species with 1 equiv of CO resulted in insertion and formation of a single product that appears to contain an oxycarbene-type ligand.

Conclusions

We have developed a methodology to prepare the first neutral, monocyclopentadienyllutetium bis(alkyl) complexes. Stepwise metathesis of the chlorides in $LuCl_3(THF)_3$, first with sodium cyclopentadienides and subsequently with lithium alkyls, allows the rational synthesis of this new class of organometallic compound. Earlier results that suggested a strong preference toward the formation of bis(cyclopentadienyl) complexes can be explained by use of ill-defined starting materials, e.g. $(LuCl_3)_n$ and/or insoluble LiC_5Me_5.

The synthesis of 1 was hampered by considerable experimental difficulties. Use of sterically more demanding cyclopentadienyl or indenyl ligands has attracted relatively little attention, and we note that the alkyl complexes derived from $[K(THF)_x]Lu(\eta^5\text{-}C_9H_4MePh_2)Cl_3$ and $Lu(\eta^5\text{-}C_5Me_3Ph_2)Cl_2(THF)_2$ possess significantly more thermal stability than their pentamethylcyclopentadienyl counterparts. Unfortunately, difficulties in the synthesis and alkylation of these starting materials prevented us from further exploiting their chemistry, although it is probable that these phenyl-substituted ligands will have an analogously greater stabilizing effect in early-transition-metal chemistry than their pentamethylcyclopentadienyl analogues.

Investigation of this chemistry has been hindered by the prevalence of salt coordination. Removal of this coordinated salt, while possible, results in major product losses due to the poor thermal stability of the salt-free systems.

The first "mixed" alkyl neutral organolanthanide complex $Lu(\eta^5\text{-}C_5Me_5)(CH_2SiMe_3)\{CH(SiMe_3)_2\}(THF)$ has been prepared. Efforts are continuing to prepare and separate a chiral $Lu(\eta^5\text{-}C_5Me_5)R'R''\cdot L$ species that may possess interesting properties.

Supplementary Material Available: Tables of hydrogen atom parameters and anisotropic thermal parameters and full listings of bond distances and angles (20 pages); listings of observed and calculated structure factors (55 pages). Ordering information is given on any current masthead page.

3-Alkylidenethiagermiranes

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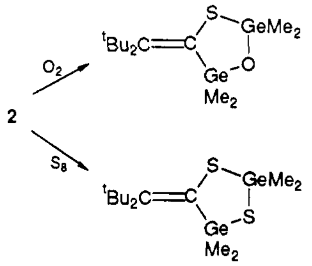
Received October 26, 1988

Dimethyl- and diphenylgermylenes react with di-*tert*-butylthioketene to give 4-alkylidene-1,2,3-thiadigermetanes 2 and 4, the products of the insertion of germylenes into 3-alkylidenethiagermiranes. Dimesitylgermylene generated by the thermolysis of hexamesitylcyclotrigermane (12) at 80 °C reacts with di-*tert*-butylthioketene to produce a stable 3-alkylidenethiagermirane, 13. Photolysis of 13 produces dimesitylgermylene and di-*tert*-butylthioketene via germathiocarbonyl ylide 17, which is intensely blue in color with a maximum band at 580 nm. 13 reacts with dimethylgermylene to yield the corresponding 4-alkylidene-1,2,3-thiadigermetane 22. Oxidation of 13 by *m*-chloroperbenzoic acid gives 3-alkylidene-1,2,4-oxathiagermetane *S*-oxide 23.

Introduction

Special interest has been focused on the synthesis of three-membered rings bearing exocyclic double bonds because the introduction of an exomethylene group to a three-membered ring is expected to increase the strain energy.[1] Some metal-group 14 three-membered heterocycles have been isolated,[2-9] but, in contrast to rather extensive studies on alkylidenecyclopropanes and their heterocyclic analogues, there is no report on the chemistry of the germanium analogues. We recently reported the synthesis and chemical properties of thiagermiranes prepared by the reaction of germylenes with thioketones.[6] To synthesize the exomethylene-containing thiagermiranes "3-alkylidenethiagermiranes", we attempted reactions of germylenes with thioketenes. We report here the synthesis of the first type of these compounds 3-alkylidenethiagermiranes, and some of the chemical properties of these.

Scheme I



Results and Discussion

Reactions of Dimethyl- and Diphenylgermylenes with Thioketenes.[10] Thermolysis of a benzene solution

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(1) (a) Dewar, M. J. S. *J. Am. Chem. Soc.* **1971**, *93*, 3081. (b) Turro, N. J. *J. Am. Chem. Soc.* **1969**, *91*, 2283. (c) Saaifrank, R. W.; Paul, W.; Wilhelm, E. *Chem. Ber.* **1982**, 155.

(2) Baudler, M. *Pure Appl. Chem.* **1980**, *52*, 755.

(3) Krebs, A.; Berndt, J. *Tetrahedron Lett.* **1983**, *24*, 4083.

(4) (a) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136. Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191. (b) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1514. (c) Weidenbruch, M.; Grimm, F.-T.; Herrndorf, M.; Schäfer, A.; Peters, K.; Schnering, G. *J. Organomet. Chem.* **1988**, *341*, 335.

(5) (a) Ando, W.; Tsumuraya, T. *Tetrahedron Lett.* **1986**, *27*, 3251. (b) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1988**, *7*, 2015.

(6) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1989**, *8*, 161.

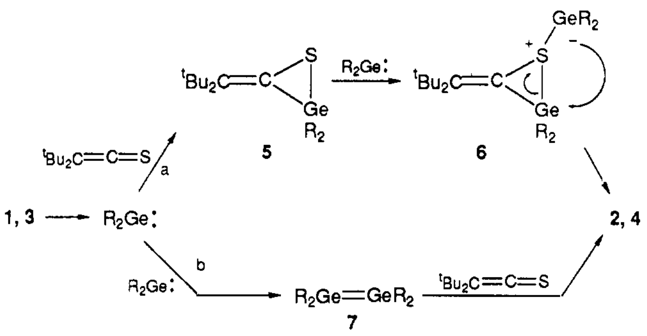
(7) (a) Ando, W.; Tsumuraya, T. *Organometallics* **1988**, *7*, 1882. (b) Batcheller, S. A.; Masamune, S. *Tetrahedron Lett.* **1988**, *29*, 3383.

