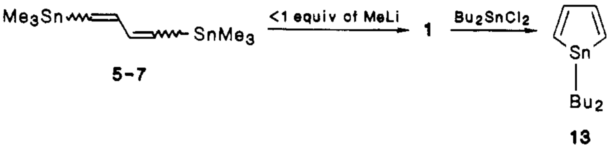
(1*E*,3*E*)-1,4-dilithio-1,3-butadiene (**3**) gives (1*E*,3*E*)-1-lithio-4-(trimethylstannyl)-1,3-butadiene (**9**) as indicated by the ^1H NMR spectrum and by acetic acid quenching to the expected (*E*)-1-(trimethylstannyl)-1,3-butadiene (**10b**).[15] However, if sufficient **7** is added to remove all the methyllithium, the ^1H NMR spectrum of **9** is replaced by that of **1**. Apparently the excess (*E*,*E*)-bis(trimethylstannyl)butadiene **7** is partially isomerized to the *Z*,*Z*-isomer **5** which then undergoes the very favorable Li/Sn exchange to the (*Z*,*Z*)-dilithiobutadiene **1** (see Scheme I). The excess bis(trimethylstannyl)butadiene is lost to polymerization. This overall conversion of **1** to **3** must be driven by the greater thermodynamic stability of **1**.

(1*E*,3*Z*)-Bis(trimethylstannyl)-1,3-butadiene (**6**) can be similarly covered to **1**. Thus, addition of excess methyllithium to **6** affords a mixture of **11** and **12**[16] as shown by acetic acid quenching to (*E*)- and (*Z*)-1-(trimethylstannyl)-1,3-butadiene (**10a**,**b**).[15] Addition of sufficient **6** to remove all the methyllithium from this mixture produces **1** and polymer. Synthetically it is most convenient to convert the mixed isomer of 1,4-bis(trimethylstannyl)-1,3-butadiene to **1**, which may be converted to 1,4-disubstituted-(1*Z*,3*Z*)-butadienes. In this manner, the reaction of **1** with dibutyltin dichloride gave 1,1-dibutylstannole (**13**) as a pale yellow oil (bp 80 °C (0.01 Torr)) in 28% yield.[17] We have been unable to obtain the stannole by the direct hydrostannation of 1,3-butadiyne.[18] Since stannoles undergo facile exchange reactions, this preparation offers an efficient method for introduction of a (1*Z*,3*Z*)-butadienyl functionality.[19]



Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. 1, 75920-66-0; 3, 75920-67-1; (1*E*,3*E*)-4, 3588-12-3; (1*E*,3*Z*)-4, 3588-13-4; (1*Z*,3*Z*)-4, 3588-11-2; 5, 112008-08-9; 6, 112008-09-0; 7, 112008-10-3; 9, 115290-35-2; 10a, 115290-38-5; 10b, 93469-37-5; 11, 115290-36-3; 12, 115290-37-4; 13, 115290-39-6; (1*Z*,3*Z*)-1,4-dideuterio-1,3-butadiene, 39768-32-6; (1*E*,3*E*)-1,4-dideuterio-1,3-butadiene, 39768-65-5; trimethylstannyl chloride, 1066-45-1; dibutyltin dichloride, 683-18-1.

Supplementary Material Available: A table C, H combustion analyses for 1,4-bis(trimethylstannyl)-1,3-butadienes (1 page). Ordering information is given on any current masthead page.

---

[15] Alvanipour, A.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1980**, *201*, 233.

[16] (1*E*,3*Z*)-1,4-Dilithio-1,3-butadiene could not be detected spectroscopically under the same condition for which the *E*,*E*- and *Z*,*Z*-isomers were formed. Qualitatively $K_{ZZ} > K_{EE} > K_{EZ}$.

