$MgCl_2$, both a high reaction rate and high selectivity (30:1) are observed. Presumably, **1** and Me_2Mg combine to form the "ate" complex **4**, which is further activated by catalytic amounts of a Lewis acid ($MgCl_2$). However, as more $MgCl_2$ is added, the Schlenk equilibrium shifts to that of "normal" Grignard solution and produces the "normal" selectivity.

Acknowledgment. This investigation was supported by grants from the NIH (GM-26908) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We acknowledge funding from the NSF (CHE-85-16614) for the purchase of a 300 MHz NMR.

Supplementary Material Available: Experimental details for Tables I and II (1 page). Ordering information is available on any current masthead page.

(Z)-1,2-Bis(2,6-diisopropylphenyl)-1,2-dimesityldigermene: Synthesis, Crystal Structure, and π-Bond Energy

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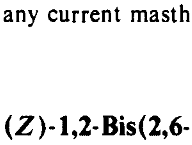
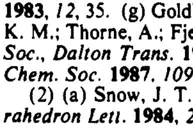
Received August 8, 1990

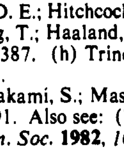
Renewed interest in the digermene (Ge=Ge) system concerns its ground-state geometry and so-called π-bond energy normally equated to the rotational barrier.[1] Since the disclosure of the molecular structure of tetrakis(2,6-diethylphenyl)digermene (**1**),[2] *which retains its structural integrity in solution*, our major efforts have been directed to the investigation of its chemical reactivity[3] and also to the synthesis of a *Z* or *E* stereoisomer of type RR'Ge=GeRR' (R ≠ R') which can provide a means of estimating the activation energy required for isomerization. This latter task turns out to be much more involved[4] than expected from the earlier work on similar disilenes,[5] as the judicious selection of R and R' is now found to be highly crucial. We report herein that (1) our final selection is R = 2,6-diisopropylphenyl and R' = mesityl, (2) the synthesized and isolated crystalline digermene **2** is the *Z* isomer (*Z*)-**2** rather than the *E* isomer, (3) (*Z*)-**2** is more stable than (*E*)-**2**, and (4) the conformation of (*Z*)-**2** shows a considerable deviation from that of **1**. Findings 3 and 4 are totally unexpected. Furthermore, digermene (*Z*)-**2** provides, for the first time, a set of kinetic parameters for the $Z \rightleftharpoons E$ isomerization of a digermene derivative.



1: M = Ge, R = R' = 2,6-diethylphenyl
2: M = Ge, R = 2,6-diisopropylphenyl, R' = Mes (2,4,6-trimethylphenyl)
3: M = Ge, R = R' = $CH(SiMe_3)_2$
4: M = Ge, R = R' = H
7: M = Si, R = 2,6-diisopropylphenyl, R' = Mes
8: M = Si, R = 2,6-diethylphenyl, R' = Mes



3a



6 : R = 2,6-diisopropylphenyl, R' = Mes

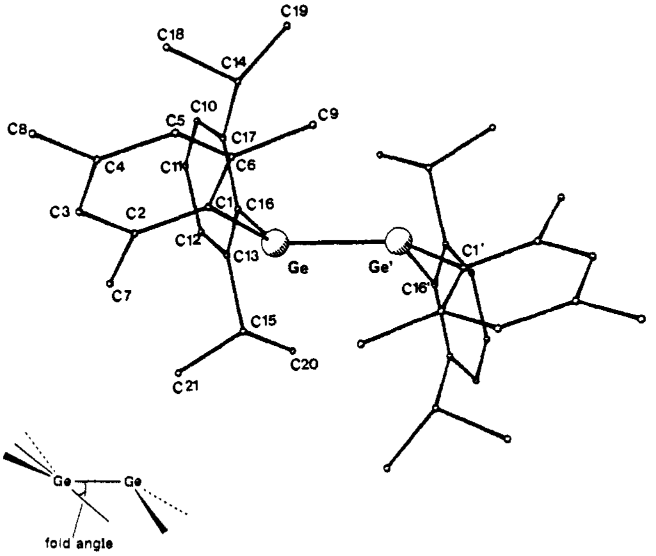


Figure 1. Crystal structure of (*Z*)-**2**. Selected bond lengths (Å) and angles (deg): Ge–Ge, 2.301 (1); Ge–C1, 1.972 (5); Ge–C16, 1.988 (5); Ge–Ge–C1, 124.0 (2); Ge–Ge–C16, 111.6 (2); C1–Ge–C16, 109.9 (2).

