(2:7:7:3, v/v/v/v). The reaction mixture was pale yellow and transparent.

Acknowledgment. We thank the Swedish Natural Science Research Council for support.

Registry No. **9**, 28830-19-5; **10**, 84057-16-9; **11**, 84057-17-0; **12**, 77136-98-2; **13**, 84057-18-1; **14**, 544-25-2; **15**, 16675-63-1; **16**, 84057-27-2; **17**, 55514-11-9; **18**, 84057-19-2; **19**, 84057-20-5; **20**, 84057-21-6; **21**, 84057-22-7; **24**, 53959-89-0; **25**, 42289-60-1; **28**, 84057-23-8; **29**, 84057-24-9; **30**, 84057-25-0; **31**, 84057-26-1.

Chemistry of Heavy Carbene Analogues R_2M (M = Si, Ge, Sn). 8.[1] Germylenes: Singlets or Triplets? [2 + 4] Cheletropic Cycloadditions of Me_2Ge and GeI_2 to Conjugated Dienes[2]

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Abstract: Thermally generated germylenes Me_2Ge undergo in solution under mild conditions (70–150 °C) concerted 1,4-additions of the linear [2 + 4] cheletropic type to certain 1,3-dienes. Thus, the highly reactive meso diallene **10a** gives, in a about 1:1 ratio, only the two isomeric 1-germacyclopentenes **11a** and **11b** expected from front- and back-side attack of Me_2Ge, whereas the D,L-diallene **10b** produces only the third isomer, **11c**, in accordance with this mechanism. The yields are about 70%; the isomer purity is ≥98%. Likewise, two other *E,E*-1,4-disubstituted 1,3-butadienes give only the corresponding cis-2,5-disubstituted 1-germacyclopentenes **7a** or **9a** in 80% or 30% yields with an isomer purity of ≥98% (limit of the NMR analysis). Similarly, with GeI_2 and **10a**, only **14a** and **14b** are found, and **14c** with **10b**, as expected for a cheletropic reaction. Methylation of **14a–c** yields the corresponding compounds **11a–c**. Other mechanisms for these 1,4-additions are discussed but are highly unlikely: thermal germylenes Me_2Ge and GeI_2 behave as singlets.

The concept of carbenes R_2C as reactive intermediates was—and still is—one of the most fruitful in organic chemistry during the last three decades both in theoretical/mechanistic and in preparative respects. For the understanding of carbene reactions, Skell's rule[4] has been quite elucidating: during addition of singlet carbenes to substituted olefins, the stereochemistry of the substituents is preserved in the cyclopropane produced, whereas a cis/trans mixture follows from addition of triplet carbenes to a sterically uniform olefin, passing a biradical.

Recently much attention has been directed toward the heavier carbene analogues, the silylenes R_2Si,[5] germylenes R_2Ge,[6] and stannylenes R_2Sn.[1,7] Also in these cases the singlet/triplet problem arises. Whereas quantum chemical calculations have shown the singlet state to be the ground state for H_2Si,[8] H_2Ge,[9,10] H_2Sn,[10] Me_2Ge,[9] and Me_2Sn[10]—in contrast to H_2C and Me_2C, where the triplet is of lower energy[11]—experimental efforts with this respect are known for silylenes only: Me_2Si gives with Me_3SiH the insertion product Me_3SiMe_2SiH and no abstraction–recombination products like Me_6Si_2.[12] This is evidence for a singlet behavior of Me_2Si. The attempted cycloaddition to suited monoolefins gave for a long time no conclusive products.[5,13] Addition to both (*E*)- and (*Z*)-2-butene immediately followed by methanolysis has resulted each time in an uniform product, allowing the conclusion that also the silylene attack to the olefin has been stereospecific.[14] Addition at 420 °C to (*E*,*E*)-2,4-hexadiene gave mixtures of *cis*- and *trans*-2,5-dimethyl-1-silacyclopent-3-ene.[5,13] Experiments with Me_2Si under milder conditions (70 °C) were unsuccessful.[15] Lastly, no addition experiments of silylenes to 1,3-dienes could be found in the literature, elucidating definitely whether there is a stereospecific (concerted) singlet or a nonstereospecific (two-step free radical, e.g.) triplet silylene reaction. Moreover, concerted 1,4-cycloaddition was precluded for the experiments mentioned above.[5,13] Thus, this situation in the case of silylenes still remains unsatisfying.

For the heavier analogues, the germylenes R_2Ge, no experiments have been reported to our knowledge concerning the singlet/triplet problem.[16] Since we have found recently a convenient source for smooth thermal generation of germylenes within the range 70–150 °C by thermolysis of 7-germanorbornadienes **1**,[17] we wish to report now cycloadditions of dimethylgermylene Me_2Ge to

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(1) Part 6: W. P. Neumann, C. Grugel, and M. Schriewer, *Angew. Chem.*, **91**, 577 (1979); *Angew. Chem., Int. Ed. Engl.*, **18**, 543 (1979). Part 7: K.-H. Scherping and W. P. Neumann, *Organometallics*, **1**, 1017 (1982).

(2) Partly published in a short communication: M. Schriewer and W. P. Neumann, *Angew. Chem.*, **93**, 1089 (1981); *Angew. Chem., Int. Ed. Engl.*, **20**, 1019 (1981).

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(4) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

(5) (a) P. P. Gaspar, "The Silylenes in Reactive Intermediates", Vol. 1, M. Jones, Jr., R. A. Moss, Eds., Wiley, New York, 1978; (b) M. Ishikawa and M. Kumada, *Adv. Organomet. Chem.*, **19**, 51 (1981).