(8) Andrianarison, M.; Couret, C.; Declercq, J.-P.; Dubourg, A.; Escudie, J.; Ranaivonjatovo, H.; Satgé, J. *Organometallics* **1988**, *7*, 1545.

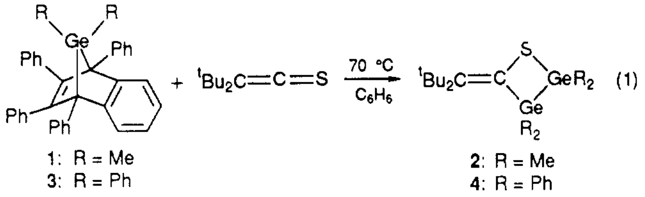
(9) Cowley, A. H.; Hall, S. W.; Nunn, C. M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 753.

(10) Ando, W.; Tsumuraya, T.; Goto, M. *Tetrahedron Lett.* **1986**, *27*, 5105.

Scheme II



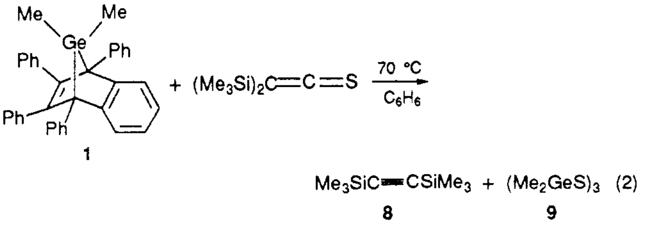
of 7,7-dimethyl-7-germanorbornadiene (1) (0.2 mmol)[11] and di-*tert*-butylthioketene (0.6 mmol)[12] at 70 °C produced mainly 4-alkylidene-1,2,3-thiadigermetane 2 (51%) along with 1,2,3,4-tetraphenylnaphthalene (eq 1). Compound



2 could be isolated by preparative GLC, but its extreme sensitivity toward air indicated that the germanium–germanium bond is easily oxidized. Elemental sulfur also reacted with 2 to yield the corresponding ring expansion product (Scheme I). Similar thermolysis of 7,7-diphenyl-7-germanorbornadiene (3) (1.0 mmol) and the thioketene (1.0 mmol) gave 4-alkylidene-1,2,3-thiadigermetane 4 (32%) which could be purified by flash column chromatography (eq 1). In contrast to the lability of 2 toward oxygen, 4 is very stable in an oxygen- or moisture-containing atmosphere. The structures of 2 and 4 were confirmed by their spectroscopic properties and also by an X-ray diffraction study of 4 as reported previously.[10]

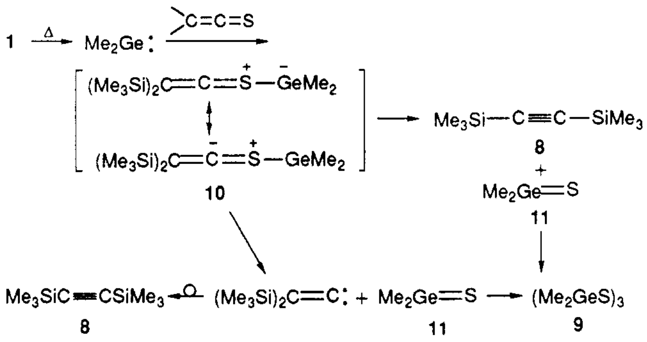
Compounds 2 and 4 appear to be derived from either the 3-alkylidenethiagermirane 5 (followed by the formation of ylide 6 and migration (path a)) or a [2 + 2]-type reaction of the thioketene with digermene 7 (path b) as shown in Scheme II.

In the reaction of dimethylgermylene with bis(trimethylsilyl)thioketene,[13] bis(trimethylsilyl)acetylene 8 (87%)[14] and the trimer of dimethylgermanethione 9 (17%)[15] were obtained along with 1,2,3,4-tetraphenylnaphthalene (eq 2). 4-Alkylidene-1,2,3-thiadigermetane was not formed in this reaction.

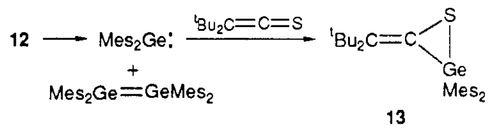


These products may be formed by the addition of dimethylgermylene to the thioketene to yield germathiocarbonyl ylide 10 which decomposes directly to the acetylene and dimethylgermanethione (11) (Scheme III). Alternatively, 10 decomposes to the alkylidenecarbene and 11, followed by migration of the trimethylsilyl group. The reason that the reactivity of bis(trimethylsilyl)thioketene toward germylene is different from that of di-*tert*-butylthioketene is not clear at the present time, but we consider that it is probably due to the great migratory aptitude of a silyl group.

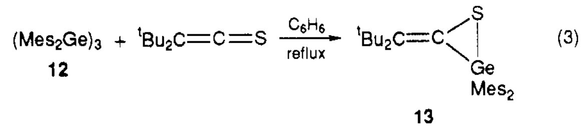
Scheme III

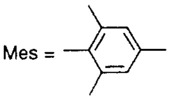


Scheme IV



Reaction of Dimesitylgermylene with Di-*tert*-butylthioketene. Isolation of 3-Alkylidenethiagermirane 13. Since the introduction of bulky substituents has been widely used for the stabilization of unstable molecules,[16] we next tried the reaction of a bulky substituted germylene, dimesitylgermylene, with the thioketene. When a benzene solution of hexamesitylcyclotrigermane (12) (0.3 mmol)[4b] and di-*tert*-butylthioketene (0.7 mmol) was heated to reflux for 10 h, 3-alkylidenethiagermirane 13 was obtained as a colorless crystalline solid in 34% yield (eq 3).





