119-121]



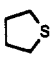
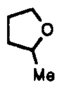
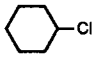
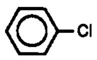
But, in the presence of a stronger reagent for $GeHal_2$, the complex is split. In these complexes with donors, the halides remain in their singlet ground state, the donor D interacts with the empty p orbital at the Ge 14, as X-ray crystallography revealed.[6,120]



14

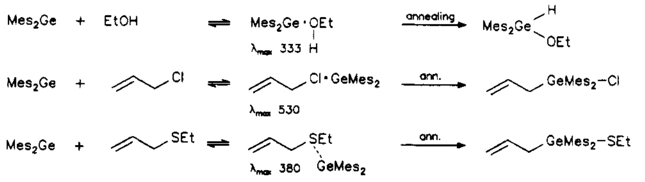
For dialkylgermylenes similar complexes, stable enough to slow down the R_2Ge polymerization, have been described in the earlier literature. For example, $Ph_3P{\cdot}GeMe_2$, measured by UV spectroscopy at 20 °C,[122] prolongated the lifetime of Me_2Ge at least five times. Pyridine·$GeEt_2$ or $Et_3N{\cdot}GeEt_2$,[72] assumed to be generated from $Et_2Ge(H)Cl$ and the base, react with oxiranes or thiiranes. $Et_3N{\cdot}GeEt_2$ is described to react only at 150 °C with MeOH, giving $Et_2Ge(H)OMe$, regarded as the insertion product. The relative stability of the pyridine complexes has been used to classify the electronegativity of Ge in a series of compounds GeX_2.[123] Some ambiguity is left by the older statement of stable complexes of Et_3N with diarylgermylenes, described to be generated from diarylchlorgermanes by dehydrochlorination,[41] since a recent report excludes stable complexes $Et_3N{\cdot}GeAr_2$ at room temperature, at least for Ar = Ph, Mes, and 2,6-Et_2-Ph, when starting from the free germylenes.[23]

TABLE II. UV Absorption Maxima (nm) of Diorganogermylene Complexes[a13]

	Me_2Ge	Ph_2Ge	Mes_2Ge	Ar_2Ge^d	Ar'_2Ge^e
3-MP[b]	420	466	550	544	558
Bu_3P			306	3147	334
		334	349	356	363
Me_2S		326	348	357	357
		332	352	359	366
		325	360	369	376
	341	374	495	508	544
	392	403	538	532	553
allyl-Cl			530		
allyl-SEt			380		
EtO-H		320	333	332	
tBuO-H		332	363[c]	367[c]	

[a] λ_{max} in 3-MP/IP(3/7) at 77 K. [b] λ_{max} in 3-MP at 77 K. [c] Digermene bands were observed during annealing. [d] Ar = 2,6-Et_2-Ph. [e] Ar' = 2,4,6-iPr_3-Ph.

A thorough UV investigation of complexes of unequivocal germylenes with donors has been carried out in hard and soft matrices. Heteroatom-containing substrates R_2O, ROH, R_2S, R_3P, R_3N, RCl, and RSR' have been shown to form adducts with typical absorption bands at shorter wavelengths compared with those of the free germylenes (see Table II).[13] As in the case of silylenes,[14] these new absorptions probably are due to n-p transitions, influenced by the substituents at the Ge.[13] Whereas germylenes are stable in hard matrices like 3-MP at 77 K, they dimerize slowly at the same temperature in soft matrices like isopentane (IP), or mixtures thereof. Thus, molecular processes could be observed and revealed, upon standing at 77 K or annealing, polymerization of the germylene $R_2Ge{\cdot}D \rightleftharpoons R_2Ge + D \rightarrow 1/n(R_2Ge)_n + D$, or, with suited complex partners, insertions (e.g. eq 45).[13]



(45)

The stability of all of these complexes is by far lower than that of the $GeHal_2$ complexes reported earlier. Thus, even $Ar'_2Ge{\cdot}PBu_3$ is stable only below −120 °C and decomposes slowly at −100 °C, giving the digermene. Its half-life time is 48 s at −79 °C. $Ar_2Ge{\cdot}SMe_2$ survives only below −140 °C. Others (see Table II) decomposed when the matrices were melted (or gave, in the cases mentioned above, the insertions indicated). Lastly, at room temperature none of these complexes survive. Therefore, several earlier observations and facts[13,124] need a new interpretation, presumably without involvement of real germylenes.

A special case is the germylene complexing ability of water. There is matrix (Ar) IR evidence for $H_2Ge{\cdot}OH_2$ and $H_2Ge{\cdot}{}^{18}OH_2$.[71] But, apparently water is involved, or can be involved in a number of germylene reactions reported, e.g., in sections C.2 and C.3. It is a matter of future research to elucidate whether, in these cases, really the germylene reacts, and water is a "brake" for its undesired, competing polymerization $R_2Ge + H_2O \rightleftharpoons R_2Ge{\cdot}OH_2 \rightarrow R_2Ge(H)OH$, or the complex itself is the reagent. Anyway, the product of the insertion into water or other acidic compounds like oximes[74] is excluded as reagent, since its consecutive reaction, e.g., with acrylonitrile[74] does not take place.[86]

It seems, anyway, that the donor complexes will have more importance in future germylene chemistry than until now.

III. Stannylenes, R_2Sn

As outlined in the introduction, such compounds R_2Sn will be dealt with in this review, where R is bound to Sn via a σ bond and consists, as far as possible, of a (monohapto) simple alkyl or aryl residue, but sometimes of a very bulky one.

Thus, π-bonded compounds like stannocenes, which also gained considerable interest, are not treated here. A good and recent treatment is available.[125]

Tin dihalides also are not covered here. Only a few examples are used, where a real stannylene-like behavior may be assumed or is established. The same is the case for tin derivatives like $Sn(OR)_2$, etc.

It is aimed to report, this should be kept in mind, on the behavior of compounds R_2Sn as heavy carbene analogues.

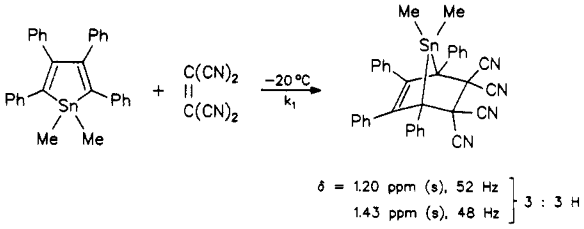
The work on stannylenes up to 1977 has been reviewed,[3a] and an account up to 1979 can be found.[126] Further on, a good but short treatment of this subject up to 1986 is available.[125] Thus, the present review considers in general, besides a number of fundamentals, the recent literature.