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(7) W. P. Neumann, "The Stannylenes R_2Sn in Organometallic and Coordination Chemistry of Ge, Sn, and Pb", M. Gielen, P. G. Harrisan, Eds., Freund Publ.: Tel Aviv, 1978.

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(13) P. P. Gaspar and R. J. Hwang, *J. Am. Chem. Soc.*, **96**, 6198 (1974).

(14) V. J. Tortorelli and M. Jones, Jr., *J. Am. Chem. Soc.*, **102**, 1425 (1980).

(15) D. Seyferth and D. C. Annarelli, *J. Am. Chem. Soc.*, **97**, 7162 (1975).

(16) After our work was finished,[2,3] stereospecific cycloaddition to (*E*,*E*)- and (*Z*,*E*)-hexa-2,4-diene in the gas phase at 540 °C with 3,5% and 0.8% yields was reported: E. C.-L. Ma, K. Kobayashi, M. W. Barzilai, and P. P. Gaspar, *J. Organomet. Chem.*, **224**, C13 (1982).

(17) W. P. Neumann and M. Schriewer, *Tetrahedron Lett.*, 3273 (1980).

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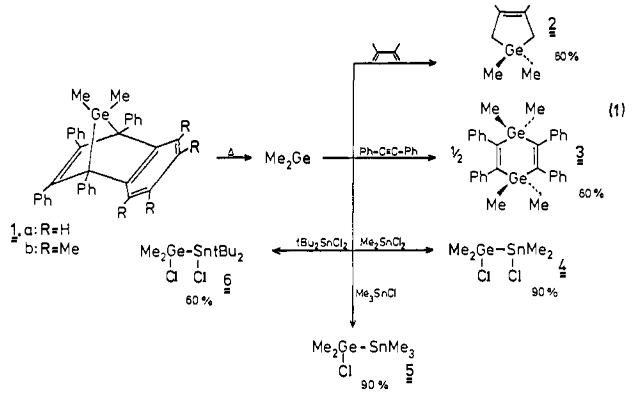
suited 1,3-dienes, proving for the first time a singlet behavior of Me_2Ge (at least the thermally generated one) and also for GeI_2 in solution.

Germylenes Me_2Ge generated thermally by this way exhibit a high reactivity in both several insertion and addition reactions, as follows from the examples given in eq 1.

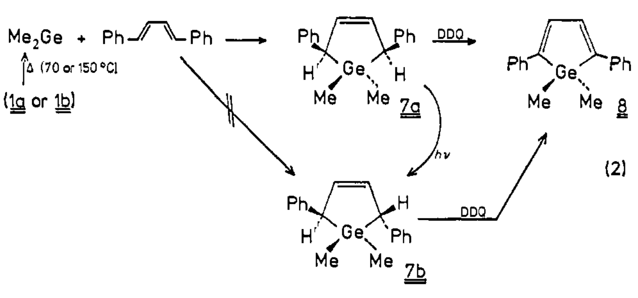


Me_2Ge adds smoothly to 2,3-dimethylbutadiene in benzene (as do Ge dihalides and RGeHal, R = alkyl, phenyl[18]) to give the corresponding germacyclopentene **2** in high yield.[17] With tolane, the 2:2 adduct **3** is formed, a 1,4-digermacyclohexadiene. Neither a 1:1 adduct, a 1-germacyclopropene, nor a 2:1 adduct, a 1-germacyclopentadiene, is built up.[17] With Me_2SnCl_2, the Sn–Cl bond is found to be a powerful germylene scavenger, giving **4** by insertion, with Me_3SnCl giving **5**. The latter result shows Me_2Ge to be a more reactive species than the corresponding stannylene Me_2Sn, which does not insert into Me_3SnCl.[19] The higher reactivity of Me_2Ge is also evidenced by its insertion into the bulky t-Bu_2SnCl_2, giving **6** with lower yield, however, not reacting with stannylenes. By these screening experiments, the usefulness of compounds **1** in synthetic germylene work is demonstrated, and especially, what is important for the following results, in the case of conjugated dienes.

The insertions mentioned above give evidence that the free germylene is formed directly from **1** here and not via a two-step mechanism with an intermediate biradical, as suggested in a preliminary short communication in an earlier stage of our investigations.[17] Any Ge radical should form, with, e.g., Me_3SnCl, if anything, a mixture of Me_2GeCl_2, $Me_3SnSnMe_3$, and $Me_2ClGeGeClMe_2$ and by no means ≥90% of $Me_2ClGeSnMe_3$ (**5**), as really found; see eq 1. In addition, thorough kinetic studies[20] have revealed exactly equal first-order degradation rates of **1a** and **1b** both in the inert solvent Ph_2O and in the efficient Ge radical scavenger $BrCCl_3$. This, again, points strongly against any Ge radical and for free Me_2Ge as the reacting species.

Results and Discussion

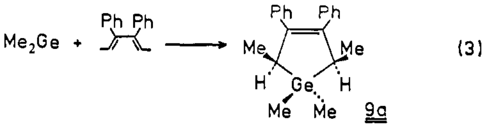
In order to make 1,4-addition of the germylene Me_2Ge conclusive for or against a concerted mechanism, we used, first, pure (E,E)-1,4-diphenylbutadiene. In its presence, **1a** is thermolyzed in benzene at 70 °C. The half-life time of the latter, $t_{1/2}$ = 47 min,[3,20] remains unchanged; its degradation is still of first order. In high yield the *cis*-2,5-diphenylgermacyclopentene **7a** is formed exclusively. Its structure can be derived from the ^1H NMR data: in a 1:1 ratio, only two Ge CH_3 singlets appear (−0.59, 0.55 ppm). The considerable high-field shift of the former obviously is caused by the strong shielding by the two phenyl groups in cis position. For further NMR information, see Table I. The trans isomer **7b** should exhibit, if present, only one singlet in an intermediate position, whereas a mixture **7a** + **7b** should be characterized by three Ge CH_3 peaks. The same result is obtained when starting from **1b** (R = CH_3), with much higher half-life time,[3,20] at 150 °C without solvent; only the cis isomer **7a** is obtained; the yield is 80%. It is colorless, well crystallized, and could be satisfyingly characterized. It is stable when air is excluded but liquefies slowly in the air. Its high reactivity follows also from its smooth dehydrogenation by DDQ to form the known[21] germol **8** (80% isolated yield), giving additional evidence for the structure of **7a** (see eq 2).