Table I. Selected Structural Parameters of Digermenes

compd	d(Ge=Ge), Å	fold angle, deg	twist angle, deg	sum of angles around Ge, deg
(*Z*)-2	2.301 (1)	36	7	345.5
1	2.213 (2)	12[a]	10[a]	358.4
3	2.347 (2)	32	0	348.5
4	2.27–2.33	34–40	0	

[a] These values are slightly different from the χ_{Ge} and τ used in ref 2.[6]

Synthesis of 2. Exposure of dichloro(2,6-diisopropylphenyl)mesitylgermane to 2 equiv of lithium naphthalenide[3c] led to the formation of two air- and moisture-sensitive digermenes A and B as the major products, as indicated by two sets of ^1H NMR signals assignable to them.[6] A series of fractional recrystallizations of the reaction mixture from THF afforded A as yellow crystals: mass spectrum (EI), m/z 700–711 (M^+ cluster); UV (methylcyclohexane, room temperature) λ_{max} (log ε) 280 (4.1), 412 nm (4.6). The structure of A was determined as (*Z*)-**2** by X-ray analysis (see below). When (*Z*)-**2** was dissolved in a hydrocarbon or ether solvent, it regenerated B to attain a 2:1 equilibrium mixture favoring (*Z*)-**2**![7] Upon concentration of this mixture, nearly all of (*Z*)-**2** and B crystallized out as pure (*Z*)-**2**. These results show that B is the *E* isomer of (*Z*)-**2**. It should be added that (1) all spectra of (*Z*)-**2** and (*E*)-**2** are consistent with the double-bond formulation[2] and (2) the existence of the corresponding germylene species in solution is excluded to the limit of spectral detection.

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(6) See supplementary material paragraph at the end of this paper.

(7) The more stable isomers of all known disilenes of type RR'Si=SiRR' have an *E* configuration (ref 5).

0002-7863/90/1512-9394$02.50/0

Table II. Kinetic Parameters for Digermene **2** Isomerization

temp, K	K_{eq}	(*Z*)-**2** → (*E*)-**2**	(*E*)-**2** → (*Z*)-**2**
290.2	0.368	$k_1 = (1.03 \pm 0.02) \times 10^{-5}\ s^{-1}$	$k_{-1} = (2.80 \pm 0.04) \times 10^{-5}\ s^{-1}$
313.3	0.490	$k_1 = (1.90 \pm 0.04) \times 10^{-4}\ s^{-1}$	$k_{-1} = (3.89 \pm 0.07) \times 10^{-4}\ s^{-1}$
		$\Delta H^‡ = 22.2 \pm 0.3$ kcal mol^{-1}	$\Delta H^‡ = 20.0 \pm 0.3$ kcal mol^{-1}
		$\Delta S^‡ = -5 \pm 1$ eu	$\Delta S^‡ = -10 \pm 1$ eu

Table III. Kinetic Parameters for Isomerizations of Disilenes **7**[a] and **8**

temp, K	K_{eq}	(*Z*)-**7** → (*E*)→**7**	(*E*)-**7** → (*Z*)-**7**
342.1	1.26	$k_1 = (1.53 \pm 0.03) \times 10^{-5}\ s^{-1}$	$k_{-1} = (1.21 \pm 0.02) \times 10^{-5}\ s^{-1}$
364.0	1.19	$k_1 = (1.67 \pm 0.04) \times 10^{-4}\ s^{-1}$	$k_{-1} = (1.41 \pm 0.02) \times 10^{-4}\ s^{-1}$
		$\Delta H^‡ = 26.3 \pm 0.5$ kcal mol^{-1}	$\Delta H^‡ = 27.0 \pm 0.5$ kcal mol^{-1}
		$\Delta S^‡ = -4.0 \pm 2.0$ eu	$\Delta S^‡ = -2.4 \pm 2.0$ eu
temp, K	**K_{eq}**	**(*Z*)-8 → (*E*)-8**	**(*E*)-8 → (*Z*)-8**
337.1	1.29	$k_1 = (1.35 \pm 0.05) \times 10^{-5}\ s^{-1}$	$k_{-1} = (1.05 \pm 0.03) \times 10^{-5}\ s^{-1}$
359.7	1.17	$k_1 = (1.59 \pm 0.03) \times 10^{-4}\ s^{-1}$	$k_{-1} = (1.37 \pm 0.02) \times 10^{-4}\ s^{-1}$
		$\Delta H^‡ = 25.6 \pm 0.8$ kcal mol^{-1}	$\Delta H^‡ = 26.7 \pm 0.8$ kcal mol^{-1}
		$\Delta S^‡ = -5.0 \pm 2.5$ eu	$\Delta S^‡ = -2.4 \pm 2.5$ eu

[a] The *Z* assignment to the isolated **7** remains tentative.