A. Generation of Stannylenes from Precursors

Certainly there are many more methods giving any type of "R_2Sn", or, more precisely, compounds $(R_2Sn)_n$ or $X-(R_2Sn)_n-X$, R = e.g. Me, Bu, Ph, than methods giving a real stannylene. For example, the attempted base-catalyzed (R_3N) dehydrohalogenation in fact generates first a distannane, which can be isolated, $R_2SnH_2 + R_2SnCl_2 \rightleftharpoons 2R_2Sn(H)Cl \rightarrow H_2 + Cl-R_2Sn-SnR_2-Cl$, but gives, with more hydride, lastly $Cl-(R_2Sn)_n-Cl$. With metals, an analogous series can be carried out: $2R_2SnCl_2 + 2Na\ (2Li,\ Mg) \rightarrow Cl-R_2Sn-SnR_2-Cl + 2NaCl\ (2LiCl,\ MgCl_2)$, etc.

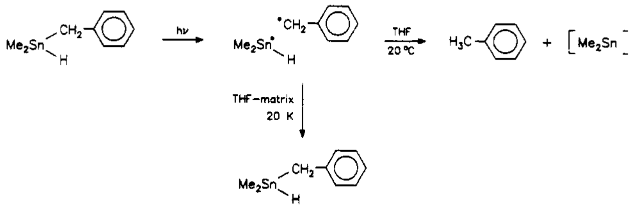
So, for long the question remained, whether there are real "simple" stannylenes, like Me_2Sn, Bu_2Sn, Ph_2Sn, as reactive intermediates, whose properties are not influenced by electronic (π-bonding like in stannocenes) or steric (kinetic) factors.

Cycloreversions starting from 7-hetero-substituted-norbornadienes have been successful in germylene generation (see section II.A.1). For stannylenes, many attempts remained unsuccessful. Lastly, a nicely crystallized 7-stannanorbornene, could be prepared at low temperature (eq 46).[127] It is the first, and also today, the only representative of this type. It decomposes even at −10 °C with $t_{1/2}$ = 17 min, $k = 6.8 \times 10^{-4}$ s^{-1}, the cycloreversion being strictly of the first order in several solvents. 5,5,6,6-Tetracyano-1,2,3,4-tetraphenylcyclohexa-1,3-diene is found quantitatively, no intermediate could be detected or trapped, and no CIDNP effects could be seen. Thus, a free stannylene Me_2Sn can be assumed.[127] But, the preparative application remained restricted so far.



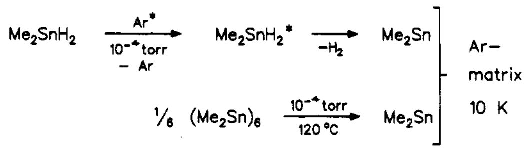
(46)

Benzyldimethyltin hydride (see eq 47) splits, upon specific irradiation in the benzyl absorption, selectively the benzyl–tin bond, which is followed by radical stabilization by means of hydrogen abstraction. At 20 °C toluene has been found quantitatively and $(Me_2Sn)_n$, very likely following from free Me_2Sn. This could be, in future, a stannylene source for preparative use. But, an attempt to trap Me_2Sn by matrix techniques at 20 K had no result: only the radical recombination was observed, presumably because of lack of activation energy for the following step (see eq 47).[128]



(47)

Me_2SnH_2 gave, after collision with activated Ar atoms in the gas phase by microwave discharge, real free dimethyl stannylene, Me_2Sn (see section B.1. and eq 48).[128]



(48)

The crystalline hexamer $[(CH_3)_2Sn]_6$[129] splits off free Me_2Sn thermally (see eq 48) but in a narrow range of temperature. Below 120 °C, the reaction is very slow, and above 130 °C, also bigger particles are split off, at first mainly Me_4Sn_2. The same has been found with the perdeuterated analogue, crystalline $[(CD_3)_2Sn]_6$,[129] splitting off free $(CD_3)_2Sn$ (see section B.1).[128]

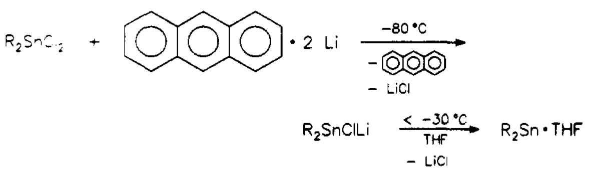
Certainly, these cyclostannanes and their analogues can also be used for preparative purposes, but the stringent conditions should be observed. Whereas in concentrated benzene solution $(Me_2Sn)_6$ remains stable at room temperature, a spontaneous and reversible equilibration both with higher and smaller rings $(Me_2Sn)_n$, n = 5,7,8, can be observed by NMR measurements. This effect becomes stronger upon heating. But, *this is by no means a proof for the existence of free stannylenes under these conditions.* On the contrary, a stannylenoid mechanism may be operative here passing through transition states with higher coordination at the tin atoms involved.[129]

The photolytical splitting of cyclic and open-chained oligostannanes should offer another way to free stannylenes,[129,130] but little certain information is available on the mechanism. For cyclostannanes, after irradiation a radical ring opening is discussed, forming a "hot" biradical, splitting off subsequently stannylenes: $(R_2Sn)_n \rightarrow R_2Sn + {}^{\bullet}(R_2Sn)^{\bullet}_{n-1}$, etc.,[3a] like with germylenes (see section II.A).

Pure $(Bu_2Sn)_6$ gives in the mass spectrometer, upon flash mass chromatography, at first mainly $(Bu_2Sn)_5$ besides $(Bu_2Sn)_7$ and the unchanged hexamer.[3a] This may indicate a split off of a Bu_2Sn particle followed by its insertion into the hexamer. Later on, larger, rearranged, and other fragment ions appear. Also in this case, a proof for a stannylene mechanism is lacking.