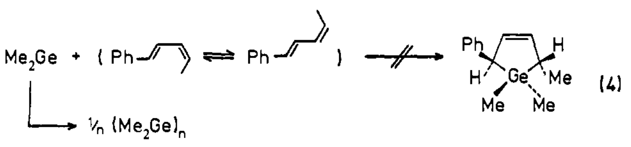
UV irradiation of pure **7a** leads to a third new Ge CH_3 peak between the two shown by **7a** (see Table I) at −0.13 ppm. The rest of the NMR spectrum remains unchanged. This indicates probably an isomerization **7a** → **7b**. In any case, treatment of the irradiation product with DDQ yields only **8**, 80% also.

These results point to a concerted cis-addition mechanism but have to be supported by a cross check with (E,Z)-1,4-diphenylbutadiene: only the trans isomer **7b** should be expected there. But this E,Z isomer rearranges, unfortunately, spontaneously both in daylight and at slightly elevated temperatures.

Other dienes had to be used. So, we chose pure (Z,Z)-3,4-diphenylhexadiene and obtained only the cis adduct **9a** with Me_2Ge, whereas the trans isomer **9b** could not be detected (eq 3). Again a cross check was not possible, unfortunately, since we were not able to prepare the corresponding Z,E isomer of the diene.



Experiments with 1-phenylpentadiene also were not successful because the Z,E isomer behaved inertly toward Me_2Ge, probably because of a concentration of the necessary s-cis conformation too low for a reaction with the short-lived germylene, the latter giving its usual and very rapid competing reaction, polymerization, to yield $(Me_2Ge)_n$ (see eq 4).



After some further attempts, our attention was drawn to a quite unusual diene, a diallene, the 2,7-diphenyl-2,3,5,6-octatetraene **10**, whose meso isomer **10a** reacts with SO_2 stereospecifically at room temperature via a concerted 1,4-addition to give a disrotatory ring closure within a few minutes.[22] Its use for our problem seemed promising: (a) its reactivity is very high because of the conjugated triene system generated; (b) the different isomers should exhibit a more or less equal reactivity since the "indicators" at the end of the chain, Me and Ph, are perpendicular to the reacting s-cis diene plane; and last but not least, (c) the outcoming isomers after the addition of Me_2Ge should be differentiatable by NMR.

Only the meso isomer **10a** is known from the literature.[22] But we succeeded also in preparing and characterizing the corre-

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(18) J. Satgé, M. Massol, and P. Rivière, *J. Organomet. Chem.*, **56**, 1 (1973).

(19) R. Moser, Dr. rer. nat. Dissertation, University of Dortmund, 1980.

(20) Kinetic and other evidence will be published elsewhere: S. Maslov and J. Köcher, unpublished work from this laboratory.

(21) T. J. Barton, A. J. Nelson, and J. Clardy, *J. Org. Chem.*, **37**, 895 (1972).

(22) (a) L. Skattebøl and K. Kleveland, *Acta Chem. Scand., Ser. B*, **B29**, 191 (1975); (b) L. Skattebøl and K. Kleveland, *Ibid.*, B29, 827 (1975).

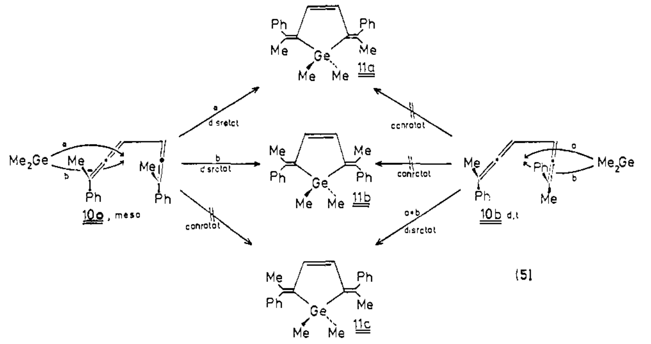
Table I. ^{1}H NMR Data of Me_2Ge and GeI_2 Adducts to 1,3-Dienes[a]

compound	7a	9a	11a	11b	11c	14a	14b	14c
$GeCH_3$	−0.59 0.55	0.32 0.42	0.66	−0.23	0.23			
CCH_3		1.15 d	2.23	2.20	2.16 2.21	2.43	2.60	2.42 2.53
C=CCH	3.32	2.10 q						
C=CH	6.10		6.30	6.73	6.53[b] 6.56[b]	6.76	6.34	6.55
C_6H_5	6.7–7.4 m	7.0 m	7.15	7.12	7.20 7.23	7.3 m	7.3 m	7.3–7.5 m

[a] δ values in CCl_4 against Me_4Si, singlets if not stated otherwise. [b] Broadened.

sponding D,L isomer **10b**. Since **10** is found to undergo unidentified transformations by prolongated heating to 70 °C, we selected the most sensitive of our germylene sources (**1a**), which is, at 70 °C in benzene, practically completely thermolyzed after 4 h.

