Organometallics 1992, *11*, 3489–3492

Rearrangement Barriers in Doubly Bonded Germanium Compounds

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Received August 25, 1992

Summary: Isomerization barriers of the doubly bonded germanium compounds $H_2Ge{=}CH_2$, $H_2Ge{=}SiH_2$, and $H_2Ge{=}GeH_2$ to the corresponding germylene isomers $HGeCH_3$, $HGeSiH_3$, and $HGeGeH_3$ have been determined by ab initio quantum-mechanical methods.

Baines and co-workers recently demonstrated that digermene[1] ($R_2Ge{=}GeR_2$) and germasilene[2] ($R_2Ge{=}SiR_2$) chemistry is complicated by these doubly bonded isomers rearranging to the corresponding germylene isomers germylgermylene ($RGeGeR_3$) and silylgermylene ($RGeSiR_3$), respectively. Baines and Cooke's germasilene chemistry[2,3] is unique, but digermenes were earlier examined in some detail,[4,5] and rearrangement to the corresponding germylgermylene isomer was never mentioned. In Ando and co-workers' tetramesityldigermene reaction studies[5b–e] (mesityl = 2,4,6-trimethylphenyl, the same substituent used by Baines and co-workers[1]), digermene generation was effected in the presence of molecules reactive toward the Ge–Ge double bond. Only Baines has investigated digermene chemistry using a reagent that reacts exclusively with the germylene.[1] Notably, Masamune's original digermene studies[4a] (using R = 2,6-dimethylphenyl) did not produce an isolable digermene in pure form, the cited reason being photoinduced digermene polymerization. In contrast, hexakis(2,6-diethylphenyl)cyclotrigermane photolysis cleanly yields the desired digermene.[4b] Perhaps the 2,6-dimethylphenyl systems were complicated by isomerization to the germylgermylenes, and bulkier aryl substituents have larger isomerization barriers. In this context, the parent germasilene and digermene isomerization barriers are of interest. Previous theoretical studies of digermene[6] and germasilene[7] did not report the isomerization barrier. In Si_2H_4, the disilene isomer lies 7 kcal mol^{-1} below silylsilylene,[8] and the classical isomerization barrier $H_2SiSiH_2 \rightarrow HSiSiH_3$ is predicted to be 17 kcal mol^{-1}.[9] Because H_2GeGeH_2 and $HGeGeH_3$ are nearly isoenergetic,[6e,f] and H_2GeSiH_2 appears to lie about 6 kcal mol^{-1} *above* $HGeSiH_3$,[7] their barriers may be even smaller than those of the disilenes.

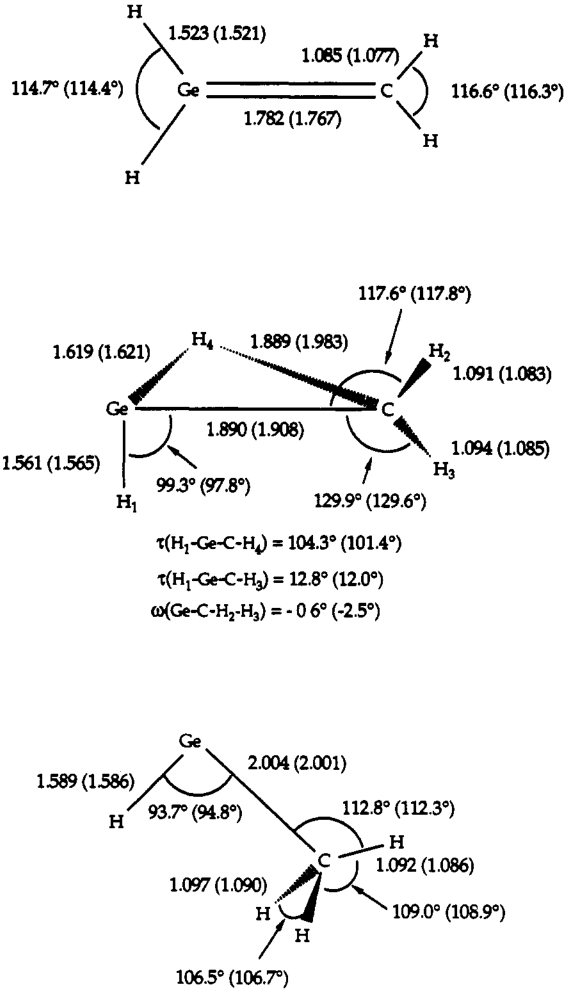

Figure 1. CISD and SCF (in parentheses) optimized geometries of germene (top), methylgermylene (bottom), and the isomerization transition state (middle) using a double-ζ plus polarization basis set. τ is a torsion angle, and ω is an out-of-plane angle. Bond distances are in Å.