Crystallographic Analysis of (*Z*)-2.[6] The structure of (*Z*)-**2** has a crystallographic 2-fold axis bisecting the Ge=Ge bond, and pertinent data are summarized in Figure 1 and Table I. The sum of the C–Ge–C and the two C–Ge–Ge′ angles is 345.5°, and there is a sizable pyramidal distortion at the germaniums, reflected in the large fold angle (36°) at these atoms. The Ge=Ge bond length is 2.301 (1) Å. These values are in contrast with those observed for **1**, where the Ge=Ge bond length is noticeably shorter and the fold angle is as small as 12°. The effectively large ligands in (*Z*)-**2** force the Ge=Ge bond to elongate to the range of distance where mixing of the homo π (b_u) orbital and the σ^* orbital becomes important with increasing fold angle and as a result (*Z*)-**2** favors a trans-bent conformation.[1] It is interesting to note that the geometries of (*Z*)-**2** and Lappert's digermene **3**[1g,8,9] are strikingly similar and happen to be in good agreement with the theoretical values (a fold angle of 30–40° and a bond length of 2.27–2.33 Å).[1] Further discussion on the electronic and steric effects of the ligands in **1**–**3** is deferred until more experimental data are accumulated.

$Z \rightleftarrows E$ Isomerization of 2 and Analogous Disilene Derivatives 7 and 8. As noted above, (*Z*)-**2** in solution is equilibrated with (*E*)-**2**: the [*E*]/[*Z*] values (K_{eq}) in C_6D_6 are 0.490 at 40.1 °C and 0.368 at 17.0 °C. The rates for the $Z \rightleftarrows E$ interconversion were measured in a standard fashion using ^{1}H NMR (500 MHz) spectroscopy, and the kinetic parameters pertinent to these first-order processes are summarized in Table II.[6,10] The rates were unaffected in the presence of 2,3-dimethyl-1,3-butadiene (**5**), an efficient germylene trapping agent. A mixture of **2** and excess **5** did not form, even after a prolonged time at 40 °C, the trapped product **6**, which was obtained upon irradiation of the mixture. Within the limits of its validity, this experiment precludes the possibility that the isomerization proceeds through a thermal dissociation–recombination pathway involving a reactive germylene species and supports the straightforward mechanism of rotation around the Ge,Ge bond axis.

For comparison, kinetic parameters were secured for the isomerization of two newly synthesized disilene derivatives with ligands shown in **7** and **8**, as summarized in Table III.[6,11] It is noted that the enthalpy of activation of the Ge=Ge bond isomerization is somewhat (4–7 kcal/mol) lower than that of the silicon isomerization. Most recent calculations arrive at an estimate of about 25 kcal/mol for the bond categories of both parent disilene and digermene.[1a] Considering the sizable ligands in the derivatives used in the experiments, one concludes that theory and experiment are in good agreement.[12]

Supplementary Material Available: The definitions of fold and twist angles, selected experiments, and listings of physical properties of new dimetallenes and additional information on the X-ray crystal analysis of (*Z*)-**2** (31 pages). Ordering information is given on any current masthead page.

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(9) Compound **3** exists as a digermene only in crystalline form and dissociates into the corresponding germylene (**3a**) in solution, an observation that distinguishes **3** from **2** and also **1** (see text). In view of the structural similarity of **3** and **2**, the small bond dissociation energy associated with **3** appears to be due largely to the unique stabilization of **3a** with the $CH(SiMe_3)_2$ group (β effect) and is not closely related to the conformation of **3**.

(10) No 1,2-diaryl rearrangement was detected during the course of these *Z* . · *E* isomerization experiments. Cf.: Yokelson, H. B.; Siegel, D. A.; Millevotte, A. J.; Maxka, J.; West, R. *Organometallics* **1990**, *9*, 1005.

(11) The parameters summarized for **8** in Table III are more accurate than those reported earlier (ref 2c).

(12) We thank Dr. R. S. Grev for providing us with a preprint of ref 1a and the National Science Foundation (Grant CHE-870670) and Kao Corporation, Japan, for financial support.

Structural Characterization of the Three Complexes $[HRe(CO)_4]_n$ (n = 2, 3, 4), Including a Rare Example of a Square Arrangement of Metal Atoms

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Received April 4, 1990

The two complexes $[Re_2(\mu\text{-}H)_2(CO)_8]$[1] and $[Re_3(\mu\text{-}H)_3(CO)_{12}]$[2] have been described as organometallic analogues of the $(CH_2)_n$ (n = 2, 3) organic molecules ethylene and cyclopropane.[1] We have now synthesized the organometallic analogue of cyclobutane and we present here the X-ray single-crystal structures of the three members of the family $[HRe(CO)_4]_n$ (n = 2, 3, and 4, compounds **1**, **2**, and **3**, respectively).[3]

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