When we heated **1a** in presence of 2 mol of **10a** (meso), we found only 30% of polygermane $(Me_2Ge)_n$ and two sets of ^{1}H NMR signals, which could be attributed, after isolation of the products, to the isomers **11a** and **11b**. No trace of the third of the possible isomers, **11c**, could be detected in the reaction mixture, including all mother liquors. On the other hand, a similar reaction with the pure D,L isomer gave exclusively this third isomer (**11c**) (see eq 5). This was the decisive cross check; the ring closure is always dirotatory and all facts available are in favor of, as far we can see, a pericyclic reaction of the germylene with the diene of the linear [2 + 4] cheletropic type and a singlet-type behavior of Me_2Ge. Not necessarily a singlet ground state can be concluded from these facts for Me_2Ge, but, since all described reactions are thermal ones under mild conditions, a singlet ground state is at least quite reasonable in accordance with quantum chemical calculations mentioned above.



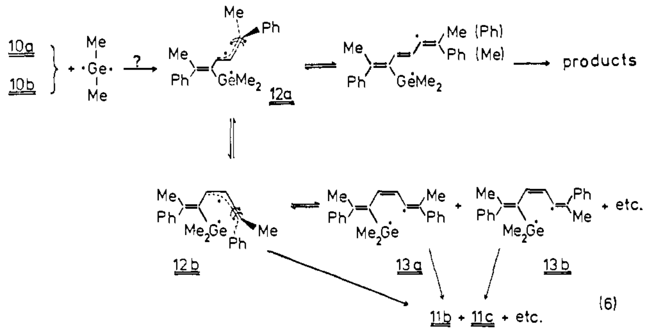
(5)

No substantial steric hindrance by the Ph groups is given, since the meso form **10a** is attacked nearly equally from the front and the back side (paths a and b in eq 5), **11a** and **11b** being generated in a 40:60 ratio. During several repetitions of the experiment, 50:50 ratios have also been obtained (Table I).

Stereospecificity is an indispensable but not a conclusive criterion for concertedness.[23] Are the cis-1,4-additions reported in eq 2, 3, and 5 really concerted? A similar problem still exists even in the well-investigated Diels–Alder reaction. There, all facts present are in favor of a concerted [4 + 2] pericyclic reaction.[23,24]

In our case, any hypothetic Ge-containing species, a radical, e.g., a triplet germylene, or a cation could add to **10**. Then, only one end of the diene system is attacked whereas the other end would not be involved. Therefore, mostly the preferred, more stable s-trans conformer of the diene should be involved and not so much the s-cis conformer, as necessary for a concerted 1,4-addition. For example, both diallenes **10a** and **10b** add easily to 1 mol of iodine even at room temperature to give the diiodide PhMeC=CIHC=CHIC=MePh with *E* configuration of the central double bond.[3] A strong driving force for this reaction certainly is the formation of the conjugated planar triene system (delocalization energy ca. 8–10 kcal/mol) connected with rotation of the terminal CMePh group clockwise *or* counterclockwise. Therefore, this 1,4-addition is *not* stereospecific; **10a** and **10b** both give the same product.

In the Ge case to be discussed here, for example, a triplet germylene should produce analogously the biradical **12a**, leading to products of higher molecular weight; nothing like this could be found. On the other hand, **12a** could rotate, overcoming the allylic stabilization (ca. 15 kcal/mol), to form **12b** and to close the ring or again build up the planar triene system, giving not less than four isomeric radicals like **13a** and **13b**. Each one of these can undergo ring closure. Thus, all three isomers **11a–c** should be formed both from **10a** and **10b** (see eq 6). But in all experiments in eq 2, 3, and 5, only the result expected for a concerted cis-1,4-addition of a germylene to the corresponding diene isomer could be detected.



(6)

Besides, we could not find any ESR or CIDNP signals in the spectra of the reacting mixtures that may (but not necessarily) arise from radical intermediates or, respectively, radical ring closure when eq 6 is followed.

Another type of two-step addition could be derived from the behavior of silylenes, which give with 1,3-dienes, first, an unstable 1,2 adduct involved in several consecutive reactions including a rearrangement to the 1,4 adduct. But this rearrangement yields a mixture of syn and anti isomers of the corresponding 1-silacyclopentene and hence is *not* stereospecific.[5,13] We find with germylenes exclusively stereospecific 1,4-additions. Of course, a stereospecific 1,2- to 1,4-rearrangement (not excluded by orbital symmetry arguments) would also be conceivable. But no intermediate, e.g., in eq 5, could be detected by NMR. If the rearrangement (hypothetically assumed to be stereospecific) is fast and the 1,2-addition rate determining, this mechanism and a real concerted 1,4-addition become indistinguishable.

To sum up, all data available at present, and especially the clearcut stereospecificity of reactions 2, 3, and 5, may best be interpreted by a concerted cis-1,4-addition of a singlet germylene to the 1,3-dienes.

This thermal [2 + 4] cheletropic Me_2Ge addition to dienes would be allowed by the Woodward–Hoffmann rules of preservation of orbital symmetries.[25] But it still has to be investigated whether the HOMO of the diene interacts with the LUMO of

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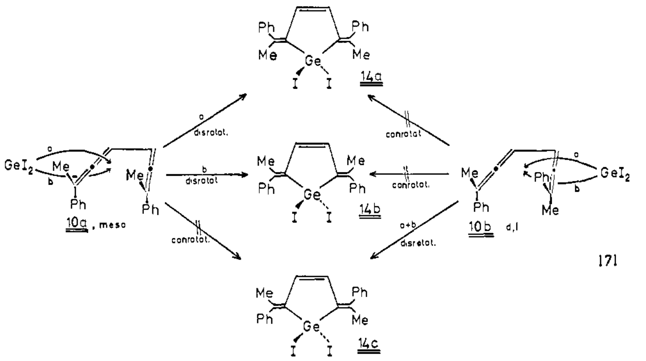
[23] R. Huisgen, *Pure Appl. Chem.*, **53**, 171 (1981). A thorough discussion of the inherent problems is given, as well as further references.