[17] **1,1-Dibutylstannole.** The mixed isomers of 1,4-bis(trimethylstannyl)-1,3-butadiene (0.96 g, 2.5 mmol) were added in 50-μL portions over 15 min to a solution containing 1.8 mL of 1.4 M methyllithium (2.5 mol) in ether and 10 mL of tetrahydrofuran at −78 °C. On warming to 25 °C, the solution became dark blue. Stirring continued for 3 h during which time the presence of **1** can be monitored by following the increase of intensity of the ^1H NMR spectral doublet at δ 8.0. The solution of **1** was then added to 1.0 g (3.3 mmol) of dibutyltin dichloride in 8 mL of tetrahydrofuran at 0 °C. After the solution was stirred for 30 min at 25 °C, the solvent was removed under reduced pressure and the residue extracted with pentane which was then washed with dilute NaOH and water. After drying, vacuum distillation gave 100 mg (28%) of 1,1-dibutylstannole (bp 80 °C (0.01 Torr)). ^1H NMR ($CDCl_3$): δ 7.16 (A_2B_2 pattern, $J_{^{119}SnH}$ = 147.2 Hz, 2 H), 6.50 (A_2B_2 pattern, $J_{^{119}SnH}$ = 156.8 Hz, 2 H), 1.55 (p, 4 H), 1.31 (sex, 4 H), 1.18 (t, 6 H), 0.87 (t, 4 H). ^{13}C NMR ($CDCl_3$): δ 145.6, 131.6, 29.6, 26.9, 13.5, 11.4. MS: *m/z* 229 ($M^+ - C_4H_9$).

[18] Mahmoud, S. Ph.D. Thesis, The University of Michigan, 1988.

[19] Substituted stannoles have been used extensively for the synthesis of heterocycles: Leavitt, F. C.; Manuel, T. A.; Johnson, F.; Matternas, L. U.; Lehman, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 5099. Atwell, W. H.; Weyenberg, D. R.; Gilman, H. *J. Org. Chem.* **1967**, *32*, 885. Killian, L.; Wrackmeyer, B. *J. Organomet. Chem.* **1977**, *132*, 213. Ashe, A. J. III; Diephouse, T. R. *J. Organomet. Chem.* **1980**, *202*, C95.

Spectroscopic Characterization of Diarylgermylene Complexes with Heteroatom-Containing Substrates

Wataru Ando,* Hiroyuki Itoh, Takeshi Tsumuraya, and Hitoaki Yoshida

Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305, Japan

Received April 13, 1988

Summary: Characteristic UV absorption bands of diarylgermylene complexes were observed in the reaction of diarylgermylenes with heteroatom-containing substrates in 3-MP/IP matrix at 77 K.

Characterizations of germylenes have been the subject of considerable interest in recent years, and a few stable diarylgermylene complexes were reported on dehydrochlorination of diarylchlorogermanes in triethylamine at room temperature by Satgé et al. in 1982.[1] Recently, however, Masamune et al.[2] claimed that diarylgermylenes did not form stable adducts with triethylamine at room temperature.

Here, we report the recent spectroscopic observation of diorganogermylenes in matrices with heteroatom-containing substrates. In our experiments diarylbis(trimethylsilyl)germanes **1a** and **1b** were photolyzed with a low-pressure mercury lamp in 3-methylpentane/isopentane (3-MP/IP = 3:7) at 77 K to give the corresponding germylene.[2-4] Dimesitylgermylene (**2a**) and bis(2,4,6-triisopropylphenyl)germylene (**2b**) showed the absorption bands with λ_{max} at 550 and 558 nm, respectively. When the matrices were annealed, the germylenes dimerized to give the digermenes **3a** and **3b** with new absorption bands at λ_{max} = 406 and 416 nm, respectively (Scheme I).

When a similar photolysis of **1a** was carried out in matrices containing triethylamine, a new band at 414 nm first appeared together with the band due to dimesitylgermylene (Figure 1).

After being allowed to stand at 77 K, the band of germylene decreased and the new band grew and was stable at 77 K. When the matrix was annealed, the new band diminished and a 406-nm band grew. Similar results were obtained for **1b** in the matrix containing triethylamine, and a new band was formed with λ_{max} = 445 nm. These new bands are very likely the diarylgermylene–triethylamine complexes **4a** and **4b**.

The new stable complexes of dimethyl- and diarylgermylenes with heteroatom-containing substrates were observed in matrices at 77 K (Table I) and are analogous to the reaction between heteroatom compounds and diarylsilylenes.[5]

Bands due to the complex of germylenes with P, N, S, and O atoms were observed widely from 306 to 376 nm in

---

[1] Rivière, P.; Castel, A.; Satgé, J. *J. Organomet. Chem.* **1982**, *232*, 123.

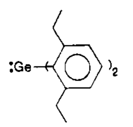
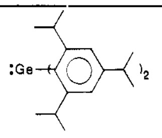
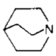
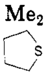
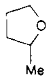
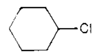
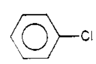
[2] Collins, S.; Murakami, S.; Snow, J. T.; Masamune, S. *Tetrahedron Lett.* **1985**, *26*, 1281.

