

## From Germenes to Transient Germanimines

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Received June 8, 1989

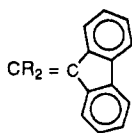
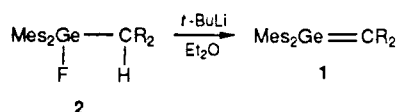
Reactions of diazo compounds  $R_2CN_2$  ( $R_2C$ : fluorenylidene) or  $Ph_2CN_2$  with germene  $Mes_2Ge=CR_2$  (1) lead to cyclodigermazanes **4** or **14** probably via transient germanimines **5** or **13** with evolution of carbene  $CR_2$  from **1**. Cyclodigermazane **4** has been isolated in the form of the cis isomer **4a**, which isomerizes slowly in solution to the trans isomer **4b**. **4a** has been characterized by X-ray diffraction:  $C_{62}H_{60}Ge_2N_4 \cdot 2C_4H_{10}O$ ;  $M_r = 1154.6$ , orthorhombic,  $Aba2$ ,  $a = 21.926$  (3),  $b = 23.134$  (3),  $c = 12.439$  (2) Å;  $V = 6310$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D(\text{calcd}) = 1.21 \text{ g}\cdot\text{cm}^{-3}$ ,  $\lambda$  (Cu K $\alpha$ ) = 1.54178 Å,  $\mu = 1.6 \text{ mm}^{-1}$ ,  $F(000) = 2432$ ,  $T = 295 \text{ K}$ , final  $R = 0.039$ , for 2896 observed reflections.

## Introduction

In recent years, much interest has been devoted to the doubly bonded main-groups elements.<sup>1</sup> In the case of germanium, some derivatives of the type  $>Ge=X$  ( $X = CR_2, NR, O, S, PR, GeR_2$ ) have been isolated or characterized as reactive intermediates.<sup>2</sup> In our group we have recently obtained the stable germene  $Mes_2Ge=CR_2$  ( $CR_2$ : fluorenylidene).<sup>3</sup> The chemistry of stable<sup>3,4</sup> or transient<sup>5</sup> germenes is now under active investigation; one of the most interesting features might be their ability to afford new doubly bonded species of germanium. In this paper we present the unexpected easy formation of germanimines  $R_2Ge=NR'$  by reaction of germene **1** with diazo compounds.

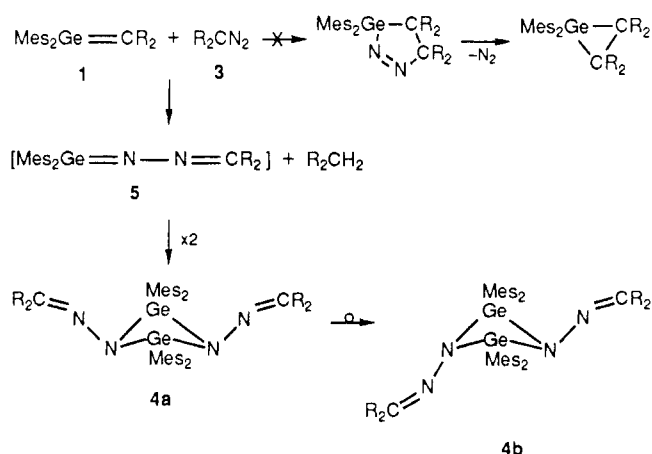
## Results and Discussion

We have recently described the synthesis of germene **1** by dehydrofluorination of fluorogermene **2** with *tert*-bu-



tyllithium,<sup>3</sup> its X-ray structure,<sup>3b</sup> and the first aspects of its chemical behavior;<sup>3a</sup> germene **1** is very reactive toward protic reagents, disulfides, and hydrides and also in [2 + 3] and [2 + 4] cycloadditions respectively with nitrones and 1,3-dienes. Another [2 + 3] cycloaddition could be expected with diazo derivatives, for example, diazofluorene **3**, with the final formation of a germacyclopropane after nitrogen evolution: such three-membered heterocycles are still unknown and, due to a highly strained ring involving probably an hyperreactive Ge-C bond, should be of great interest. Similar reactions of diazo derivatives with doubly bonded main-group derivatives leading to three-membered rings have been observed from diphosphenes,<sup>6</sup> disilenes,<sup>7</sup> and digermenes.<sup>8</sup> We have in fact observed a completely different and unexpected reaction, affording the cyclo-

## Scheme I



digermazane **4a**, probably via germanimine intermediate **5** (Scheme I).