[24] See, e.g., B. Prantl, E. Eibler, and J. Sauer, *Tetrahedron Lett.*, **23**, 1139 (1982). Discussion and further references are given.

[25] I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", Wiley, New York, 1976.

Me_2Ge or the reverse. Both possibilities are open and allowed here in principle.

The singlet/triplet problem is found also for germanium dihalides, but no decisive experiment is known in this respect. GeI_2 reacted with (2,3-substituted) butadiene but not with 1,4-disubstituted butadienes.[26] So we used the highly reactive diallene systems **10a** and **10b**, and we[27] matched exactly the stereospecificity found with Me_2Ge (see eq 7). Only disrotatory ring closures occurred in every case. Path a in eq 7 is slightly preferred compared with (b), indicating a slight steric hindering of the approach of GeI_2 by two Ph groups; the ratio **14a**:**14b** is 60:40. **14a–c** can be isolated, but they are not indefinitely stable in solution at 20 °C: from pure **14c** in CCl_4 after 24 h, substantial amounts of **14a** are formed (not of **14b**, which incidates again steric strain in or during formation of **14b**), and some **14c** can be detected after some time in a solution containing originally exclusively **14a** and **14b**.



(7)

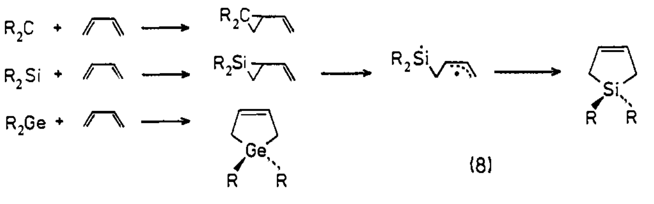
By treatment of **14a–c** with MeMgI in ether, we obtained three Me_2Ge derivatives precisely identical with compounds **11a–c**. This provides independent proof for the structure of the latter:

$$\mathbf{14a} \xrightarrow{2\text{MeMgI}} \mathbf{11a}$$

$$\mathbf{14b} \xrightarrow{2\text{MeMgI}} \mathbf{11b}$$

$$\mathbf{14c} \xrightarrow{2\text{MeMgI}} \mathbf{11c}$$

It is of more general interest now to compare the reactivity of the formally "two-valent species" of group 4 toward 1,3-dienes. Whereas carbenes give only 1,2-addition not affecting the second double bond, resulting in vinyl cyclopropanes, the silylenes form ("at least on the superficial level of our present knowledge of silylene reaction mechanisms"[5a]) primary products very similar to those of carbenes, i.e., by 1,2-addition[28] too, but facile rearrangements by various paths follow very quickly, often ending up with the nonstereospecific formation of the stable 1,4 adduct. With singlet germylenes, no longer can a 1,2-addition to conjugated dienes be observed. Instead, a cheletropic [2 + 4] reaction is found, at least in all examples studied so far, with 1,4 adduct formed stereospecifically being the primary and final product (see eq 8).



(8)

For the heavier homologues, the stannylenes Me_2Sn, no additions to carbon–carbon double bonds are known with certainty so far. It should be supposed that 1,2-additions no longer occur, but 1,4-additions may be possible with diene systems of sufficiently high reactivity.[29]

Experimental Section

General Procedures. All reactions were carried out under dry argon. Benzene and *n*-hexane were freshly distilled from $LiAlH_4$. All NMR spectra were taken on a 60-MHz Varian EM 360A spectrometer. Chemical shifts were measured against Me_4Si.

1,4,5,6-Tetraphenyl-2,3-benzo-7,7-dimethyl-7-germanorborna-2,5-diene (1a). To 0.42 g (17 mmol) of magnesium, activated with iodine under argon, and 5.30 g (11.3 mmol) of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene[30] was added 50 mL of dry THF by distillation from another flask containing $LiAlH_4$. After 3.04 g (17.4 mmol) of 2-bromofluorobenzene were added slowly at 0–5 °C, the mixture was stirred at 20 °C until nearly all of the Mg was dissolved. Then the THF is evaporated at 12 torr, and the residue is resolved in 50 mL of CH_2Cl_2 and filtered from the remaining Mg. After addition of 50 mL of EtOH, the product **1a** crystallizes upon cooling and is filtered off. In this case, some 1-germacyclopentadiene is still admixed; purification by column chromatography (silica gel, pentane/Et_2O (19:1)) is effective. Yield of pure product is 4.4 g, 71%: mp 138 °C dec; ^1H NMR (CCl_4) δ 0.2 (s, 3 H, Ge Me), 0.88 (s, 3 H, Ge Me), 6.5–7.5 (m, 24 H, Ph); MS (70 eV), *m/e* 432 (100%, M − Me_2Ge). Anal. Calcd for $C_{36}H_{30}Ge$: C, 80.78; H, 5.65. Found: C, 80.76; H, 5.78.

After thermolysis of **1a** in CCl_4 (4 h, 70 °C), a quantitative amount of 1,2,3,4-tetraphenylnaphthalene is precipitated by EtOH; mp 205 °C. Me_2GeCl_2 and C_2Cl_6 are estimated by GLC: 95% and 100%, respectively. By NMR, ca. 5% of another product, δ 1.0 (s, Ge Me), could be seen, presumably $Me_2GeClCCl_3$.