[3] Ando, W.; Tsumuraya, T.; Sekiguchi, A. *Chem. Lett.* **1987**, 317.

[4] Konieczny, S.; Jacobs, S. J.; Wilking, J. K. B.; Gaspar, P. P. *J. Organomet. Chem.* **1988**, *224*, C17.

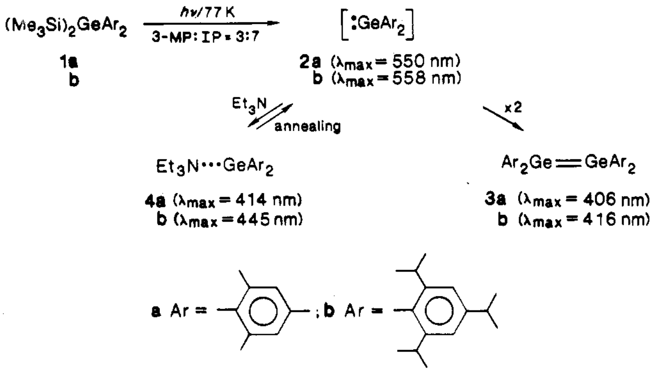
[5] Ando, W.; Sekiguchi, A.; Hagiwara, K.; Sakakibara, A.; Yoshida, H. *Organometallics* **1988**, *7*, 558.

Table I. UV Absorption Maxima (nm) of Diorganogermylene Complexes[a]

	:GeM$_2$[b] 420	:GePh$_2$ 463	:GeMes$_2$ 550	 544	 558
^{n}Bu$_3$P			306	314	334
		334	349	356	363
Me$_2$S		326	348	357	357
		332	352	359	366
		325	360 (373)[c]	369	376
	341	374	495	508	544
	392	403	538	532	553

[a] λ_{max} in 3-MP:IP = 3:7 at 77 K. [b] Generated from 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-germanorborna-2,5-diene. [c] λ_{max} in 2-MeTHF at 77 K.

Scheme I



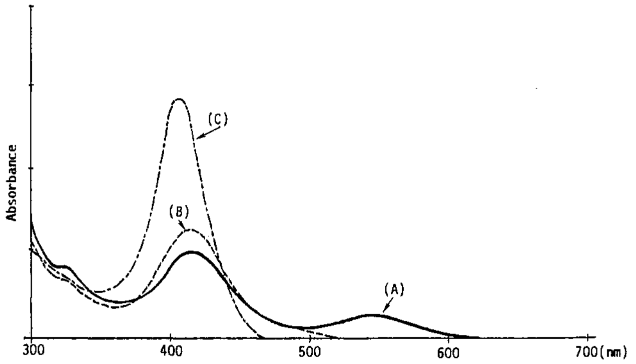
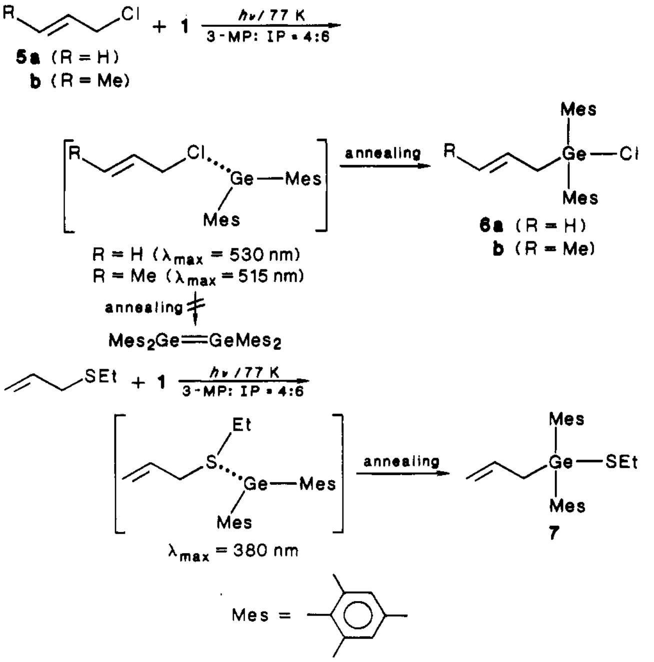