After 1 week at room temperature in diethyl ether solution, **4a** ( $R_2CN$  in the cis position) is quantitatively isomerized in **4b** ( $R_2CN$  in the trans position). Why the exclusive cis isomer **4a** is initially formed is not yet un-

(1) For reviews on  $M=M$  compounds, see the following. (a) Si=Si: West, R. *Science* (Washington, D.C.) **1984**, *225*, 1109-14. West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201-11. (b) Si=M ( $M =$  group 14 and 15 elements): Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419-509. (c) Si=C: Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1-44. (d) Si=C (or N) and Ge=C (or N): Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141-77. (e) Ge=M ( $M =$  group 14 and 15 elements): Satgé, J. *Adv. Organomet. Chem.* **1982**, *21*, 241-87. (f)  $M=M'$  ( $M, M' =$  Si, Ge, Sn, P, As, Sb): Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1-63. (g)  $P=X$  ( $X =$  group 14 and 15 elements): Lochschmidt, S.; Schmidpeter, A. *Phosphorus Sulfur* **1986**, *29*, 73-109.

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(3) (a) Couret, C.; Escudié, J.; Satgé, J.; Lazraq, M. *J. Am. Chem. Soc.* **1987**, *109*, 4411-4412. (b) Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J.; Dräger, M.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 828-829.

(4) Two other stable germenes have been prepared at the same time as **1** by Berndt et al.: (a) Meyer, H.; Baum, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 798-799. (b) Berndt, A.; Meyer, H.; Baum, G.; Massa, W.; Berger, S. *Pure Appl. Chem.* **1987**, *59*, 1011-1014.

(5) (a) Wiberg, N.; Kim, Ch. K. *Chem. Ber.* **1986**, *119*, 2966-2979, 2980-2994. (b) Wiberg, N.; Karampatses, P.; Kim, Ch. K. *Chem. Ber.* **1987**, *120*, 1203-1212.

(6) Etemad-Moghadam, G.; Bellan, J.; Tachon, C.; Koenig, M. *Tetrahedron* **1987**, *43*, 1793-1797.

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

(8) (a) Ando, W.; Tsumuraya, T. *Organometallics* **1988**, *7*, 1882-1883. (b) Batcheller, S. A.; Masamune, S. *Tetrahedron Lett.* **1988**, *29*, 3383-4.

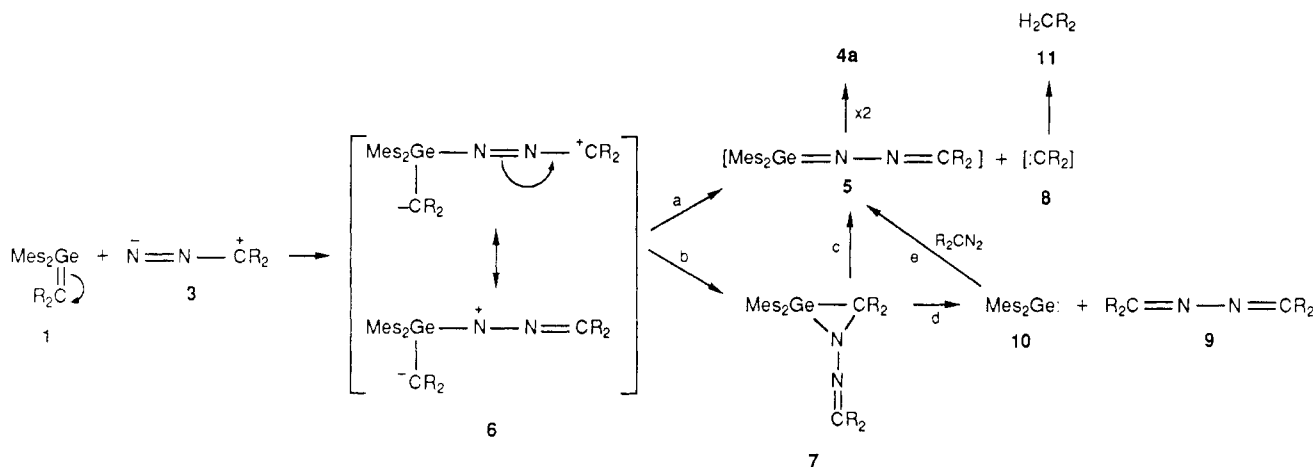
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Scheme II