1,4,5,6-Tetraphenyl-2,3-tetramethylbenzo-7,7-dimethyl-7-germanorborna-2,5-diene (1b). Analogously to the foregoing procedure, 6.5 g (14.1 mmol) of the same germacyclopentadiene[30] is reacted with 4.1 g (17.6 mmol) of 1,2,3,4-tetramethyl-5-bromo-6-fluorobenzene.

1b: yield 6.7 g, 80%, mp 180 °C dec; ^1H NMR (CCl_4) δ 0.16, 0.23 (2 s, 3 H each, Ge Me), 1.9, 2.1 (2 s, 6 H each, Ar Me), 6.4–7.2 (m, 20 H, Ph). Anal. Calcd for $C_{40}H_{38}Ge$: C, 81.24; H, 6.48. Found: C, 81.24; H, 6.49.

After thermolysis of **1b** in CCl_4, a quantitative yield of 1,2,3,4-tetramethyl-5,6,7,8-tetraphenylnaphthalene can be precipitated by EtOH; mp 250 °C.

1,1,3,4-Tetramethyl-1-germacyclopent-3-ene (2). A sample of 1.09 g (2.03 mmol) of **1a** and 1.45 g (17.7 mmol) of 2,3-dimethylbutadiene in 5 mL of benzene is heated to 70 °C for 3 h. After cooling, the product is identified by NMR, identical with that reported in the literature,[26] yield 80% (GLC).

1,1,4,4-Tetramethyl-2,3,5,6-tetraphenyl-1,4-digermacyclohexa-2,5-diene (3). A 2.0-g (3.7 mmol) sample of **1a** and 3.2 g (18.0 mmol) of tolane are heated for 3 h at 70 °C. After cooling, the reaction mixture is dissolved in 15 mL of CH_2Cl_2. Addition of 15 mL of EtOH causes crystallization of 1.1 g (58%) of a colorless product, mp 295 °C, identical with an authentic sample of **3**.[31]

Insertion Products of Me_2Ge into Organotin Halides (Eq 1). A mixture of 53 mg of **1a** (0.1 mmol) and 0.2 mmol of the corresponding organotin halide in 1 mL of benzene is heated in a closed NMR tube for 3 h at 70 °C. The reaction products have the following NMR absorptions: $ClMe_2SnGeMe_2Cl$ δ 0.50 (s, 6 H, Me Sn, ^2J = 52 Hz), 0.71 (s, 6 H, Me Ge, ^3J = 16 Hz); $Me_3SnGeMe_2Cl$ δ 0.17 (s, 9 H, Me Sn, ^2J = 48 Hz), 0.65 (s, 6 H, Me Ge, ^3J = 16 Hz); Cl-*t*-$Bu_2SnGeMe_2Cl$ δ 0.80 (s, 6 H, Me Ge, ^3J = 7 Hz), 1.28 (s, 18 H, *t*-Bu Sn, ^2J = 86 Hz).

Products of abstraction–recombination reactions like Me_6Sn_2 and $Me_2GeClGeClMe_2$ in the case of insertion into Me_3SnCl are not present (GLC).

1,1-Dimethyl-2,5-diphenyl-1-germacyclopent-3-ene (7a). A 2.75-g (4.6 mmol) sample of **1b** and 2.10 g (10.0 mmol) of (*E*,*E*)-1,4-diphenylbutadiene are heated at 150 °C for 1.5 h. After cooling, the solid reaction mixture is pulverized. From the NMR (see Table I) of a sample resolved in CCl_4, it is found that **7b** is absent (≤2%); thus the isomer purity of **7a** formed is ≥98%. After 0.5 h of stirring with 25 mL of EtOH and filtering off insoluble $(Me_2Ge)_n$ (30%) and 1,2,3,4-tetraphenyl-5,6,7,8-tetramethylnaphthalene, one evaporates the filtrate to half its volume in vacuo. In a CO_2 bath, first the remaining diphenylbutadiene precipitates, and then 0.5 g (30%) of pure **7a** in colorless crystals; mp 52 °C. The mother liquor contains another 50% yield and some butadiene derivative. For NMR data, see Table I. Anal. Calcd for $C_{18}H_{20}Ge$: C, 69.98; H, 6.53. Found: C, 70.32; H, 6.30.

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(26) P. Mazerolles and G. Manuel, *Bull. Soc. Chim. Fr.*, 327 (1966).

(27) In cooperation with W. Reimann in this laboratory (undergraduate research work).

(28) Formation of silacyclopropanes from silylenes and monoolefins and their reactivity have been demonstrated earlier: D. Seyferth and D. C. Annarelli, *J. Organomet. Chem.*, **117**, C51 (1976); M. Ishikawa and M. Kumada, *Ibid.*, **81**, C3 (1974).

(29) Work is in progress in this laboratory.

(30) N. K. Hota and C. J. Willis, *J. Organomet. Chem.*, **15**, 89 (1968).

(31) M. E. Volpin, Yu. D. Koreshkov, V. G. Dulova, and D. N. Korsanov, *Tetrahedron*, **18**, 107 (1962).

A sample of **7a** is stirred in benzene with an equimolar amount of **DDQ** for 15 min at 25 °C. After separation of the insoluble hydroquinone, the solvent is removed completely. The resulting residue is crystallized from $CH_2Cl_2/EtOH$ to yield 80% of the germol **8**; mp 128 °C (lit. 20 mp 128 °C).