Figure 1. Photolysis of dimesitylbis(trimethylsilyl)germane in the presence of triethylamine matrix: (A) after photolysis of **1a** with a low-pressure mercury lamp for 40 min in the presence of triethylamine in 3-MP:IP = 3:7 at 77 K (—); (B) the above sample was allowed to stand in the dark at 77 K for 30 min (- - -); (C) the above sample was allowed to anneal (- - -).

comparison to those of silaylides.[5] The germylene–chlorine complexes revealed spectra of the red shift in the region 346–553 nm. The shift among heteroatoms is probably due to the stability of germylene–heteroatom complexes, which is in accord with the differences between germylenes and silylenes.[5]



In order to determine the stability of these complexes, we irradiated **1b** in a matrix (3-MP/IP = 3:7) containing Bu$_3$P or dimethyl sulfide at an elevated temperature. In the experiments in Bu$_3$P, only one band, 334 nm, appeared at −120 °C after prolonged standing with no band corresponding to tetrakis(2,4,6-triisopropylphenyl)digermene (**3b**). However, two bands appeared at −100 °C. Thus, the diarylgermylene–phosphine complex appears to be stable at −120 °C but to slowly decompose at −100 °C. The half-life of the bis(2,4,6-triisopropylphenyl)germylene–tributylphosphine complex was 48 s at −79 °C. The diarylgermylene–dimethyl sulfide complex was stable below −140 °C.

The photolysis of **1a** in the matrices (3-MP/IP=4:6) containing crotyl chloride at 77 K produced a band at 515 nm, and no digermene was formed upon annealing. Analysis of the photolysate by GC–MS showed the formation of chlorocrotyldimesitylgermane (**6b**), direct insertion of the germylene into carbon–chlorine bond in quantitative yield, and no 2,3-sigmatropic rearranged product.[6]

Irradiation of **1a** at 77 K in matrices (3-MP/IP = 4:6) containing allyl sulfide led to the formation of a new band at 380 nm. Annealing of the solution discharged the band with the formation of the C-S insertion product of dimesitylgermylene. These data are consistent with 515- and 380-nm bands of dimesitylgermylene–chlorine and –sulfur complexes and contrast markedly with the behavior of silylene or carbene with allylic compounds.[7]

Acknowledgment. Financial support for this research was provided by a Grant-in Aid for Special Project Research (No. 63106003) from the Ministry of Education, Science, and Culture of Japan.

---

(6) In thermal reaction of dimethylgermylene with crotyl chloride two products, direct insertion and rearranged, were obtained in the ratio 1:3.

(7) Ando, W. *Acc. Chem. Res.* **1977**, *10*, 179.

Digermirane and Azadigermiridine: Synthesis and Reactions

Wataru Ando* and Takeshi Tsumuraya

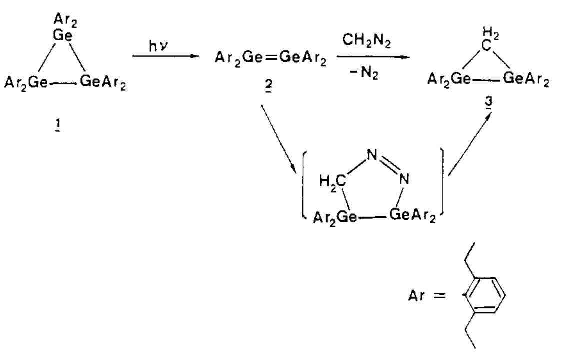
Department of Chemistry, The University of Tsukuba
Tsukuba, Ibaraki 305, Japan

Received April 14, 1988

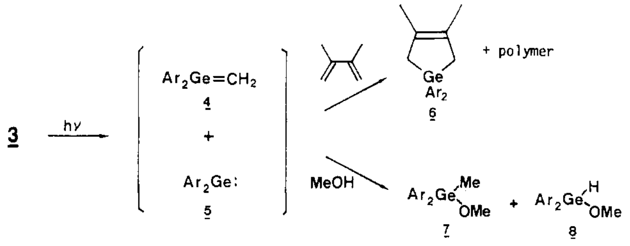
Summary: 1,1,2,2-Tetrakis(2,6-diethylphenyl)digermirane (**3**) was prepared by the reaction of tetrakis(2,6-diethylphenyl)digermene (**2**) with diazomethane. The photolysis of **3** with a high-pressure mercury lamp yields germene **4** and germylene **5**. The digermirane **3** reacts with pyridine *N*-oxide, sulfur, and selenium to yield the insertion products of O, S, and Se into the germanium–germanium bond. 2,2,3,3-Tetrakis(2,6-diethylphenyl)azadigermiridine (**12**) was prepared by the reaction of **2** with phenyl azide.