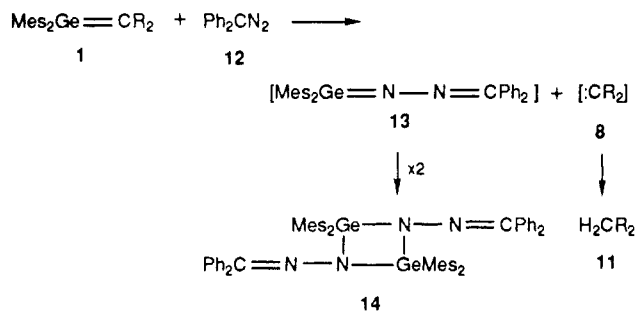
derstood. Compounds **4a** and **4b** are stable compounds that can be handled in air, in contrast with compounds with a Ge–N bond, which are generally very air sensitive.<sup>9</sup> No reaction with methanol is observed, even in solution. Such relative inertness of the Ge–N bond is probably due to the large steric hindrance, which prevents the attack of the protic reagent on nitrogen lone pair. **4a** has been characterized by NMR and mass spectrometry and particularly by X-ray analysis.

**Description of the Structure.** **4a** crystallizes with two molecules of diethyl ether and possesses a 2-fold axis perpendicular to the center of the Ge<sub>2</sub>N<sub>2</sub> ring. The central lozengic cyclodigermazane core deviates significantly from planarity as is evident from the Ge(1)N(1)Ge'(1)N'(1) torsion angle of 25°. The dihedral angle between the planes Ge(1)N(1)N'(1) and Ge'(1)N(1)N'(1) is 34°, and between the planes Ge(1)Ge'(1)N(1) and Ge(1)Ge'(1)N'(1) is 38°. This rather important fold angle is comparable to that observed in cyclobutanes (35°)<sup>10</sup> but much higher than in other four-membered rings with two main-group elements: for example, 8.8 and 8.4° in 1,3-cyclodigermozane,<sup>11</sup> 2.4–5.9<sup>12</sup> and exceptionally 17.9°<sup>13</sup> in 1,3-disilacyclobutanes. The two R<sub>2</sub>CN groups are in the cis position: N(2) and N'(2) are 0.14 Å above the mean plane through Ge(1)–Ge'(1)N(1)N'(1).

The Ge–N bonds (1.894, 1.895 Å) are somewhat longer than others recorded (1.82–1.86 Å);<sup>14</sup> elongations of these bonds are probably due to the steric congestion caused by mesityl and fluorenylidene groups. The Ge–C(Mes), N–N, and N=C bonds lie in the normal range.

The data for the fluorenylidene moiety are in good agreement with the literature<sup>3b,15</sup> for C(20)–C(21), C-

Scheme III



(21)–C(22), and C(22)–C(23) bonds. The C(19)–C(20) and C(19)–C(23) bonds, respectively 1.487 (7) and 1.490(6) Å, are slightly longer than the normal value and at the upper limit of the fluctuation for such bonds;<sup>15</sup> such slight elongations might indicate a lower conjugation with the C=N bond than expected. The Ge(1)N(1)Ge'(1) bond angle lies in the normal range for such an angle in a cyclodigermazane (92.6° in compound of ref 14a), but the N(1)Ge(1)N'(1) angle (79.6 (2)°) is lower than in similar compounds (87.1° in cyclodigermazane,<sup>14</sup> 87.6° in 1,3-cyclodigermozane<sup>11</sup>).

The bond lengths and bond angles within the mesityl groups and phenyl of the fluorenylidenes lie in the normal range and deserve no special comment.