Irradiation of 7a. A sample of **7a** (0.1 g) in 5 mL of cyclohexane is irradiated with a high-pressure mercury lamp (TQ 150 Hanau) for 3 h. After removal of the solvent, the residue is dissolved in CCl_4. The NMR spectra shows a new Ge CH_3 absorption at −0.13 ppm probably due to the isomer **7b** (ca. 10%). Upon treatment with **DDQ**, only the germol **8** appears (yield, 80 mg, 80%).

1,1,2,5-Tetramethyl-3,4-diphenyl-1-germacyclopent-3-ene (9a). **1b** (2.0 g, 3.4 mmol) and 2.3 g (10.0 mmol) of (*E*,*E*)-3,4-diphenylhexa-2,4-diene are heated to 130 °C for 3 h. After cooling, the reaction mixture is stirred with 25 mL of EtOH. The remaining solids are separated, and the filtrate is evaporated to dryness in vacuo. The residue is dissolved in a little CH_2Cl_2 (it contains a 30% yield of **9a** as estimated by NMR), and remaining hexadiene is converted to its adduct by just sufficient amounts of tetracyanoethylene (NMR). Silica gel layer chromatography (pentane/Et_2O (19:1)) gives **9a**: mp 65 °C (MeOH); yield 100 mg. Anal. Calcd for $C_{20}H_{24}Ge$: C, 71.28; H, 7.18. Found: C, 71.52; H, 7.09.

(*E*,*E*)- and (*Z*,*Z*)-1,1-Dimethyl-2,5-bis(1-phenylethylidene)-1-germacyclopent-3-ene (11a and 11b). **1b** (1.5 g, 2.8 mmol) and 1.1 g of meso-diallene **10a**[22a] (4.3 mmol) are heated for 3 h at 70 °C in 10 mL of benzene and then almost evaporated in vacuo. The residue contains 70% **11a** + **11b** and ca. 30% $(Me_2Ge)_n$ (NMR). It is taken up in 10 mL of pentane, filtered through 10-cm silica gel, evaporated to two-thirds of the volume, and mixed 1:1 with EtOH. Upon cooling, ca. 300 mg of **11a** and **11b** are precipitated (58:42) in three fractions. A further yield can be obtained from the liquor. **11c** cannot be detected (≤2%) (NMR).

D,L-2,7-Diphenylocta-2,3,5,6-tetraene (D,L-Diallene) (10b). (Information for the preparation of **10a** in literature[22] is used.) 1-Bromo-2-phenyl-1-propene (150 g, 0.76 mol) is irradiated (TQ 150) in 1 L of pentane in the presence of 15 g (80 mmol) of benzophenone until the *E*/*Z* isomer ratio has reached ca. 50:50 (NMR). After evaporation of the solvent, 140 g of the *E*/*Z* mixture is isolated by distillation; bp 105–110 °C (15 torr). The corresponding Grignard derivative (THF) is reacted at −60 °C with CuCl, and after the usual workup, 50 g of a mixture of the three stereoisomeric hexadienes is isolated: 45% *E*,*Z*; 23% *Z*,*Z*, and 32% *E*,*E* (NMR). The *E*,*Z* isomer, the only one of interest here, is isolated: the mixture is shaken with 300 mL of pentane and 12–15 g of pure *E*,*E* isomer remain insoluble and are separated; mp 138 °C. Upon cooling of the mother liquor at 5 °C after 24 h, 18 g of the *E*,*Z* isomer are precipitated, together with ca. 5% *E*,*E* isomer. A sample is purified from $CH_2Cl_2/EtOH$: mp 70–71 °C; ^1H NMR (CCl_4) δ 2.25 (s, 6 H, Me), 6.5 (s, 2 H, vinyl), 7.0–7.6 (m, 10 H, Ph).

From the remaining mother liquor, a mixture of a little *E*,*Z* and much *Z*,*Z* isomers crystallizes slowly, giving pure (*Z*,*Z*)-diphenylhexadiene from pentane: mp 78–80 °C; ^1H NMR (CCl_4) δ 2.05 (s, 6 H, Me), 6.15 (s, 2 H, vinyl), 7.3 (s, 10 H, Ph).

The dibromocarbene adduct is prepared by suspending 12.4 g (53 mmol) of (*E*,*Z*)-diphenylhexadiene and 25 g (220 mmol) of *t*-BuOK in 250 mL of pentane and adding dropwise at −15 °C 56 g (220 mmol) of $CHBr_3$. After warming to 20 °C, the mixture is stirred overnight. Then, diluted hydrochloric acid is added, the mixture is shaken, and the organic layer is separated and dried with $MgSO_4$. Pentane is evaporated, and the residue is taken up in EtOH. Upon cooling, the colorless product crystallizes: yield 6.7 g, 22%; mp 134 °C. Further, impure fractions can be collected (5 g): ^1H NMR (CCl_4) δ 1.75 (s, 2 H, CH), 1.8 (s, 6 H, Me), 7.0–7.7 (m, 10 H, Ph). Anal. Calcd for $C_{20}H_{18}Br_4$: C, 41.56; H, 3.14. Found: C, 41.93; H, 3.56.

10b is formed when 6.7 g (11.5 mmol) of this intermediate in 10 mL of Et_2O is mixed at −70 °C with 40 mmol of $MeLi/Et_2O$ and the temperature is raised to −20 °C during 1 h of stirring. After hydrolysis with 20 mL of H_2O, the organic layer is separated and dried with $MgSO_4$. Evaporation of the ether yields a slightly yellow oil (sufficiently pure for further use), which crystallizes from EtOH: yield 2.6 g, 90% **10b**, ^1H NMR (CCl_4) δ 2.15 (m, 6 H, Me) 5.9 (m, 2 H, C=C=CH), 7.0–7.5 (m, 10 H, Ph).