The structure of 13 was confirmed by ^{1}H and ^{13}C NMR and mass spectroscopic analyses and elemental analysis. 3-Alkylidenethiagermirane 13 is stable toward atmospheric oxygen and moisture and does not decompose even when heated to its melting point of 120–121 °C.

3-Alkylidenethiagermirane 13 probably arises from the direct reaction of dimesitylgermylene (generated from the thermolysis of cyclotrigermane 12) with di-*tert*-butylthioketene (Scheme IV). Although the generation of germylenes and digermenes by the photolysis of cyclotrigermanes is well-known.[4a,5b,6] thermolysis of cyclotrigermanes has not been studied. This is the first generation of a germylene from a cyclotrigermane by thermolysis.[17]

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(11) Schriewer, M.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897.

(12) Elam, E. U.; Rash, F. H.; Dougherty, J. T.; Goodlett, V. W.; Brannock, K. C. *J. Org. Chem.* **1968**, *33*, 2738.

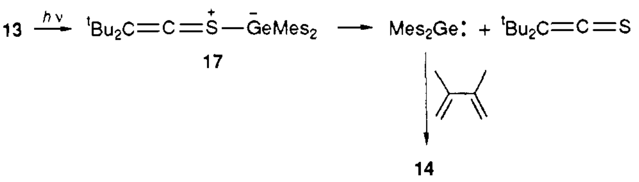
(13) Harris, S. J.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1976**, 1008.

(14) Frisch, K. C.; Young, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 4853.

(15) Barrau, J.; Ben Hamida, N.; Satgé, J. *J. Organomet. Chem.* **1985**, *282*, 315.

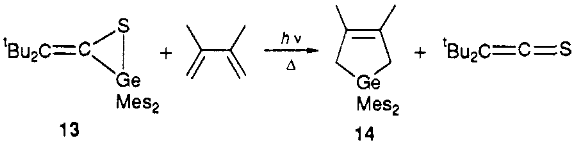
(16) (a) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. (b) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

Scheme V



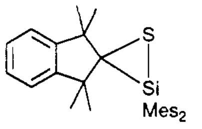
Under the reaction conditions, trapping products from tetramesityldigermene were not obtained, probably due to the steric factors. A similar reaction of dimesitylgermylene, generated photochemically from cyclotrigermane **12**, did not give 3-alkylidenethiagermirane **13** probably because of the instability of **13** toward photolysis.

Photolysis and Pyrolysis of 3-Alkylidenethiagermirane 13. Although 3-alkylidenethiagermirane **13** is thermally stable, **13** was easily decomposed by photolysis with a low-pressure mercury lamp. When a cyclohexane solution of **13** (0.1 mmol) and 2,3-dimethyl-1,3-butadiene (5 mmol) was irradiated with a low-pressure mercury lamp at room temperature, germacyclopentene **14** and di-*tert*-butylthioketene were obtained in 50% and 33% yields, respectively (eq 4). Similar results were obtained in a flow copyrolysis (at 500 °C) of **13** and 2,3-dimethyl-1,3-butadiene, although under these conditions di-*tert*-butylthioketene decomposed further and was not isolated.

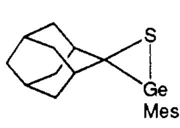


(4)

Since **14** appears to arise from the addition of dimesitylgermylene to the butadiene,[18] it is clear that **14** undergoes cycloelimination during the photolysis or the pyrolysis to produce dimesitylgermylene and di-*tert*-butylthioketene. As in the case of thiasilirane **15**[19] or thiagermirane **16**,[6] the reaction seems to proceed via germathiocarbonyl ylide **17** (Scheme V).



15



16

The low-temperature matrix-isolation technique has been used widely for the observation of reactive compounds.[20] We next tried to detect germathiocarbonyl ylide **17** spectroscopically. Irradiation of 3-alkylidenethiagermirane **13** in a 3-methylpentane (3-MP) matrix at 77 K with a low-pressure mercury lamp led to the appearance of a new band at 580 nm in the UV–vis spectrum, and the matrix became intensely blue in color (Figure 1). This absorption band was indefinitely stable at 77 K. However, it immediately disappeared on brief irradiation with a xenon lamp ($\lambda > 460$ nm) or when the matrix was allowed to melt. The colored species also was observed at 582 nm in the photolysis product of **13** in a 3-MP/isopentane (IP) (1/4) glass at 77 K.[21]

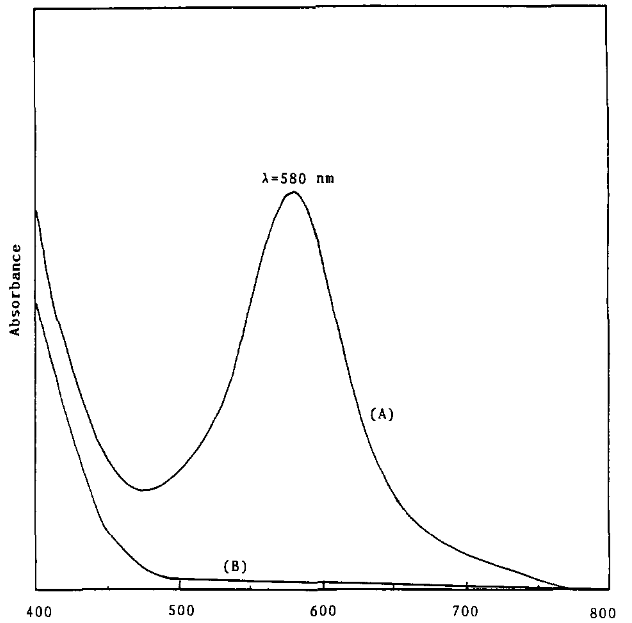
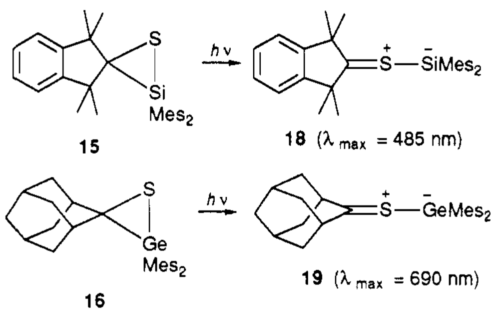
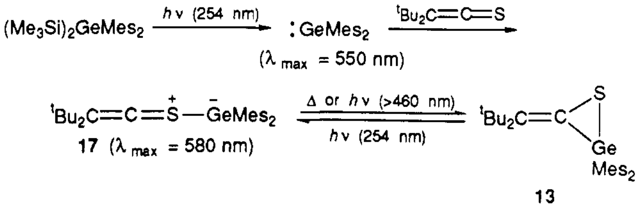