**Proposed Mechanism for the Formation of 4.** The first step of this reaction is probably the complexation of germanium by nitrogen; such a complexation has already been observed between 1 and ethers or amines.<sup>3a</sup> From intermediate 6 (Scheme II), two mechanisms might be postulated: an elimination reaction (route a), with intermediate formation of germylimine 5 and carbene 8, leading finally to cyclodigermazane **4a** and fluorene **11** after abstraction of hydrogen from the solvent; a cyclization reaction (route b), with the germylaziridine intermediate 7, followed by [2 + 1] decomposition leading to germylimine 5 and carbene 8 (reaction c). Route b is unlikely because such three-membered heterocycles generally decompose by formation of germylene and imine (reaction d).<sup>17,18</sup> In this case the germylene **10** could react

(9) Rivière, P.; Rivière-Baudet, M.; Satgé, J. *Germanium. Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1982; Vol. 2, Chapter 10.

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(12) Baines, K. M.; Brook, A. G.; Lickiss, P. D.; Sawyer, J. F. *Organometallics* **1989**, *8*, 709–716.

(13) Fritz, G.; Thomas, J.; Peters, K.; Peters, E. M.; Von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1984**, *514*, 61.

(14) (a) Pfeiffer, J.; Maringgele, W.; Noltemeyer, M.; Meller, A. *Chem. Ber.* **1989**, *122*, 245–252. (b) Lappert, M. F.; Sanger, A. R.; Power, P. P.; Srivastava, R. C. *Metal and Metalloid Amides*; Wiley: Chichester, UK, 1980.

(15) For a normal fluorenylidene group, the mean distances (Å) in the five-membered ring (with standard deviations of the mean value) obtained from analysis of 27 structures<sup>16</sup> are as follows: C(19)–C(20), 1.472 (16); C(20)–C(21), 1.405 (12); C(21)–C(22), 1.459 (1) (individual fluctuations respectively 1.440–1.496, 1.381–1.432, 1.436–1.487). In fluorenyl groups, the mean C(19)–C(20) distance from 45 structures<sup>16</sup> is 1.519 (12) Å (individual fluctuation 1.489–1.541 Å).

(16) The Cambridge Crystallographic Data Centre: Computer-Based Search, Retrieval, Analysis and Display of Information: Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr.* **1979**, *B35*, 2331–2339. Inaccurate structure determinations and questionable cases of bonding have not been taken into consideration.

(17) Rivière, P.; Rivière-Baudet, M.; Richelme, S.; Castel, A.; Satgé, J. *J. Organomet. Chem.* **1979**, *168*, 43–52.

with part of the starting diazofluorene to afford, according to a Glidewell-type reaction,<sup>19</sup> the germanimine **5** (reaction e). But the absence of diimine **9** seems to eliminate route d. So **4a** is probably formed by route a, with transient formation of germanimine **5**.

The formation of fluorenyl carbene **8** (Scheme III) from the fluorenyl group bound to germanium and not from the diazofluorene is proved unambiguously by the reaction between germene **1** and diphenyldiazomethane **12**: this reaction leads exclusively, via carbene **8** and probably germanimine **13**, to cyclodigermazane **14** and fluorene **11**. Diphenylmethane Ph<sub>2</sub>CH<sub>2</sub> and cyclodigermazane **4** have not been observed.

**14** has a good thermal stability: it is recovered unchanged after 2 months in solution at room temperature and a further 8 h at 80 °C in a sealed tube and is for this reason identified as the thermodynamic trans isomer **14b**. If the cis isomer **14a** is first formed in this reaction, it must isomerize very rapidly to **14b**, contrary to **4a**, which isomerizes slowly in ether solution (*t*<sub>1/2</sub> = 4 days) to the trans isomer **4b**. The stability of **4a** compared to **14a** is probably due to the bulkier and less flexible group fluorenylidene.

In spite of the substitution on germanium by two bulky mesityl groups and possibilities of mesomeric effects between the Ge=N double bond and the N=CR<sub>2</sub> moiety, **5** dimerizes rapidly. Let us note that germanimines with rather similar structures [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Ge=N-N=C-(COOMe)<sub>2</sub><sup>19</sup> recently prepared by Glidewell from electron-rich germylene and the corresponding diazo compounds are stable, probably due to the bulkier bis(trimethylsilyl)amino groups on germanium.