In recent time, cyclotristannanes with bulky substituents gained attention, $(R_2Sn)_3$, R = 9-phenanthryl,[131,132] 2,6-Et_2Ph,[133] 2,4,6-iPr_3Ph.[134] They can be regarded as thermal and photolytical stannylene sources. With R = 2,4,6-iPr_3Ph, the cyclotristannane is thermodynamically stable at 0 °C or below. But, at room temperature or above, a rapid equilibrium with the dimer $(Ar_2Sn)_2$ occurs, the latter being favored at higher temperatures. Indeed, the stannylene Sn(2,4,6-$iPr_3Ph)_2$ could be trapped from such mixtures with reagents like 2,3-dimethyl-1,3-butadiene or Bu_3Sn-H.[134] (For the reactions occurring, see below). But, no further application has been done so far, it seems, and mostly the remaining distannene, $R_2Sn{=}SnR_2$, has attracted attention.[29b] For additional information on crowded stannylenes or, respectively, oligomers, compare ref 125. Mostly, the arylation reaction is used, e.g. $SnCl_2$ + 2ArLi → "Ar_2Sn", but also for simple "stannylenes", see above.

In one case of the latter type, an interesting insight into elimination mechanisms could be obtained, when THF was used as a strong complexing agent (see eq 49).[150]

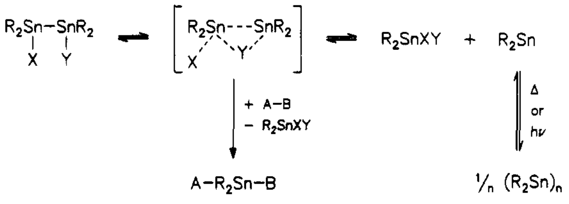


(49)

R = Me, CD_3, Et, tBu

In the future, the insertion of Sn atoms into certain σ bonds might become a stannylene source. At present, it may be assumed that the synthesis 2 R–Hal + Sn → R_2SnHal_2, which has been, in E. Frankland's hands,[1] the beginning of organotin chemistry in 1849, could start with such an insertion, R–Hal + Sn → RSnHal, involving probably single electron transfer (SET). *Intense attempts have been made to use this reaction also for technical syntheses, and a considerable progress has been achieved.* Many catalysts have been used,[135] and the efforts are continued.[136]

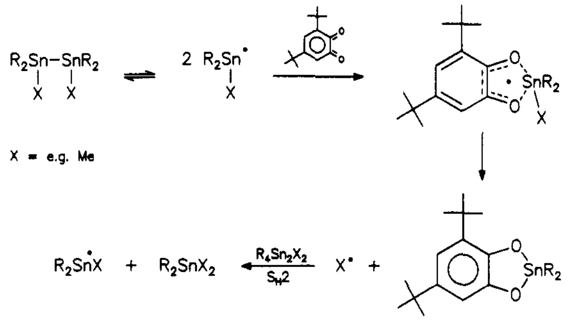
In preparative scale, a group of 1,2-shifts, formal α-eliminations, is used for doing "stannylene" chemistry.[3] There might be, in one case or the other, a free stannylene. But, mostly internal complexes or transition states have to be assumed (eq 50).[137,138] All the migration groups indicated have been used, but SPh seems to have the best migratory aptitude, both thermally and photochemically.[137,138]



(50)

X = Y or X ≠ Y = alkyl, Hal, OAc, SnR_3, $(-R_2Sn-)_n$, SPh

But, care should be taken. Another splitting of di- and oligostannanes may occur, and a radical one, both thermally and photolytically,[139] established (e.g. eq 51).[140] This mechanism can be in operation also with cyclic α-keto oxime ethers or α-keto Schiff bases. The intermediate, five-coordinate tin-containing radical mostly can be detected by ESR spectroscopy, and sometimes reaches high steady concentrations.



(51)

Since the very rapid polymerization of free stannylenes like Me_2Sn, Bu_2Sn, and Ph_2Sn occurs even at low temperatures such as −30 °C or below, it needs apparently no activation energy, $k = 10^8\ M^{-1}\ s^{-1}$. This often impedes reactions needing activation energy, and therefore higher temperatures.

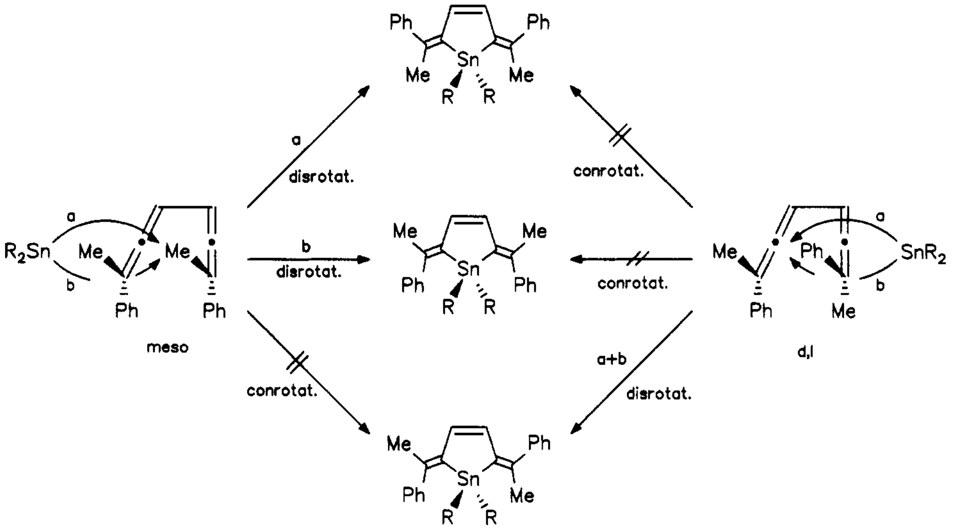
In many cases, a slowdown or even prevention of the polymerization of R_2Sn has to be achieved for preparative stannylene reactions. In future, some hope may be given by a complexation of R_2Sn by strong donors, like in the R_2Ge case (see section II.C.4). Apparently, the THF action in eq 49 can be considered as a first hint. Therefore, at present those stannylenes often are used which are stabilized electronically or sterically, or both. In practice, these are the well-known Lappert's dialkyl stannylene $Sn[CH(SiMe_3)_2]_2$[141] and diamino stannylene $Sn[N(SiMe_3)_2]_2$[141] and Veith's diamino stannylene $Sn(NtBu)_2SiMe_2$.[64] With the amino stannylenes, both stannylene and non-stannylene mechanisms have to be expected, see below.