Figure 1. (A) After photolysis of **13** with a low-pressure mercury lamp (254 nm) for 1 h in 3-MP at 77 K. (B) After annealing the matrix and recooling to 77 K. In (A) and (B), the starting material was subtracted.

Scheme VI



Scheme VII



This colored species was independently generated by the reaction of dimesitylgermylene with di-*tert*-butylthioketene. Thus, irradiation of dimesitylbis(trimethylsilyl)germane in the presence of di-*tert*-butylthioketene in a 3-MP matrix at 77 K with a low-pressure mercury lamp produced a purple species with λ_{max} at 550 nm which was

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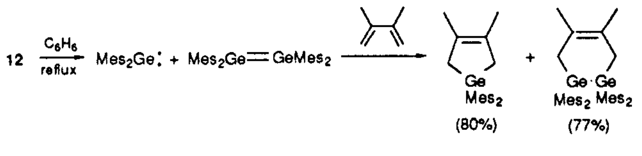
(17) Thermolysis of hexamesitylcyclotrigermane (**12**) in benzene at 80 °C afforded dimesitylgermylene and tetramesityldigermene, which could be trapped effectively by 2,3-dimethyl-1,3-butadiene as shown. Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.*, in press.



(18) Riviere, P.; Castel, A.; Satgé, J. *J. Organomet. Chem.* **1982**, *232*, 123.

(19) Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270.

(20) (a) Chapmann, O. L. *Pure Appl. Chem.* **1974**, *40*, 511. (b) Dunkin, I. R. *Chem. Soc. Rev.* **1980**, *9*, 1.

(21) The 2-nm shift of the absorption maximum in going from 3-MP to 3-MP/IP (1/4) is probably due to a solvent effect.

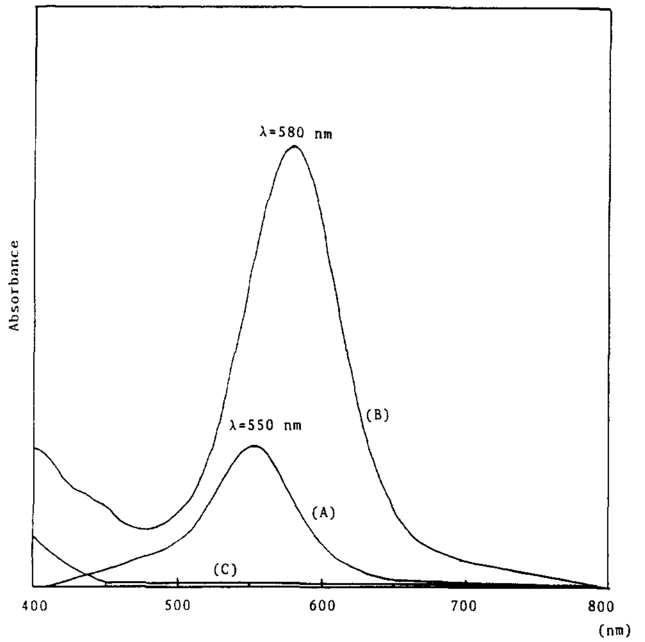
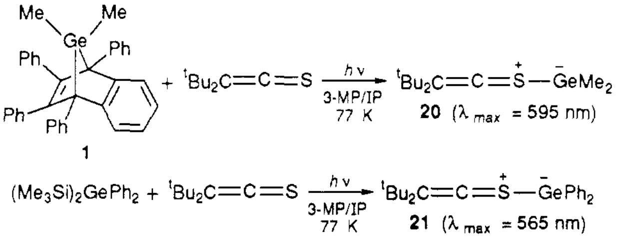


Figure 2. (A) After photolysis of **18** with a low-pressure mercury lamp (254 nm) for 30 min in the presence of di-*tert*-butylthioketene in 3-MP at 77 K. (B) The above sample was allowed to melt carefully and recooled to 77 K. (C) After complete warming to room temperature and recooling to 77 K. In (A)–(C), the starting material was subtracted.

Scheme VIII

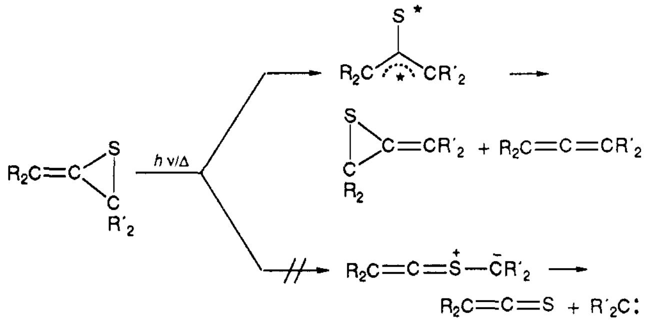


assigned to dimesitylgermylene.[22] After careful annealing and recooling of the matrix, this band diminished and a blue species with λ_{max} at 580 nm was formed. Dimesitylgermylene thus reacted with di-*tert*-butylthioketene to give a species with λ_{max} at 580 nm when the matrix was annealed (Figure 2).