### Concluding Remarks

Reactions of germene **1** with diazo derivatives lead to the formation of new doubly bonded derivatives of germanium: there is formation of a >Ge=N— derivative from another doubly bonded compound of this metal. These reactions are new routes to germanimines >Ge=N—. Such reactions from more sterically hindered germenes and diazo derivatives should lead to stable germanimines. These reactions are now under active investigation.

### Experimental Section

All syntheses were performed under an atmosphere of dry nitrogen using standard Schlenk or high-vacuum line techniques. Solvents were dried by distillation from sodium benzophenone immediately prior to use. <sup>1</sup>H NMR spectra were recorded on a Varian EM 360 A at 60 MHz and on a Bruker AM 300 WB spectrometer at 300 MHz. Mass spectra were performed on a Varian MAT 311 A or on a Nermag R10-10H spectrometer. Experimental molecule peak patterns were assigned after comparison with theoretical peak patterns calculated on a Tektronics 4051. Melting points were determined on a Reichert apparatus.

The highly air and moisture sensitive solutions of **1** in Et<sub>2</sub>O were prepared as previously described<sup>3</sup> by addition of *tert*-butyllithium to the corresponding fluorogermane at -40 °C followed by warming to room temperature.

**Synthesis of 4a.** To an orange solution of germene **1** (3.20 mmol) in Et<sub>2</sub>O (30 mL), prepared from fluorogermane **2** (1.62 g, 3.27 mmol) and an equivalent of *tert*-butyllithium 1.7 N in pentane) cooled at 0 °C was added a solution of diazofluorene **3**<sup>20</sup> (0.62 g, 3.23 mmol) in Et<sub>2</sub>O (10 mL). The reaction mixture becomes brown and then red after 2 h of stirring at room temperature. Gas chromatography and NMR showed the formation of fluorene. Solvents were eliminated in vacuo, and the residue

**Table I.** Important Interatomic Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for **4a**

bond distances		bond angles	
N(1)-Ge(1)	1.894 (3)	Ge(1)-N(1)-Ge'(1)	94.5 (2)
N'(1)-Ge(1)	1.895 (3)	N(1)-Ge(1)-N'(1)	79.6 (2)
N(2)-N(1)	1.398 (4)	C(1)-Ge(1)-N(1)	110.7 (1)
C(19)-N(2)	1.277 (6)	C(10)-Ge(1)-N(1)	119.0 (2)
C(1)-Ge(1)	1.984 (5)	C(10)-Ge(1)-C(1)	109.6 (2)
C(10)-Ge(1)	1.967 (4)	N(2)-N(1)-Ge'(1)	129.1 (2)
C(19)-C(23)	1.490 (6)	N(2)-N(1)-Ge(1)	119.4 (2)
C(23)-C(22)	1.397 (7)	C(19)-N(2)-N(1)	118.0 (4)
C(22)-C(21)	1.456 (8)	C(23)-C(19)-C(20)	105.7 (4)
C(21)-C(20)	1.425 (6)	C(20)-C(19)-N(2)	134.7 (4)
C(20)-C(19)	1.487 (7)	C(23)-C(19)-N(2)	119.3 (4)
Ge(1)-Ge'(1)	2.783 (1)		
torsion angles		plane angles	
N(1)Ge(1)N(1)Ge'(1)	-25	Ge(1)N(1)N'(1)-Ge'(1)N(1)N'(1)	34
		Ge(1)Ge'(1)N(1)-Ge(1)Ge'(1)N'	38