B. Isolation and Identification of Free Stannylenes

1. Matrix Spectroscopy and Trapping

A real, free stannylene Me_2Sn, a heavy carbene analogue, does exist: By starting from crystalline $(Me_2Sn)_6$[129] thermally at 120 °C, and independently from Me_2SnH_2 by splitting off H_2 by using microwave-activated Ar, Me_2Sn could be isolated in an Ar matrix at 5 K. Well-resolved and intense IR spectra

SCHEME VI



have been obtained. All 10 bands could be assigned by normal coordinate analysis to monomeric, strongly bent Me_2Sn. The symmetry is C_{2v}. The H_3C–Sn valence stretches are $\nu_s = 504$ cm^{-1}, $\nu_{as} = 518$ cm^{-1}.[128] The Raman spectrum is in accordance with this, and Sn–Sn vibrations are absent, as to be expected.[129] Tempering the matrix up to 30 K caused no alterations in the IR spectrum.

To support these conclusions and the assignments further on, crystalline $[(CD_3)_2Sn]_6$ has been prepared[129] and thermolyzed, giving free $(CD_3)_2Sn$ in an equal Ar matrix. Again, good IR spectra obtained by this way could be used for a normal coordinate analysis, the D_3C–Sn valence stretches being $\nu_s = 462$ cm^{-1}, $\nu_{as} = 476$ cm^{-1}, in accordance with what had to be expected.

2. *Chemical Techniques*

To decide whether a free stannylene is really reacting, and whether it has a singlet or a triplet state, the stereospecific reaction of adequately 1,4-disubstituted 1,3-dienes with R_2Sn has been used. But, neither starting from the 7-dimethylstannanorbornene described in section A, nor starting from $(Me_2Sn)_6$, thermal additions to (*E,E*)-1,4-diphenyl-1,3-butadiene or the stereo isomers of the 1,1,6,6-tetrasubstituted diallene used in sections II.B.2 and II.C.3 could be achieved so far. Only the polystannane was obtained or recovered.[129]

Finally, clear results could be obtained at room temperature with Lappert's dialkyl stannylene and the meso or, respectively, *d/l* isomers of the diallenyl derivative (see Scheme VI) R = $CH(SiMe_3)_2$. Quantitative yields have been obtained, and only those products could be observed which have to follow from disrotatory ring closure corresponding to a thermal [4 + 2] chelotropic pericyclic reaction in accord with the Woodward–Hoffmann rules.[142] The cross-check, given by the application of both isomers indicated, is conclusive.

The singlet state, well established for this stannylene (see section B.3.) is confirmed chemically, therefore. It behaves as a donor in these cycloadditions, reacting, more rapid with electron poor dienes (see section III. C.3).[142] This corresponds to a HOMO-stannylene/LUMO-diene interaction, in accord with the orbital situation at this stannylene (see section B.3). But also Veith's diaminostannylene, $R_2 = (NtBu)_2SiMe_2$, and $SnCl_2$, $SnBr_2$, and SnI_2 as well (suspended in dry benzene) behaved likewise: only disrotatory thermal ring closure has been observed in all cases. Because of the different HOMO/LUMO situation of this diaminostannylene (if one follows the MNDO calculations, see section B.3.), results of additions to dienes of different π-electron density would be of importance.

3. *Quantum Chemical Considerations and Calculations*

For SnH_2, a singlet ground state $^1A_1$ resulted from ab initio, double-ζ quality calculations in the valence region, the bond length has been calculated to be Sn–H = 1.756 ± 0.005 Å, and the angle H–Sn–H = 92.7 ± 0.5°. For the excited triplet $^3B_1$ state, likewise 1.707 Å and 118.2° followed by the same way, the S/T gap being 25 kcal/mol.[54] In later information, 23 kcal/mol has been given.[53] Another group used SCF MO calculations and found for SnH_2 a Sn–H distance of 1.77 Å, and ∠ H–Sn–H = 93° in the S ground state.[55]

For Me_2Sn a singlet ground state followed from ab initio SCF calculations by using a given pseudopotential method with C–Sn = 2.203 Å, and ∠ C–Sn–C = 95.3°, a S/T separation of 22 kcal/mol, and a dipole moment of 0.43 D.[128] These findings are in agreement with the IR measurements and normal coordinate calculations, see above.

By a MNDO SCF MO method, for Me_2Sn also a singlet ground state has been calculated, but a much shorter C–Sn distance of 2.03 Å, and a higher C–Sn–C bond angle of 99.1° followed there, as well as a high dipole moment of 2.94 D.[143] (As stated there, MNDO consistently underestimates bond lengths to tin.)

A later investigation of Me_2Sn also using an MNDO MO method,[144] ends up, without referring to the earlier results, in the S ground state of Me_2Sn with ∠ C–Sn–C = 101.2°, which also seems surprisingly high (net charge at the Sn = +0.56). The HOMO of Me_2Sn is the in-plane lone electron pair on tin, and the LUMO the out-of-plane unoccupied 5p orbital on tin.

For Lappert's dialkylstannylene, R_2Sn, R = $CH(SiMe_3)_2$, in the gas phase followed from electron diffraction measurements, a long bond length of C–Sn = 2.22 Å, and an angle C–Sn–C = 97°,[56] (another value is 96°) which indicates only little distortion by the bulky

R groups, less than for the corresponding R_2Ge (see section II.B.3). This certainly is due to the longer Sn covalent radius. For the diamino stannylene, R = $N(SiMe_3)_2$, the angle N–Sn–N is 96°, too, in the gas phase, but 104.7° in the crystalline monomer.[56] The former dialkyl stannylene, on the other hand, gives a dimer in the solid state (see section C.1).

Whereas for R_2Sn, R = $CH(SiMe_3)_2$, the HOMO/LUMO situation is the same as for Me_2Sn, see above, for the diaminostannylene only the LUMO situation remains unchanged (again a 5p orbital, orthogonal to the N–Sn–N plane). The HOMO and also the next bound orbital, however, are calculated to be localized, surprisingly, on the nitrogen atoms, as lone pairs. The tin lone pair (normally presenting in stannylenes the HOMO), here is admixed with σ (Sn–N), more than 1 eV lower in energy than the HOMO.[144] These conclusions should be considered when mechanisms of diaminostannylenes are discussed.

A thorough study, using a MNDO SCF MO model, has been concentrated on R_2Sn and the mechanisms of its insertion and cycloaddition reactions.[143] For example, a synchronous mechanism of the 1,4-cycloaddition of $SnBr_2$ to 1,3-dienes with a symmetrical transition state has been calculated to be more favorable than a two-step mechanism. Following the same study, for insertions of Me_2Sn into $Me_2ClSn–Cl$ and $Me_3Sn–Cl$, a concerted, one-step mechanism without an intermediate has been calculated to be preferred, but a radical abstraction–recombination one for the insertion into MeI.