Synthesis of small-ring systems involving a germanium–germanium bond have received considerable attention because of interest in the reactivity of the reactive germanium–germanium bonds in the ring.[1-6] However, digermiranes and azadigermiridines have not been isolated or very well characterized, although recently synthesis of a disilirane[7] and an azadisiliridine[8] was reported by Masamune and West. Here, we report the first synthesis and reactions of a novel digermirane and an azadigermiridine.

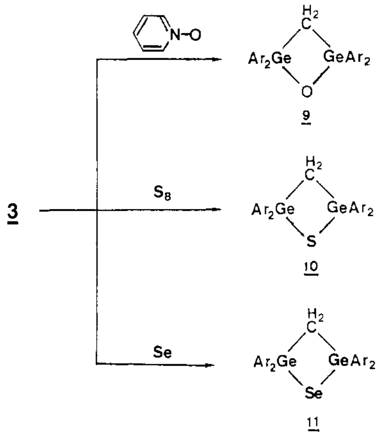
Scheme I



Scheme II



Scheme III



Irradiation of a cyclohexane solution of hexakis(2,6-diethylphenyl)cyclotrigermane (1)[3b,4] at room temperature with a low-pressure mercury lamp afforded tetrakis(2,6-diethylphenyl)digermene (2) in good yield.[3b] A cyclohexane solution of 2 (prepared from 0.5 mmol of 1) was transferred to an ethereal solution of diazomethane (ca. 5 mmol, dried by KOH and degassed) under argon at −78 °C. After the addition was completed, the resulting mixture was warmed to room temperature. During the reaction, dinitrogen was evolved and the solution became pale yellow. Crystallization of the residue from hexane afforded 1,1,2,2-tetrakis(2,6-diethylphenyl)digermirane (3) as colorless crystals in 72% yield (based on the cyclotrigermane 1 used) (Scheme I).

The structure of 3 was confirmed by spectroscopic analysis [^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 7 Hz, 24 H, CH_3), 1.30 (s, 2 H, $GeCH_2Ge$), 2.76 (q, J = 7 Hz, 8 H, CH_2), 2.91 (q, J = 7 Hz, 8 H, CH_2), 6.8–7.4 (m, 12 H, Ar); ^{13}C NMR ($CDCl_3$) δ 6.99 (t, $GeCH_2Ge$), 15.32 (q, CH_3), 30.12 (t, CH_2), 125.41 (d, Ar), 128.75 (d, Ar), 138.85 (s, Ar), 149.77 (s, Ar);

---

(1) (a) Ando, W.; Tsumuraya, T.; Sekiguchi, A. *Tetrahedron Lett.* **1985**, *26*, 4523. (b) Ando, W.; Tsumuraya, T. *Tetrahedron Lett.* **1986**, *27*, 5105.

(2) (a) Ando, W.; Tsumuraya, T. *Tetrahedron Lett.* **1986**, *27*, 3251. (b) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics*, in press.

(3) (a) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136. (b) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191. (c) Collins, S.; Murakami, S.; Snow, J. T.; Masamune, S. *Tetrahedron Lett.* **1985**, *26*, 1281.

(4) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1514.

(5) (a) Espenbetov, A. A.; Struchkov, Yu. Y.; Kolesnikov, S. P.; Nefedov, O. M. *J. Organomet. Chem.* **1984**, *275*, 33. (b) Nefedov, O. M.; Egorov, M. P.; Gal'minas, A. M.; Kolesnikov, S. P.; Krebs, A.; Berndt, J. *J. Organomet. Chem.* **1986**, *301*, C21.

(6) Barrau, J.; Hamida, N. B.; Agrebi, A.; Satge, J. *Organometallics* **1987**, *6*, 659.

(7) Masamune, S.; Murakami, S.; Tobita, H. *J. Am. Chem. Soc.* **1983**, *105*, 7776.

(8) Gillette, G. R.; West, R., presented at the 19th Organosilicon Symposium, Baton Rouge, LA, April 26–27, 1985.

0276-7333/88/2307-1882$01.50/0