was crystallized from Et<sub>2</sub>O at -20 °C to afford red crystals (0.54 g, 31%) of **4a**·0.6 Et<sub>2</sub>O: mp 266–267 °C; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 2.05 (s, 12 H, *p*-Me), 2.48 (s, 24 H, *o*-Me) (NMR was performed at 25 °C; at this temperature, the flipping of the ring in solution relative to the NMR time scale makes the mesityl groups magnetically equivalent), 6.61 (s, 8 H, Ar Mes), four doublets of doublets which actually appear as triplets due to accidental overlap at 6.64 (<sup>3</sup>J(HH) = 7.5 Hz), 6.97 (<sup>3</sup>J(HH) = 7.5 Hz), 7.16 (<sup>3</sup>J(HH) = 6.7 Hz) and 7.18 (<sup>3</sup>J(HH) = 6.7 Hz, 8 H, H bound to C(25), C(26), C(29), C(30), C'(25), C'(26), C'(29), C'(30)), four doublets at 7.38 (<sup>3</sup>J(HH) = 7.5 Hz), 7.46 (<sup>3</sup>J(HH) = 6.7 Hz), 8.03 (<sup>3</sup>J(HH) = 6.7 Hz), and 8.72 (<sup>3</sup>J(HH) = 7.5 Hz, 8 H, H bound to C(24), C(27), C(28), C(31), C'(24), C'(27), C'(28), C'(31)); mass spectrum (EI, 70 eV, <sup>74</sup>Ge), *m/e* (rel intensity) 1006 (M, 15), 814 (M - R<sub>2</sub>CN<sub>2</sub>, 10), 694 (M - Mes<sub>2</sub>Ge, 5), 635 (M - 2R<sub>2</sub>CN - Me, 40), 504 (M/2, 15), 474 (M/2 - 2Me, 40) 430 (M/2 - 5 Me + H, 100).

For compounds **4a** and **4b**, according to the different fractions of crystallization, and even in the same fraction, we see in <sup>1</sup>H NMR at 300 MHz various quantities of Et<sub>2</sub>O, from 0 to 2 Et<sub>2</sub>O per mole; so the analyses we have performed vary between the expected values (73.99 for C, 6.01 for H, and 5.57 for N in **4a** and 72.81 for C, 6.98 for H, and 4.85 for N in **4a**·2Et<sub>2</sub>O. For example, found for **4a**·0.6Et<sub>2</sub>O: C, 73.57; H, 6.38; N, 5.44. The X-ray study proved unambiguously the structure of **4a** with the R<sub>2</sub>CN<sub>2</sub> groups in a cis position.

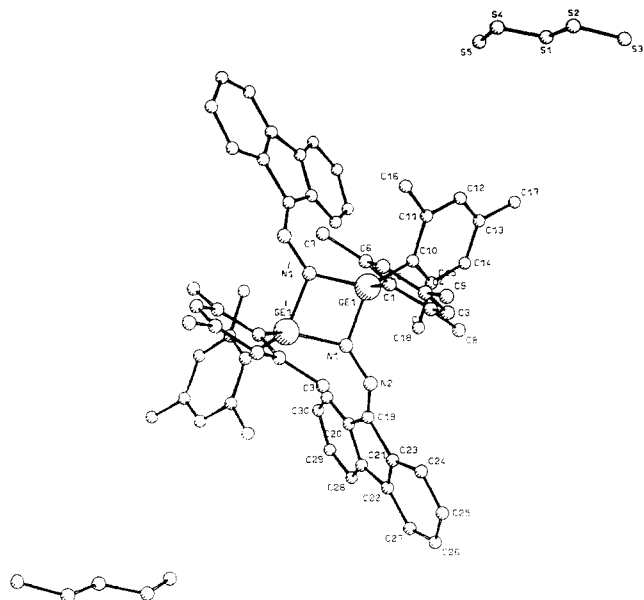
**Synthesis of 4b.** After a week in solution at room temperature, **4a** was quantitatively isomerized to **4b** (R<sub>2</sub>CN<sub>2</sub> groups in the trans position). **4b** was crystallized in Et<sub>2</sub>O at -20 °C to afford red crystals of **4b**·0.9Et<sub>2</sub>O: mp 304–305 °C; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 2.07 (s, 24 H, *o*-Me), 2.14 (s, 12 H, *p*-Me), 6.48 (s, 8 H, Ar Mes), four doublets of doublets (<sup>3</sup>J(HH) = 7.6 Hz) at 6.33, 6.95, 7.14, and 7.23 (8 H, H bound to C(25), C(26), C(29), C(30), C'(25), C'(26), C'(29), C'(30)), four doublets (<sup>3</sup>J(HH) = 7.6 Hz) at 7.41, 7.48 (2d), 8.14 (8 H, H bound to C(24), C(27), C(28), C(31), C'(24), C'(27), C'(28), C'(31)); mass spectrum (EI, 70 eV, <sup>74</sup>Ge), *m/e* (rel intensity) 1006 (M, 10), 814 (M - R<sub>2</sub>CN<sub>2</sub>, 8), 635 (M - 2R<sub>2</sub>CN - Me, 25), 504 (M/2, 15), 474 (M/2 - 2Me, 30), 430 (M/2 - 5Me + H, 80). For example, found for **4b**·0.9Et<sub>2</sub>O: C, 73.51; H, 6.55; N, 5.29. Single crystals of **4a**, obtained by slow crystallization in Et<sub>2</sub>O, are not air- and moisture-sensitive and can be handled in air.