When a similar photolysis of the bis(trimethylsilyl)germane in the presence of di-*tert*-butylthioketene was carried out in a 3-MP/IP (1/4) matrix, only a band with λ_{max} at 582 nm was observed but no absorption bands due to dimesitylgermylene. These results indicate that dimesitylgermylene reacts with di-*tert*-butylthioketene in a soft matrix at 77 K without annealing.[23] Irradiation of the solution of the 582 nm species with a wavelength of light greater than 460 nm or melting the matrix resulted in production of the 3-alkylidenethiagermirane **13**.

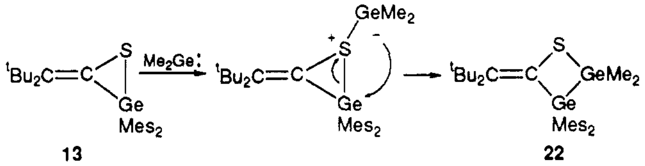
We recently succeeded in the spectroscopic detection of sila- and germathiocarbonyl ylides **18**[19] and **19**[6] which were generated by the photolysis of thiasilirane **15** and thiagermirane **16** in hydrocarbon matrices at 77 K (Scheme VI). On the basis of these earlier results, it is quite reasonable to assume that the colored species most probably is the germathiocarbonyl ylide **17** (Scheme VII).

Scheme IX[a]

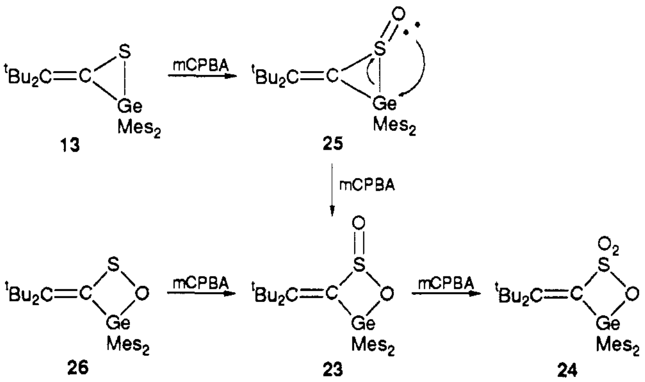


[a] The asterisk = ion/radical.

Scheme X



Scheme XI



In a similar manner, germathiocarbonyl ylides **20** (λ_{max} = 595 nm) and **21** (λ_{max} = 565 nm) were generated in a 3-MP/IP (1/4) matrix at 77 K by the reaction of di-*tert*-butylthioketene with dimethyl- or diphenylgermylenes (Scheme VIII).

These findings are in contrast to the thermal or photochemical behavior of allene episulfide in the carbon system. Allene episulfides undergo isomerization or desulfurization via ring opened type "thioxyallyl" intermediates and do not generate thiocarbonyl ylides or carbenes (Scheme IX).[24]

Ring Expansion Reactions of 3-Alkylidenethiagermirane 13. Dimethylgermylene generated by the thermolysis of 7,7-dimethyl-7-germanorbornadiene **1** at 70 °C reacted with 3-alkylidenethiagermirane **13** to give 4-alkylidene-1,2,3-thiadigermetane **22** in 74% yield, which could be purified by flash column chromatography. The structure of **22** was confirmed by ^1H and ^{13}C NMR and mass spectroscopic analyses and elemental analysis. The generally accepted mechanism involves the formation of an ylide that subsequently rearranges to the ring expansion product (Scheme X). These results are consistent with the mechanism of the formation of 4-alkylidene-1,2,3-

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[22] (a) Ando, W.; Tsumuraya, T.; Sekiguchi, A. *Chem. Lett.* **1987**, *317*. (b) Ando, W.; Itoh, H.; Tsumuraya, T.; Yoshida, H. *Organometallics* **1988**, *7*, 1880.

[23] The 3-MP/IP(1/4) matrix is a relatively soft matrix compared to the 3-MP matrix. The viscosities of the matrices at 77 K are as follows: 3-MP/IP(1/4), 1.8 × 10^7 P; 3-MP, 9.4 × 10^{11} P. Lambardi, J. R.; Raymonda, J. W.; Albrecht, A. C. *J. Chem. Phys.* **1964**, *40*, 1148. Without any trapping reagent dimesitylgermylene dimerizes to tetramesityldigermene in a 3-MP/IP (1/4) matrix at 77 K. Ando, W.; Itoh, H.; Tsumuraya, T., submitted for publication. Dimerization of silylenes at 77 K in soft matrices; see: Sekiguchi, A.; Hagiwara, K.; Ando, W. *Chem. Lett.* **1987**, 209.

[24] Ando, W.; Itami, A.; Furuhata, T.; Tokitoh, N. *Tetrahedron Lett.* **1987**, *28*, 1787.

thiadigermetanes **2** and **4** (path a in Scheme II) in the reaction of dimethyl- or diphenylgermylenes with di-*tert*-butylthioketene.

Similar to thiagermirane **16**,[6] alkylidenethiagermirane **13** was readily oxidized by 2 equiv of *m*-chloroperbenzoic acid (mCPBA) in dichloromethane at 0 °C to give the 3-alkylidene-1,2,4-oxathiagermetane *S*-oxide **23**. The latter was oxidized further by treatment with mCPBA to afford 3-alkylidene-1,2,4-oxathiagermetane *S*,*S*-dioxide **24**. The formation of **23** can be explained by either direct oxidation of 3-alkylidenethiagermirane *S*-oxide **25** or its rearrangement product **26** (Scheme XI).