C. Reactions of Stannylenes

1. Oligo- and Polymerization, Influence of Bulky Substituents[29b]

Simple stannylenes like Me_2Sn, Bu_2Sn, and Ph_2Sn polymerize very rapidly, $k = 10^8\ M^{-1}\ s^{-1}$, forming, dependent on the conditions, smaller or larger cyclostannanes $(R_2Sn)_n$, n = 3,4,5,6... with real Sn–Sn σ bonds and sp^3 hybridization around the tin. Structures with tetrahedral building blocks are formed, as established by X-ray crystallography (one of the earliest examples is $(Ph_2Sn)_6$ which has, in crystalline state, a chair conformation[1]) and also by NMR techniques, especially ^{119}Sn NMR.[129] A thermal depolymerization takes place, for $(Me_2Sn)_6$ at 120 °C (see section B.1), but also photolytically at room temperature.[130,138] During photolysis, attention should be given, for preparative use, to unwanted C–Sn splitting besides the desired Sn–Sn splitting.

With bulky substituents, the polymerization is slowed down, becomes reversible, or is prevented completely. For example, R_2Sn, R = 2,4,6-iPr_3Ph, gives a cyclic trimer below 0 °C, which is, at room temperature in equilibrium with the dimer, and the stannylene can be trapped.[29b,134] Lappert's dialkyl stannylene R_2Sn, R = $CH(SiMe_3)_2$, is monomeric in the gas phase, whereas in solution there is a monomer–dimer equilibrium, and the crystalline solid phase is formed by the dimer.[145] No higher oligomers have been observed. The dimer, however, is not built up by a normal Sn—Sn or Sn═Sn bond. The distance being 2.76 Å (quite near, by coincidence, to the "normal" Sn—Sn bond), but structure and bonding are much more complicated here. A bent, centrosymmetric structure has been found for $[R_2Sn{\cdot}SnR_2]$, and an overlap of the nonbonding orbital of each monomer unit with the orthogonal vacant p_z orbital of the other has been concluded.[145] Following MNDO calculations,[144] a distannene structure Sn═Sn also cannot be sustained (the Sn—Sn bond order is only 0.17, as calculated), the structure mentioned above is questioned, and a cyclic dimer with ligand participation is discussed, and probable for diamino and dialkoxy stannylenes.

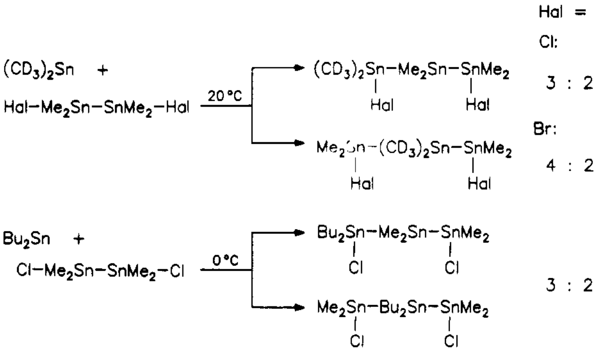
Lappert's stannylene remains monomeric even in the crystal, when the H in its substituted methyl group is replaced by 2-pyridinyl.[146]

Also for diaminostannylenes, a reversible dimerization in solution has to be considered. $Sn(NiPr)_2SiMe_2$ is, e.g., dimeric in solution and has, at room temperature, a fluxional structure. The dynamic behavior is interpreted as an intramolecular process.[147]

2. Insertion into σ Bonds

Free stannylenes Me_2Sn, generated from the 7,7-dimethyl-7-stannanorbornene, or Et_2Sn, generated from Et_2SnCl_2 with anthracene–lithium (see section III.A) give, when partners are lacking, exclusively $(Me_2Sn)_n$ or, respectively, $(Et_2Sn)_n$. These are detected quantitatively after aeration as $(Me_2SnO)_n$ or $(Et_2SnO)_n$. In the presence of excess Me_2SnCl_2, however, substantial amounts of e.g. $ClMe_2Sn–SnEt_2Cl$ have been isolated.[148,149] This indicates clearly an insertion into Sn–Cl bonds. With the less electron deficient tin in $Me_3Sn–Cl$, however, this bond is inert at 20 °C.

The Sn–Sn bond in hexaalkyl distannanes Me_6Sn_2 and Et_6Sn_2 behaved inert under mild conditions, i.e. at or below 20 °C. (This does not exclude insertions at higher temperatures like 100–140 °C, starting from other stannylene sources.[3a]) But, in 1,2-dihalo distannanes, the Sn–Sn bond, being more electron deficient, proved to be nearly as active as the Sn–Hal bonds even at 20 °C, when starting from the corresponding 7-stannanorbornene (eq 52).[150] With $(CD_3)_2Sn$, under appropriate conditions, the overall yield is nearly a quantitative one; with the more bulky Bu_2Sn only a 2% yield has been found. For the analysis of these mixtures, besides NMR techniques in situ, a derivatization of the halide products using RMgI at 0 °C with consecutive GLC has been used.[150]



(52)

Also $Me_3Sn–Sn(C_6F_5)_3$ proved to be active enough at 20 °C for an insertion of free Me_2Sn into its Sn–Sn bond.[150]

Sn–Br and Sn–SPh bonds in Me_2SnBr_2 and $Me_2Sn(SPh)_2$ also do insert free Me_2Sn at 20 °C.[150] But, at 80 °C, this reaction becomes reversible, and an equilibrium with $(Me_2Sn)_n$ is reached after 1 h[137] (see eq 50).

During these reactions, the first-order rate of the thermolysis of the stannylene (Me_2Sn) source, the 7-stannanorbornene, remained unchanged. The insertions mentioned above can be considered, therefore, as reactions of real, free Me_2Sn.

The R_2SnCl_2/anthracene·2Li source gave, in all of these cases, the same results. For details, see ref 150.

$(Me_2Sn)_6$ is a thermal stannylene source, as shown at least at 120 °C (see section III.B.1).. In solution, it is inert toward organotin chlorides or Bu–Br at 20 °C, but at 80 °C the insertion product $Bu–Me_2Sn–Br$ appears. Also MeI inserts Me_2Sn at higher temperatures.[3a]

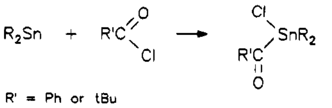
Care should be taken, again, when considering mechanisms. For example, pure $(Me_2Sn)_6$ is inert at 20 °C toward Me_2SnCl_2 and Bu_2SnCl_2 in THF, see above. Admixing of a little LiCl to the THF solution did not affect the hexamer, but the dialkyltin dichloride (^{119}Sn NMR). Then, the hexamer reacts smoothly, giving a 75% yield of $Cl–Me_2Sn–SnMe_2–Cl$ with Me_2SnCl_2, and a 60% yield of $Cl–Et_2Sn–SnMe_2–Cl$ with Et_2SnCl_2, after 2–4 h.[129,151] Formal Me_2Sn insertion products are built up, but no free Me_2Sn is involved here, presumably. The kind of LiCl catalysis still requires further investigation.