**Synthesis of 14b.** To a solution of germene **1** (prepared from 0.50 g (1.0 mmol) of **2** and the equivalent amount of *tert*-butyllithium in pentane) in 15 mL of Et<sub>2</sub>O was added a solution of diphenyldiazomethane Ph<sub>2</sub>CN<sub>2</sub><sup>24</sup> (0.19 g, 1.0 mmol) in Et<sub>2</sub>O at room temperature. The reaction mixture became red immediately. After this stirred at room temperature overnight, gas chromatography and NMR showed the formation of fluorene and the absence of diphenylmethane. After elimination of the solvents in vacuo, crude **14b** was recrystallized in pentane to afford yellow crystals (0.15 g, 30%, mp 284–285 °C); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 2.16 (s, 12 H, *p*-Me), 2.42 (s, 24 H, *o*-Me), 6.65 (s, 8 H, Ar Mes), 6.64–7.54 (m, 20 H, Ph); mass spectrum (EI, 70 eV, <sup>74</sup>Ge), *m/e* (rel intensity) 1010 (M, 10), 637 (M - Ph<sub>2</sub>CN<sub>2</sub> - Mes - 4Me, 15),

(18) Attempts to synthesize the three-membered ring **7** by other routes have been unsuccessful.

(19) Glidewell, C.; Lloyd, D.; Lombard, K. W.; McKechnie, J. S. *Tetrahedron Lett.* 1987, 28, 343–344.

(20) Schonberg, A.; Awad, W. I.; Latif, N. *J. Chem. Soc.* 1951, 1368.



**Figure 1.** PLUTO view of **4a** showing the crystallographic numbering for half of the molecule. Primed atoms are related to those without a prime by a crystallographic 2-fold axis.

**Table II. Crystallographic Data for **4a** and Structure Determination Details**

formula	$C_{62}H_{60}Ge_2N_4 \cdot 2C_4H_{10}O$
$M_r$	1154.6
cryst syst	orthorhombic
space group	$Aba2$
cryst dimens, mm	prism with hexagonal basis, $0.5 \times 0.5 \times 0.5$
cryst color	red
unit-cell dimens ( $\text{\AA}$ ) determined from 25 rflctns with $11^\circ \leq 2\theta \leq 50^\circ$	$a = 21.926$ (3), $b = 23.134$ (3), $c = 12.439$ (2)
$V, \text{\AA}^3$	6310 (1)
$Z$	4
$D(\text{calcd}), \text{g cm}^{-3}$	1.21
$F(000)$	2432
$T, \text{K}$	295
$\mu(\text{Cu } K\alpha), \text{mm}^{-1}$	1.6
radiatn	Cu $K\alpha$
$\lambda, \text{\AA}$	1.54178
diffractometer	Huber 424 + 511
coll mode	$\omega/2\theta$ scans
indep rflctns	2994
obsvd rflctns [ $I \geq 2.5\sigma(I)$ ]	2896
$2\theta_{\text{max}}, \text{deg}$	135
$R$	0.039
$R_w$	0.047
$w$	$1/(\sigma^2(F) + 0.00516F^2)$
electron density in the final difference synthesis, $e \text{\AA}^{-3}$	+0.31/-0.41
$\Delta/\sigma_{\text{max}}$	0.55
$S$	0.93

622 (M -  $\text{Ph}_2\text{CN}_2$  - Mes - 5Me, 20), 506 (M/2, 25), 431 (M/2 - 5Me, 100), 312 (Mes<sub>2</sub>Ge, 50). Anal. Calcd for  $C_{62}H_{64}N_4Ge_2$ : C, 73.70; H, 6.38; N, 5.54. Found: C, 73.99; H, 6.17; N, 5.51.