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of dry argon. The ^{1}H NMR spectra were recorded on Varian EM 360 A and JEOL PMX 60 SI spectrometers. ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. UV–vis spectra were measured on a JASCO Ubest 50 spectrometer. IR spectra were recorded on a Hitachi 260-50 spectrometer. Mass spectra were obtained on Hitachi RMU-6M and JEOL JMS-DX300 mass spectrometers. Preparative HPLC were carried out on a LC-08 (Japan Analytical Ind. Co., Ltd.). Preparative gas chromatographic separations were carried out on a Ohkura gas chromatograph with a 8 mm × 1.5 m glass column of 10% SF-96 on Celite 545. All melting points were uncorrected.

Materials. 2,3-Benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorborna-2,5-diene (**1**)[11] was prepared according to literature procedures. 2,3-benzo-1,4,5,6,7,7-hexaphenyl-7-germanorborna-2,5-diene (**3**) was synthesized by the reaction of 1,1,2,3,4,5-hexaphenylgermole and benzyne generated by 1-aminobenzotriazole and $Pb(OAc)_4$.[25] Hexamesitylcyclotrigermane (**12**) was prepared by reductive coupling of dichlorodimesitylgermane with Mg and $MgBr_2$ in THF as reported previously.[4b] Di-*tert*-butylthioketene[12] and bis(trimethylsilyl)thioketene[13] were synthesized according to literature procedures. Benzene, cyclohexane, 3-methylpentane, isopentane, and tetrahydrofuran (THF) used as solvents were dried over lithium aluminum hydride and distilled before use. Hexamethylphosphoramide (HMPA) was dried over a 4A molecular sieve and distilled before use. Dichloromethane was dried over calcium chloride and then distilled.

Thermolysis of 2,3-Benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanorborna-2,5-diene (1) with Di-*tert*-butylthioketene. A solution of **1** (107 mg, 0.2 mmol), di-*tert*-butylthioketene (102 mg, 0.6 mmol), and benzene (1.3 mL) was heated at 70 °C for 2.5 h. Separation of the reaction mixture by preparative GLC gave **2** (51%). **2** purified by GLC was contaminated by a small amount of the oxidized product. For **2**: ^{1}H NMR ($CDCl_3$) δ 0.72 (s, 6 H), 0.77 (s, 6 H), 1.21 (s, 9 H), 1.53 (s, 9 H); MS *m/e* (relative intensity) 376 (2, M^+), 319 (30, $M^+ - {}^tBu$), 206 (100, $Me_2Ge{=}GeMe_2$), 185 (76, $Me_2Ge{=}C{=}C^tBu$); High-resolution MS calcd for $C_{14}H_{30}S^{72}Ge^{74}Ge$ 376.0501, found 376.0547.

After the above reaction was completed, the reaction mixture was exposed to air and subsequent separation by preparative GLC gave the oxidized product 4-alkylidene-1,3,2,5-oxathiadigermolane: ^{1}H NMR ($CDCl_3$) δ 0.70 (s, 6 H), 0.77 (s, 6 H), 1.36 (s, 9 H), 1.63 (s, 9 H); MS *m/e* (relative intensity) 392 (25, M^+), 335 (46, $M^+ - {}^tBu$), 254 (28, $M^+ - {}^tBu_2C_2$), 238 (39, $M^+ - {}^tBu_2C_2 - Me$), 206 (59, $Me_2Ge{=}GeMe_2$), 123 (100); High-resolution MS calcd for $C_{14}H_{30}OS^{72}Ge^{74}Ge$ 392.0449, found 392.0443.

A reaction similar to that described above was carried out, and a benzene solution (3 mL) of sulfur (100 mg, 3.1 mmol) was added to the reaction mixture. Separation of the mixture by preparative GLC gave the ring expansion product 5-alkylidene-1,3,2,4-dithiadigermolane: ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 12 H), 1.40 (s, 9 H), 1.62 (s, 9 H); MS *m/e* (relative intensity) 408 (7, M^+), 351 (16, $M^+ - {}^tBu$), 270 (8, $M^+ - {}^tBu_2C_2$), 255 (36, $M^+ - {}^tBu_2C_2 - Me$), 238 (18, $Me_2Ge - GeMe_2 - S$), 223 (49, $Me_2Ge - GeMe_2 - S - Me$), 123 (100); high-resolution MS calcd for $C_{14}H_{30}S_2{}^{72}Ge^{74}Ge$ 408.0221, found 408.0223.

Thermolysis of 2,3-Benzo-1,4,5,6,7,7-hexaphenyl-7-germanorborna-2,5-diene (3) with Di-*tert*-butylthioketene. A mixture of **3** (660 mg, 1 mmol), di-*tert*-butylthioketene (170 mg, 1 mmol), and benzene (5 mmol) was heated at 70 °C for 3 h. The solvent was evaporated at room temperature under reduced pressure, and the residue was subjected to flash column chromatography (silica gel, benzene/hexane = 1/3, N_2 pressure) to give **4** (32%). For **4**: mp 150–152 °C; ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 9 H), 1.74 (s, 9 H), 7.3–7.9 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 32.4 (q), 33.3 (q), 41.3 (s), 41.7 (s), 128.1 (d), 128.5 (d), 129.0 (d), 132.7 (s), 134.2 (d), 134.6 (d), 136.9 (s), 139.7 (s), 162.0 (s); MS *m/e* (relative intensity) 624 (2, M^+), 567 (7, $M^+ - {}^tBu$), 486 (2, $M^+ - {}^tBu_2C_2$), 454 (27, $Ph_2Ge{=}GePh_2$), 305 (100, Ph_3Ge), 228 (10, Ph_2Ge). Anal. Calcd for $C_{34}H_{38}SGe_2$: C, 65.45; H, 6.14. Found: C, 65.53; H, 6.27.

Thermolysis of 1 with Bis(trimethylsilyl)thioketene. A solution of **1** (53.4 mg, 0.1 mmol), bis(trimethylsilyl)thioketene (101 mg, 0.5 mmol), and benzene (2 mL) was heated at 70 °C for 3 h. Separation of the reaction mixture by preparative GLC gave **8** (87%) and **9** (17%).

All spectral data obtained for **8**[14] and **9**[15] were identical with those of authentic samples.