Characterization of 10b with SO_2. A 200-mg sample of **10b** is desolved in 1.5 mL of *n*-heptane and 1.5 mL of benzene, and SO_2 is bubbled through the mixture for 30 min at 20 °C. Then the solvents are evaporated at 12 torr, and the residue is recrystallized from acetone/H_2O, yielding 200 mg (80%) of (*E*,*Z*)-2,5-bis(1-phenylethylidene)-2,5-dihydrothiophene 1,1-dioxide: mp 140 °C; IR (KBr) 1120, 1135, 1290, 1300 (SO_2) cm^{-1}; ^1H NMR ($CHCl_3$) δ 2.3, 2.46 (2 s, 3 H each, Me), 6.57, 6.62 (2 s, 1 H each, C=CH), 7.2–7.6 (m, 10 H, Ph), no indication for the presence of the corresponding SO_2 adduct of **10a**.[22] Anal. Calcd for $C_{20}H_{18}O_2S$: C, 74.50; H, 5.58. Found: C, 74.93; H, 5.31.

(*E*,*Z*)-1,1-Dimethyl-2,5-bis(1-phenylethylidene)-1-germacyclopent-3-ene (11c). Obtained in a similar manner to **11a** and **11b** from **1b** and D,L-diallene **10b**; mp 98 °C. Neither **11a** nor **11b** is present (≤2%, NMR). Anal. Calcd for $C_{22}H_{24}Ge$: C, 73.19; H, 6.70. Found: C, 73.38; H, 6.70.

(*E*,*E*)- and (*Z*,*Z*)-1,1-Diiodo-2,5-bis(1-phenylethylidene)-1-germacyclopent-3-ene (14a and 14b). The meso diallene (0.5 g, 2.0 mmol) and 1.3 g of GeI_2[32] (3.9 mmol) in 10 mL of *n*-hexane are heated to reflux for 1 h. After cooling, excess GeI_2 is separated by filtration. The filtrate is evaporated to dryness. The residue consists of the two diiodogermacyclopentenes **14a** and **14b** (63:37, yield ca. 80%). **14c** is not detectable (≤2%). The residue is dissolved in little pentane. Cooling to −70 °C causes crystallization of a mixture of **14a** and **14b** (25:75), yield 400 mg (37%).

(*E*,*Z*)-1,1-Diiodo-2,5-bis(1-phenylethylidene)-1-germacyclopent-3-ene (14c). Obtained in a similar manner to **14a** and **14b** from the D,L-diallene **10b** and GeI_2; mp 117–118 °C. Anal. Calcd for $C_{20}H_{18}I_2Ge$: C, 41.07; H, 3.10. Found: C, 40.20; H, 3.34.

After standing overnight, a solution of pure **14c** shows considerable amounts of **14a**, whereas **14b** is not detectable.

Alkylation of the Germacyclopentenes 14a and 14b. A mixture of **14a** and **14b** (ca. 60:40) is treated with excess MeMgBr in Et_2O at −70 °C. After warming to room temperature, the reaction mixture was stirred for 30 min. After hydrolysis, the organic layer is dried over Na_2SO_4 and then evaporated to dryness. The yellow residue is dissolved in CCl_4. The NMR spectrum shows the presence of the two isomers **11a** and **11b** (ca. 60:40). **11c** is not formed.

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Registry No. **1a**, 76054-64-3; **1b**, 76054-69-8; **2**, 5764-66-9; **3**, 915-38-8; **4**, 84174-06-1; **5**, 84174-07-2; **6**, 84174-08-3; **7a**, 80262-45-9; **7b**, 84174-01-6; **8**, 28124-19-8; **9a**, 80242-28-0; **10a**, 42525-52-0; **10b**, 80242-33-7; **11a**, 80242-30-4; **11b**, 80242-29-1; **11c**, 80242-31-5; **14a**, 84174-02-7; **14b**, 84174-03-8; **14c**, 84192-52-9; $Me_2GeClCCl_3$, 84174-04-9; Me_2Ge, 74963-95-4; $(Me_2Ge)_n$, 82401-03-4; $CHBr_3$, 75-25-2; GeI_2, 13573-08-5; MeBr, 74-83-9; *t*-Bu_2SnCl_2, 19429-30-2; Me_2SnCl_2, 753-73-1; Me_3SnCl, 1066-45-1; 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene, 20991-88-2; 2-bromofluorobenzene, 1072-85-1; 1,2,3,4-tetraphenylnaphthalene, 751-38-2; 1,2,3,4-tetramethyl-5-bromo-6-fluorobenzene, 84174-05-0; 1,2,3,4-tetramethyl-5,6,7,8-tetraphenylnaphthalene, 51227-24-8; 2,3-dimethylbutadiene, 513-81-5; tolane, 501-65-5; (*E*,*E*)-1,4-diphenylbutadiene, 538-81-8; (*E*,*E*)-3,4-diphenylhexa-2,4-diene, 24815-65-4; 1-bromo-2-phenyl-1-propene, 3360-53-0; (*E*)-1-bromo-2-phenyl-1-propene, 16917-35-4; (*Z*)-1-bromo-2-phenyl-1-propene, 19647-26-8; (*E*,*Z*)-diphenylhexadiene, 84174-09-4; (*Z*,*Z*)-diphenylhexadiene, 84174-10-7; (*E*,*E*)-diphenylhexadiene, 16914-12-8; benzophenone, 119-61-9; (*E*,*Z*)-2,5-bis(1-phenylethylidene)-2,5-dihydrothiophene-1,1-dioxide, 84174-11-8.

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(32) Prepared from GeI_4 and H_3PO_2: G. Brauer, "Handbuch der präpar. anorgan. Chemie", 3rd ed., Verlag, Stuttgart, 1978.