Long-waved irradiation of $(Me_2Sn)_6$, or $(Bu_2Sn)_n$, however, initiates insertions of Me_2Sn or Bu_2Sn units into, e.g., the C–Hal bonds of MeBr, BuBr, allylCl, and benzylCl, the Sn–H bonds of Me_3SnH and Me_2SnH_2, the C–Sn bonds of Me_4Sn, and the Sn–Sn bonds of Me_6Sn_2, forming the corresponding products, in the last example, e.g., $Me_3Sn–Bu_2Sn–SnMe_3$. Likewise, the O–O bonds in tBu_2O_2 or $(PhCO)_2O_2$ do insert Me_2Sn or Bu_2Sn, as do the S–S bonds in Et_2S_2, tBu_2S_2, Ph_2S_2, and $(PhCO)_2S_2$, forming, each time, the Me_2SnX_2 or Bu_2SnX_2 products which are expected.[130] In all of these cases, again, a stannylene mechanism is assumed, but remains to be established finally.

And, even in an established stannylene insertion, both a one-step and a two-step mechanism (radical abstraction–recombination) have to be envisaged following MO calculations.[143] Moreover, a preceding complexation of R_2Sn by the partner or the solvent may be discussed (see section III.C.4).

A rapid stannylene insertion into the very strained C–Sn bond of a stannirene, generated by R_2Sn addition to a strained alkyne (see section III.C.3) is assumed at room temperature, even in a rather crowded environment. Anyway, there is clear evidence for the 1,2-distannacyclobut-3-ene.[152]

Much insertion work with "simple" stannylenes remains to be done, since the crowded (but not easy to prepare) stannylenes indicated a high and versatile reactivity. Thus, Lappert's dialkylstannylene, R_2Sn, R = $CH(SiMe_3)_2$, inserts easily into C–Hal bonds of alkyl, aryl, and even acyl halides[153,154] (see, e.g., eq 53). And,



(53)

R' = Ph or tBu

the corresponding diaminostannylene, R = $N(SiMe_3)_2$, likewise inserts into C–Hal bonds of BuCl, MeBr, EtBr, PrBr, tBuBr, PhBr, MeI, EtI, iPrI, BuI, PhI, CCl_4, $CHCl_3$, and CH_2Cl_2.[154] Veith's diaminostannylene, R_2Sn, R_2 = $(NtBu)_2SiMe_2$, gave, with open-chained or cyclic 1,2-dichloro or 1,2-dibromo derivatives, the corresponding olefins[155] and no detectable insertion products.

Anyway, no stannylene insertions into C–H or C–C bonds are known so far.

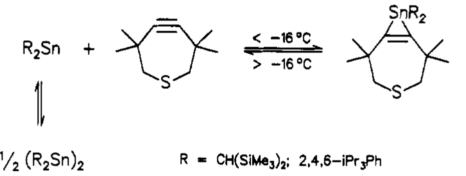
In summing up, the presently restricted number of insertions of Me_2Sn, Ph_2Sn, etc. certainly is handicapped by the rapid polymerization of these stannylenes, but certainly not has come to its end.

3. Addition to Unsaturated Systems

Reactions of isolated C=C groups with stannylenes seem not to be known, neither with short-lived nor with persistent "pilot" ones.

For the addition of H_2Sn to acetylene HC≡CH, MO calculations predict a thermoneutral, easily reversible addition.[156] No experiments with unstrained, nonactivated alkynes are published.

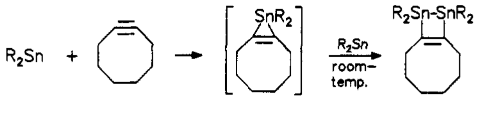
With strained cycloalkynes, however, successful additions could be carried out under very mild conditions. If the steric bulk both of the stannylene and the alkyne environment is sufficient, the stannirene could be obtained and characterized by X-ray crystallography (eq 54).[157]



(54)

R = $CH(SiMe_3)_2$; 2,4,6-iPr_3Ph

If there is more space available than in this case, a rapid insertion of a second bulky stannylene occurs, giving the 1,2-distanniacyclobut-3-ene, which is stable at room temperature against air and moisture, and is evidenced both by X-ray crystallography and chemical reactions (eq 55).[152]



(55)

R = $CH(SiMe)_2$

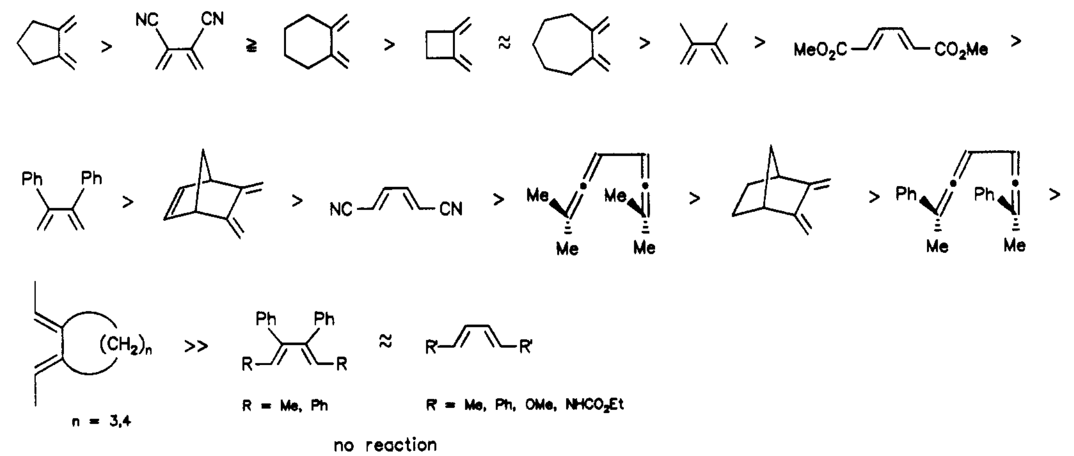
With 2 moles of R_2Sn, R_2 = $(NtBu)_2SiMe_2$, and the thiacycloheptyne, the first distannacyclobutene has been found and unequivocally proved by X-ray analysis.[91] In contrast to the cyclooctyne product mentioned above, this four-membered ring is easily split by warming it, giving the educts. In light of the investigations discussed above, in this case a transient stannirene may also be supposed, followed by the insertion of the second mole R_2Sn.