Thermolysis of Hexamesitylcyclotrigermane (12) with Di-*tert*-butylthioketene. A solution of **12** (280 mg, 0.3 mmol), di-*tert*-butylthioketene (119 mg, 0.7 mmol), and benzene (5 mL) was heated to reflux for 10 h. The solvent was evaporated at room temperature under reduced pressure, and the residue was separated by preparative HPLC to give **13** (34%). For **13**: mp 120–121 °C; ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 9 H), 1.49 (s, 9 H), 2.24 (s, 6 H), 2.39 (s, 12 H), 6.80 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.1 (q), 23.7 (q), 30.7 (q), 32.2 (q), 39.8 (s), 40.2 (s), 125.6 (s), 129.3 (d), 134.0 (s), 139.3 (s), 142.9 (s), 151.3 (s); MS *m/e* (relative intensity) 482 (3, M^+), 425 (1, $M^+ - {}^tBu$), 344 (2, $Mes_2Ge{=}S$), 312 (100, Mes_2Ge). Anal. Calcd for $C_{28}H_{40}SGe$: C, 69.87; H, 8.37. Found: C, 69.55; H, 8.48.

Photolysis of 13 with 2,3-Dimethyl-1,3-butadiene. A solution of **13** (48.1 mg, 0.1 mmol), 2,3-dimethyl-1,3-butadiene (410 mg, 5 mmol), and cyclohexane (5 mL) was irradiated with a low-pressure mercury lamp for 6 h at room temperature. Separation of the reaction mixture by preparative TLC (silica gel, benzene/hexane = 1/3) gave **14** (50%) and di-*tert*-butylthioketene (33%).

All spectral data obtained for **14**[18] was identical with those of an authentic sample.

Pyrolysis of 13 with 2,3-Dimethyl-1,3-butadiene. The pyrolysis apparatus consisted of a 28 cm × 1 cm Pyrex tube packed with Pyrex chips. The upper end of the tube was equipped with a rubber cap for syringe introduction of the sample and a nitrogen inlet. The pyrolysis tube was maintained at 500 °C, and the nitrogen flow was ca. 10 mL/min. The sample was introduced drop by drop by using a syringe. The pyrolysate was trapped in a receiver cooled by dry ice–MeOH. A solution of **13** (48.1 mg, 0.1 mmol), 2,3-dimethyl-1,3-butadiene (410 mg, 5 mmol), and benzene (1 mL) was pyrolyzed at 500 °C under flowing nitrogen. Separation of the reaction mixture by preparative TLC (silica gel, benzene/hexane = 1/3) gave **14** (22%).

Photolysis of 13 in Hydrocarbon Matrices at 77 K. A mixture of **13** (ca. 1 mg) and 3-MP (5 mL) was placed in a quartz UV cell and degassed for several times. The mixture was cooled to 77 K, and the resulting matrix was irradiated with a low-pressure mercury lamp. The UV–vis absorptions were taken at periodic intervals. An absorption band with a maximum at 580 nm appeared and grew on irradiation. On annealing the matrix this band immediately disappeared. Similarly, **13** was irradiated in 3-MP/IP (1/4) at 77 K, giving absorption bands at 582 nm.

Preparation of Bis(trimethylsilyl)germanes. A solution consisting of 10 mL (80 mmol) of Me_3SiCl and 3.0 g (123 mmol) of Mg turnings in 43 mL of dry HMPA was heated to 90 °C. Dichlorodimesitylgermane (7.0 g, 18 mmol) dissolved in 22 mL of dry THF was added dropwise to the heated mixture. The colorless mixture immediately turned yellow, giving a deep orange solution after 40 h of heating. After the solution had cooled, the solution was filtered to remove excess Mg, and hexane was added. The resulting mixture was hydrolyzed with 10% HCl, and the hexane layers were washed with water. Concentration of the solution in vacuo yielded 5.6 g (70%) of a white powder. Subsequent recrystallization from hexane and ethanol gave pure dimesitylbis(trimethylsilyl)germane. Dimesitylbis(trimethyl-

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silyl)germane: mp 183–184 °C; ^{1}H NMR (CCl_4) δ 0.20 (s, 18 H), 2.14 (s, 12 H), 2.23 (s, 6 H), 6.75 (s, 4 H); MS *m/e* (relative intensity) 458 (2, M^+), 443 (6, M^+ – Me), 385 (9, M^+ – Me_3Si), 226 (89, M^+ – Mes – Me_3Si), 177 (100); high-resolution MS calcd for $C_{24}H_{40}Si_2Ge$ 458.1880, found 458.1871.

Bis(trimethylsilyl)diphenylgermane[26] was prepared by a reaction similar to that described above and was purified by column chromatography (silica gel, hexane): colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 18 H), 7.2–7.6 (m, 10 H); MS *m/e* (relative intensity) 374 (2, M^+), 359 (M^+ – Me), 224 (56, M^+ – Ph – Me_3Si), 135 (100); high-resolution MS calcd for $C_{18}H_{28}Si_2Ge$ 374.0941, found 374.1010.

Reactions of Germylenes with Di-*tert*-butylthioketene in Hydrocarbon Matrices. A mixture of dimesitylbis(trimethylsilyl)germane (ca. 1 mg) and 3-MP (5 mL) was placed in a quartz UV cell and degassed several times. The mixture was cooled to 77 K, and the resulting matrix was irradiated with a low-pressure mercury lamp. The UV–vis absorption band with λ_{max} at 550 nm appeared and grew on irradiation. Annealing the matrix resulted in an immediate disappearance of this band with concurrent formation of a new band with λ_{max} at 580 nm, due to germathiocarbonyl ylide **17**. On annealing the matrix or irradiation of the solution with a wavelength of light greater than 460 nm resulted in disappearance of this band.