**X-ray Crystal Structure.** Standard reflection 3,7,2 was measured every 50 reflections; no significant variation. The molecule was determined by direct methods using SHELXS-86<sup>21</sup>

**Table III. Fractional Atomic Coordinates ( $\times 10^4$ ) for Half of the Molecule of **4a** and Equivalent Temperature Factors ( $\text{\AA}^2$ )**

	$x$	$y$	$z$	$B_{\text{eq}}$
Ge(1)	563 (1)	277 (1)	0	2.52
N(1)	256 (1)	-465 (1)	-343 (3)	2.64
N(2)	593 (1)	-955 (1)	-61 (5)	2.88
C(1)	860 (2)	301 (1)	1506 (4)	2.98
C(2)	1407 (2)	-13 (2)	1708 (4)	3.70
C(3)	1620 (2)	-59 (3)	2764 (5)	4.85
C(4)	1320 (3)	197 (3)	3606 (6)	6.05
C(5)	799 (3)	504 (2)	3403 (4)	5.02
C(6)	567 (2)	572 (2)	2361 (4)	3.81
C(7)	-4 (2)	922 (2)	2261 (4)	4.05
C(8)	1779 (2)	-280 (2)	819 (6)	4.87
C(9)	1582 (7)	144 (7)	4731 (9)	11.26
C(10)	1172 (2)	633 (2)	-955 (4)	3.11
C(11)	1363 (2)	1194 (2)	-716 (4)	3.45
C(12)	1837 (2)	1443 (2)	-1330 (5)	4.02
C(13)	2105 (2)	1154 (2)	-2155 (4)	3.79
C(14)	1912 (2)	599 (2)	-2396 (4)	3.93
C(15)	1448 (2)	336 (2)	-1829 (5)	3.63
C(16)	1067 (2)	1552 (2)	155 (5)	4.19
C(17)	2645 (2)	1416 (3)	-2794 (6)	5.59
C(18)	1271 (3)	-268 (2)	-2146 (5)	5.26
C(19)	555 (1)	-1399 (2)	-666 (4)	2.91
C(20)	274 (2)	-1520 (2)	-1731 (4)	3.48
C(21)	442 (2)	-2093 (2)	-2030 (5)	4.38
C(22)	820 (2)	-2343 (2)	-1188 (5)	4.42
C(23)	899 (2)	-1933 (2)	-375 (4)	3.73
C(24)	1261 (3)	-2049 (2)	497 (6)	5.11
C(25)	1538 (3)	-2583 (3)	590 (8)	7.11
C(26)	1463 (3)	-2997 (2)	-246 (9)	7.21
C(27)	1107 (3)	-2885 (2)	-1114 (7)	5.72
C(28)	276 (3)	-2302 (3)	-3041 (6)	5.51
C(29)	-53 (3)	-1944 (4)	-3737 (6)	7.00
C(30)	-226 (3)	-1405 (3)	-3438 (6)	6.10
C(31)	-60 (2)	-1183 (2)	-2424 (4)	4.12
S1(O)	2895 (4)	3208 (4)	2917 (8)	13.05
S2(C)	3125 (7)	3256 (7)	3962 (11)	17.13
S3(C)	3781 (7)	3114 (7)	3827 (16)	15.83
S4(C)	2280 (4)	3331 (5)	2949 (10)	12.72
S5(C)	2040 (5)	3275 (5)	1815 (10)	12.35

<sup>a</sup>Coordinates of the second half of the molecule are generated by the symmetry operation  $-x, -y, +z$ .  $B_{\text{eq}} = 8/3 \times (\Pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^*)$ .

(only half of the atoms). The first isotropic refinement showed one molecule of solvent ( $\text{Et}_2\text{O}$ ) in the asymmetric unit. Least-squares refinement was performed by SHELX-76<sup>22</sup> with anisotropic temperature factors, isotropic solvent, and H atoms in calculated positions. The molecular structure was drawn with PLUTO<sup>23</sup> (Figure 1). Important distances and bond angles for **4a** are given in Table I; crystallographic data for **4a** are given in Table II; fractional atomic coordinates for **4a** are given in Table III.

**Supplementary Material Available:** Listings of bond lengths, bond angles, and torsion angles of compound **4a** (2 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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