A 1-phospha-3,4-distannacyclobut-1-ene, prepared from tBuC≡P and R_2Sn, R = $CH(SiMe_3)_2$, and clearly evidenced,[158] should close here this triple bond series. An addition of the stannylene's dimer has been proposed,[158] but regarding the arguments given above a stannylene addition–insertion sequence also could be thought of, it seems.

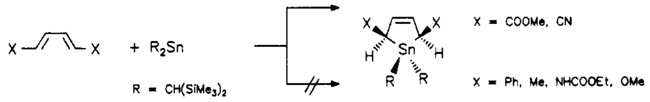
The conjugated dienes and hetero dienes offer an interesting field both for synthetic and mechanistic studies.

With respect to the mechanistic point, and in order to check the singlet state of the reacting stannylenes, 1,4-cycloadditions to 1,4-disubstituted 1,3-dienes have

SCHEME VII



been dealt with in section III.B.2. A chelotropic [4 + 2]-pericyclic reaction with disrotatory ring closure has been established at 20 °C. Only those stannylenes reacted that are monomeric under these conditions, or at least are in equilibrium with the monomers. For the dialkylstannylene, R_2Sn, R = $CH(SiMe_3)_2$, a reactivity has been found only toward those 1,4-disubstituted dienes (*E*,*E* isomers) bearing electron-withdrawing groups (X = e.g., COOMe, CN), whereas electron neutral or donating ones diminished or nullified the reactivity even at 80 or 110 °C (X = e.g., Ph, Me, NHCOOEt, OMe) (see eq 56).[142] Only the thermodynamically less favored syn isomers have been detected (see eq 56). Again, a disrotatory ring closure follows. Moreover, the stannylene is seen to act as a donor, that means an interaction of this HOMO (the lone pair at the tin atom) with the LUMO of the diene can be derived, like with germylenes. Quite a number of further 1,3-dienes gave corresponding stannacyclopent-3-enes, too, and different functional groups can be carried by the dienes, also in 2- or 2,3-positions. It follows that FMO considerations alone are not satisfying to explain the reactivity of 1,3-dienes toward R_2Sn: Free terminal CH_2 groups do enhance the reactivity, as does a higher (or exclusive) content of the s-cis conformer. Lastly, the following reactivity sequence for dienes could be set up in competition experiments, 1,2-bismethylene cyclopentane being the most reactive (see Scheme VII).[159]

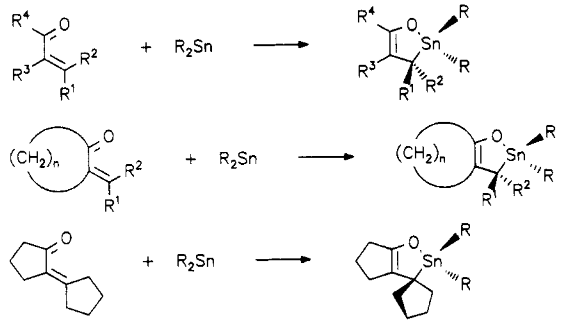


(56)

In no case could any other products like 1,2-adducts, dimers thereof, or insertion derivatives of a second olefin into them be observed. This is a clear difference between stannylenes and germylenes (see section II. C.3).

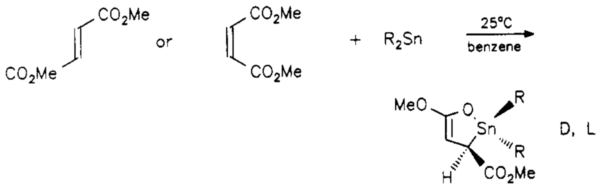
All these experiments with dienes (except those with diallenes) have only been done with the stannylene, R_2Sn, R = $CH(SiMe_3)_2$. It would be of interest to check here other stannylenes, especially diaminostannylenes, also with respect to the calculated difference in their HOMO situation (see section III.B.3).

Considerable work has been done with oxa dienes. With R_2Sn, R = $CH(SiMe_3)_2$, both open-chained and cyclic s-cis fixed vinyl ketones, and aldehydes as well (R^4 = H), gave quantitative yields of the substituted oxa-2-stannacyclopent-4-enes (stannyl enolates) when stirred in benzene at room temperature. Several esters (R^4 = OMe) also belong to this group giving, surprisingly, the corresponding ester enolates slowly and in 30% yield (see eq 57).[160]



(57)

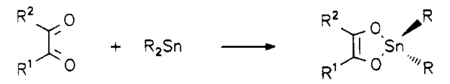
This prompted the investigation of maleinic and fumaric acid esters. Both gave, very slowly, the same cycloadduct in 60% yield (eq 58).[160]



(58)

No intermediates could be detected. The mechanism remains open, at first. A concerted 1,4-addition as with dienes is possible, but a 1,2-addition of R_2Sn across the CO or the vinyl group of the oxadiene with subsequent rearrangement to the oxastannacyclopentene cannot be excluded. Anyway, the carbonyl activity is not dominant, ketones react as fast (or faster) as aldehydes.

The same stannylene also added to a selection of 1,2-diketones, open-chained and cyclic ones, giving good yields of 1,3-dioxa-2-stannacyclopent-4-enes, which also can be considered as stannylenediolates (see eq 59).[160]



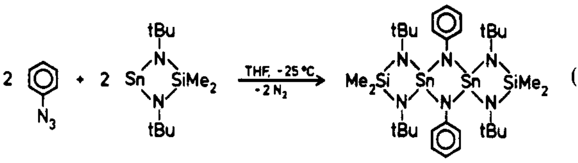
(59)

In competition experiments using derivatives with comparable structures the following reactivity sequence has been established toward the same stannylene R_2Sn: 1,2-diketones > vinyl ketones > 1,3-dienes.[160]

Other heterodienes seem not to have been investigated so far, with one neighboring exception: 4,4-bis(trifluoromethyl)-substituted dihetero dienes $(CF_3)_2C{=}N{-}CR{=}X$, X = O, S, NR, gave 1,4-cycloadducts with $SnCl_2$. In one of the CF_3 groups in the product, the F substituents became mobile and useful for further syntheses.[161]