Similarly, the bis(trimethylsilyl)germane was irradiated in 3-MP/IP(1/4) glass at 77 K, giving absorption bands at 582 nm due to **17**. Melting the matrix or irradiation with $\lambda > 460$ nm resulted in immediate disappearance of this band with concurrent formation of 3-alkylidenethiagermirane **13** which was detected by MS.

Irradiation of **1** or bis(trimethylsilyl)diphenylgermane with di-*tert*-butylthioketene in a 3-MP/IP(1/4) matrix at 77 K with a low-pressure mercury lamp produced absorption bands at 595 or 565 nm, respectively, due to the corresponding germathiocarbonyl ylide.

Reaction of Dimethylgermylene with 13. A solution of **1** (107 mg, 0.2 mmol), **13** (48.1 mg, 0.1 mmol), and benzene (5 mL) was heated at 70 °C for 4 h. Separation of the reaction mixture by flash column chromatography (silica gel, benzene/hexane = 1/3, N_2 pressure) to give **22** (74%). For **22**: mp 170–172 °C; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 3 H), 0.98 (s, 3 H), 1.26 (s, 9 H), 1.69 (s, 9 H), 2.04 (s, 6 H), 2.31 (s, 3 H), 2.33 (s, 3 H), 2.75 (s, 3 H), 2.85 (s, 3 H), 6.80 (s, 1 H), 6.85 (s, 1 H), 6.94 (s, 1 H), 6.97 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 2.6 (q), 5.4 (q), 21.0 (q), 22.6 (q), 22.9 (q), 23.5 (q), 24.7 (q), 32.3 (q), 32.4 (q), 40.7 (s), 40.9 (s), 128.8 (d), 129.0 (d), 129.1 (d), 129.8 (d), 136.9 (s), 137.8 (s), 138.3 (s), 140.6 (s), 141.7 (s), 142.0 (s), 142.6 (s), 142.7 (s), 143.2 (s), 156.5 (s); MS *m/e* (relative intensity) 584 (2, M^+), 569 (3, M^+ – Me), 527 (4, M^+ – ^tBu), 446 (6, M^+ – $^tBu_2C_2$), 414 (100, $Me_2Ge{=}GeMes_2$), 393 (19, $Mes_2Ge{=}C{=}C^tBu$), 170 (46, $^tBu_2C{=}C{=}S$). Anal. Calcd for $C_{30}H_{46}SGe_2$: C, 61.70; H, 7.94. Found: C, 61.71; H, 8.07.

Oxidation of 13 with mCPBA. To a mixture of **13** (48.1 mg, 0.1 mmol) and dichloromethane (10 mL) was added *m*-chloroperbenzoic acid (mCPBA) (0.2 mmol) at 0 °C. The reaction mixture was separated by preparative TLC (silica gel, dichloromethane) to give **23** (quant). **23** was further oxidized to **24** by the treatment of mCPBA. For **23**: mp 196–197 °C; ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 9 H), 1.56 (s, 9 H), 2.26 (s, 3 H), 2.28 (s, 3 H), 2.38 (s, 6 H), 2.47 (s, 6 H), 6.85 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.1 (q), 23.5 (q), 31.2 (q), 34.5 (q), 40.7 (s), 42.2 (s), 129.7 (d), 130.0 (d), 136.0 (s), 137.9 (s), 140.1 (s), 140.8 (s), 141.2 (s), 142.7 (s), 161.6 (s), 167.6 (s); IR (KBr) 1100 cm^{-1} (–SO–O–); MS *m/e* (relative intensity) 450 (13, M^+ – SO_2), 393 (100, M^+ – SO_2 – ^tBu), 328 (16, $Mes_2Ge{=}O$), 312 (25, Mes_2Ge). Anal. Calcd for $C_{28}H_{40}O_2SGe$: C, 65.52; H, 7.85. Found: C, 65.78; H, 8.11. For **24**: mp 262–263 °C; ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 9 H), 1.64 (s, 9 H), 2.28 (s, 6 H), 2.40 (s, 12 H), 6.88 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.1 (q), 23.4 (q), 31.7 (q), 33.0 (q), 41.1 (s), 41.8 (s), 130.1 (d), 133.2 (s), 141.1 (s), 142.7 (s), 151.9 (s), 172.5 (s); IR (KBr) 1300, 1150 cm^{-1} (–SO_2–O–); MS *m/e* (relative intensity) 530 (9, M^+), 393 (26, M^+ – SO_3 – ^tBu), 328 (37, $Mes_2Ge{=}O$), 312 (86, Mes_2Ge), 193 (100, MesGe). Anal. Calcd for $C_{28}H_{40}O_3SGe$: C, 63.54, H, 7.61. Found: C, 63.41, H, 7.71.

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Registry No. **1**, 76054-64-3; **2**, 110889-95-7; **3**, 107824-82-8; **4**, 110889-96-8; **8**, 14630-40-1; **9**, 16090-54-3; **12**, 107824-84-0; **13**, 120033-92-3; **14**, 83686-73-1; **17**, 120058-70-0; dimesitylbis(trimethylsilyl)germane, 111655-80-2; **22**, 120033-93-4; **23**, 120033-94-5; **24**, 120033-95-6; *t*-$Bu_2C{=}C{=}S$, 16797-75-4; $(Me_3Si)_2C{=}C{=}S$, 62827-97-8; $CH_2{=}C(CH_3)C(CH_3){=}CH_2$, 513-81-5; $(Me_3Se)_2GePh_2$, 111655-78-8; $GeCl_2Ph_2$, 1613-66-7; MeS_2Ge, 72176-49-9; Me_2Ge, 74963-95-4; Ph_2Ge, 68816-03-5; 1,1,2,3,4,5-hexaphenylgermole, 15922-94-8; benzyne, 462-80-6; dichlorodimesitylgermane, 96481-42-4; 4-(di-*tert*-butylmethylidene)-1,3,2,5-oxathiadigermolane, 110889-97-9; 5-(di-*tert*-butylmethylidene)-1,3,2,4-dithiadigermolane, 110889-98-0.

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