Allenes and diphenylketene did not react with Me_2Sn or R_2Sn, $R_2 = (NtBu)_2SiMe_2$.[109,162] A stable stannaethene, $(Me_3Si)_2C(BtBu)_2C{=}Sn[CH(SiMe_3)_2]_2$, has been obtained from the recombination of the R_2Sn with the diborylcarbene, and has been evidenced by X-ray analysis.[163]

This stroll across the additions of stannylenes to unsaturated systems should be concluded by meeting the exotic products of a number of azides $R{-}N_3$, R = alkyl, aryl, acyl, sulfonyl, as elaborated independently by two groups.[109,110,164,165] A dispirodistannadecane could be established by X-ray crystallography (see eq 60).[164]



(60)

Also a stanna tetrazoline could be found, analogous to the germylene case. In accordance with all findings, an intermediate with something like a Sn=N bond can be assumed, which either dimerizes forming the dispiro derivatives, or adds to a second azide molecule via a 1,3-dipolar cycloaddition, forming the tetrazoline (compare Scheme V and section II.C.3.f).

4. Complexation by Donors or Acceptors

Both acceptors and donors are invited by dialkyl stannylenes R_2Sn to complex formation, acceptors via the lone pair of electrons (HOMO), donors via the empty 5p orbital (LUMO) at the tin atom. In fact, these stannylenes act as donors in many reactions, see above, likewise replace, e.g., CO from $MO(CO)_6$, and exhibit an extense coordination chemistry, as had been stated even in early days of R_2Sn, R = $CH(SiMe_3)_2$,[112,125] e.g. with many transition-metal compounds. Since long, similar complexes also of simple stannylenes, R = Me, Bu, tBu are known, and even complexes formed with a donor and an acceptor simultaneously, e.g. in[166] $^1/_2[Bu_2Sn{\cdot}Fe(CO)_4]_2 + THF \rightleftharpoons THF{\cdot}Bu_2Sn{\cdot}Fe(CO)_4$. With EtI at 65 °C, the Bu_2Sn unit leaves from this complex in a quite stannylene-like, nonradical reaction forming Bu_2EtSnI. With I_2 at 20 °C, Bu_2SnI_2 is easily formed.[167] Nothing is known about the mechanism. In the case of the insertion of free Me_2Sn into Me–I, on the other hand, an intermediate donor complex $MeI{\cdot}SnMe_2$ has been calculated to be formed exothermally,[143] which undergoes then a radical abstraction–recombination process ending up with Me_3SnI.

The donor capability of diaminostannylenes is less expressed.[112] Sometimes, moreover, they can be regarded, overall, as Lewis acids.[64]

But, interesting donor complexes $R_2Sn{\cdot}D$ should exist, D = e.g R_2O, R_3N, ROH, RSH, H_2O, and the like, even more characteristic as it has been found in the germylene case (see section II.C.4) since the coordination tendency of Sn can generally be regarded as superior compared with that of Ge. The complexation of R_2Sn, R = Me, Et, Pr, by THF at -40 °C, seems to be, however, one of the few observations of this type of complex, hindering or at least slowing down the rate of the polymerization of R_2Sn,[150] see above. The complex $R_2Sn{\cdot}THF$, evidenced both by ^{13}C and ^{119}Sn NMR spectroscopy, is interpreted by interaction of the donor THF with the empty 5p orbital at the tin.[151]

It can be expected that these complexes should give much impact to the chemistry of simple stannylenes, now impeded by their very rapid polymerization.

IV. Conclusion

The chemistry of germylenes and stannylenes has reached a volume that probably nobody could predict 15 years ago. Certainly, much impact has been given by the concept of carbenes which has been, and still is, one of the most exciting and fruitful in organic chemistry. Its extension first to the silylenes and, more recently, to the germylenes and stannylenes opened the view to the "heavy carbene analogues". This was a challenge to compare and to look for carbene-like as well as for independent, non-carbene-like properties and reaction schemes.

The Ge and Sn singlet–triplet gap has been detected to be much bigger. For all germylenes and stannylenes known so far, the s state is the ground state. And in fact, all reactions investigated until now are recognized as those of the singlet state; they might be derived from short-lived or persistent (kinetically stable) R_2Ge or R_2Sn, from thermal or photolytic mechanisms.

Insertions into σ bonds are widespread, but more selective and specific than for carbenes or silylenes. But, intramolecular insertions forming double bonds, like $XC{-}CH_3 \rightarrow XCH{=}CH_2$, $XSi{-}CH_3 \rightleftharpoons XSiH{=}CH_2$, are not found with the heavier "analogues", although a number of germenes $R_2Ge{=}CR_2$ and stannenes $R_2Sn{=}CR_2$ could be identified as products of other reactions.

The character of the double bond changes in quality. Whereas the group C=C is one of the oldest subjects in organic chemistry, Si=Si was established, after discussions full of spirit, about 20 years ago (it was hard for some contemporaries to leave the beloved "double-bond rule"), and Ge=Ge followed later, for example via dimerization of two germylenes. But, it seems now, that a bond Sn=Sn does not really exist. "Distannenes" in fact are much more complicated in bonding, although formed by dimerization of stannylenes $2R_2Sn \rightleftharpoons R_2Sn{\cdot}SnR_2$.

A versatile addition of germylenes to most of the important unsaturated systems (except to isolated C=C groups, so far) has been found. With conjugated systems, 1,4-additions are preferred, but 1,2-additions do occur, also. The latter dominates absolutely with carbenes and silylenes. With stannylenes, 1,4-additions by far are dominating. 1,2-additions have often been postulated, but only in very recent time could a few examples of stannirenes be evidenced.

Until now, most of the research was directed toward mechanistic, structure, spectroscopic, and coordination problems. For a broader synthetic application, there is a need for additional germylene or stannylene sources. The present unequivocal ones mostly are somewhat hard to prepare, at least in larger scale. For engaged researchers, however, this was—and is—no handicap. Here is a challenge for future research and synthesis.

Anyway, the germylene and stannylene concept opened new fields of synthetic chemistry and brought new insights into mechanisms and driving forces, and into molecular behavior. And last, but not least, it offers a rich harvest of new or, even more, novel chemical compounds. A number of them are of potential or already factual synthetic or biological interest.

The present article tries to give a synopsis of what is going on with germylenes and stannylenes at present, and why, for the benefit of future work. Plenty of data had to be evaluated. The selection is governed by the space available, but also, what seems unavoidable, by the individual aspects of the author, to whom complaints may be addressed.

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