Here we report the structures, and energies, of the species involved in the rearrangements

$$H_2GeCH_2 \rightarrow HGeCH_3 \tag{1}$$

$$H_2GeSiH_2 \rightarrow HGeSiH_3 \tag{2}$$

$$H_2GeGeH_2 \rightarrow HGeGeH_3 \tag{3}$$

The doubly bonded and corresponding germylene isomer geometries, as well as the connecting transition states, were

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Table I. Relative Energies (in kcal/mol) of the Doubly Bonded Isomers, the Corresponding Germylene Isomers, and the Transition State

	germene → methylgermylene			germasilene → silylgermylene			digermene → germylgermylene		
	H_2GeCH_2	transition state	$HGeCH_3$	H_2GeSiH_2	transition state	$HGeSiH_3$	H_2GeGeH_2	transition state	$HGeGeH_3$
SCF/DZP[a]	0.0	38.4	−20.1	0.0	15.5	−13.0	0.0	12.3	−7.6
CISD/DZP[b]	0.0	37.5	−15.9	0.0	15.0	−7.7	0.0	12.9	−2.3
CISD+Q/DZP[b]	0.0	35.6	−14.4	0.0	15.4	−5.6	0.0	13.6	−0.2
CCSD/DZP[b]	0.0	35.7	−14.9	0.0	15.5	−5.9	0.0	13.6	−0.5
CCSD(T)/DZP[b]	0.0	34.3	−13.0	0.0	15.7	−3.7	0.0	14.0	1.7
CCSD/ANO[b]	0.0	35.8	−14.7	0.0	14.4	−5.6	0.0	13.1	−0.1
CCSD(T)/ANO[b]	0.0	34.5	−12.6	0.0	14.4	−3.2	0.0	13.4	2.3
$\Delta\Delta H$(0 K)[c]	0.0	33.1	−11.4	0.0	13.0	−3.2	0.0	12.0	2.0

[a] At the SCF/DZP optimized geometry. [b] At the CISD/DZP optimized geometry. [c] CCSD(T)/ANO relative energies plus zero-point energies from scaled SCF harmonic vibrational frequencies.

completely optimized using self-consistent-field (SCF) methods. The resulting stationary points were characterized by SCF harmonic vibrational frequency analysis as minima or transition states. Subsequently, the geometries were refined using configuration interaction methods[10] including all valence-electron single and double excitations (CISD); i.e., the carbon 1s-like, silicon 1s2s2p-like, and germanium 1s2s2p3s3p3d-like orbitals were frozen in the CI procedure. Double-ζ plus polarization (DZP) quality basis sets[11] were used in the SCF and CISD geometry optimizations. Relative energy predictions were refined by adding the Davidson correction[12] for unlinked quadruple excitations (CISD+Q), and by coupled cluster methods[13] including all single and double excitations (CCSD),[14] as well as the CCSD(T) method,[15] which includes connected triple excitation effects via perturbation theory. Our best energy predictions use polarized triple-ζ quality atomic natural orbital (ANO) basis sets[16,17] and the CCSD(T) method.

The SCF and CISD optimized structures are shown in Figures 1–3. Focusing on the isomerization transition state structures (shown in the middle of Figures 1–3), we find a near constancy in the geometry about the incipient germylene center. In each case, the distance from germanium to the migrating hydrogen, H_4, is 1.62 Å. Remarkable, too, are the nearly identical values of the Ge–M and M–H_4 distances in each transition state, especially at the CISD level of theory. The H_1–Ge–M angles are invariably close to the corresponding values in the germylene product. The geometry about the M center is always nearly planar, as given by the out-of-plane angle ω; in contrast, the corresponding doubly bonded compounds (see the top structure in each figure) are decidedly nonplanar in the case of M = Si, Ge. In all, refining the SCF geom-

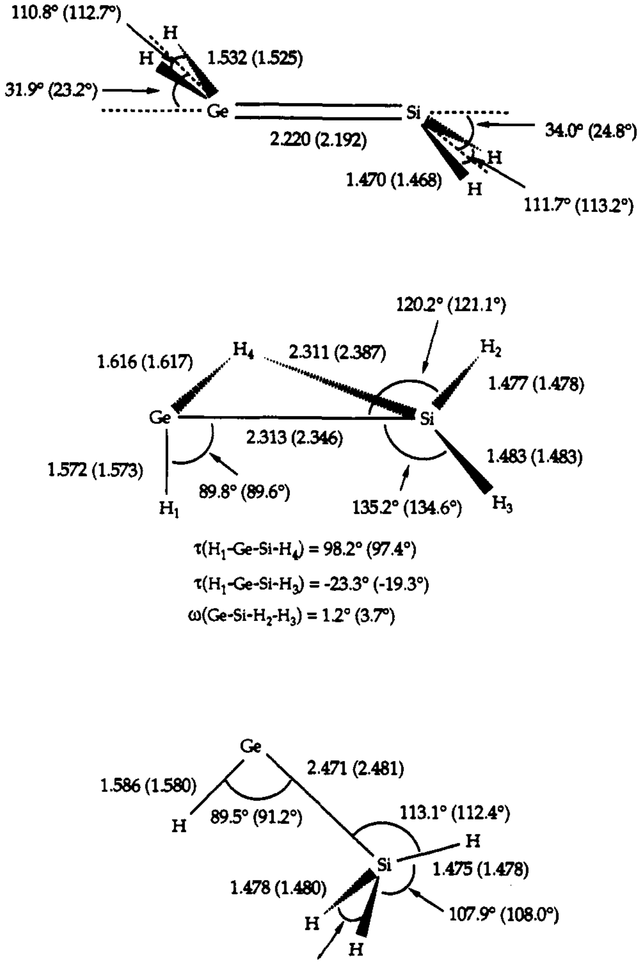

Figure 2. CISD and SCF (in parentheses) optimized geometries of germasilene (top), silylgermylene (bottom), and the isomerization transition state (middle) using a double-ζ plus polarization basis set. τ is a torsion angle, and ω is an out-of-plane angle. Bond distances are in Å.

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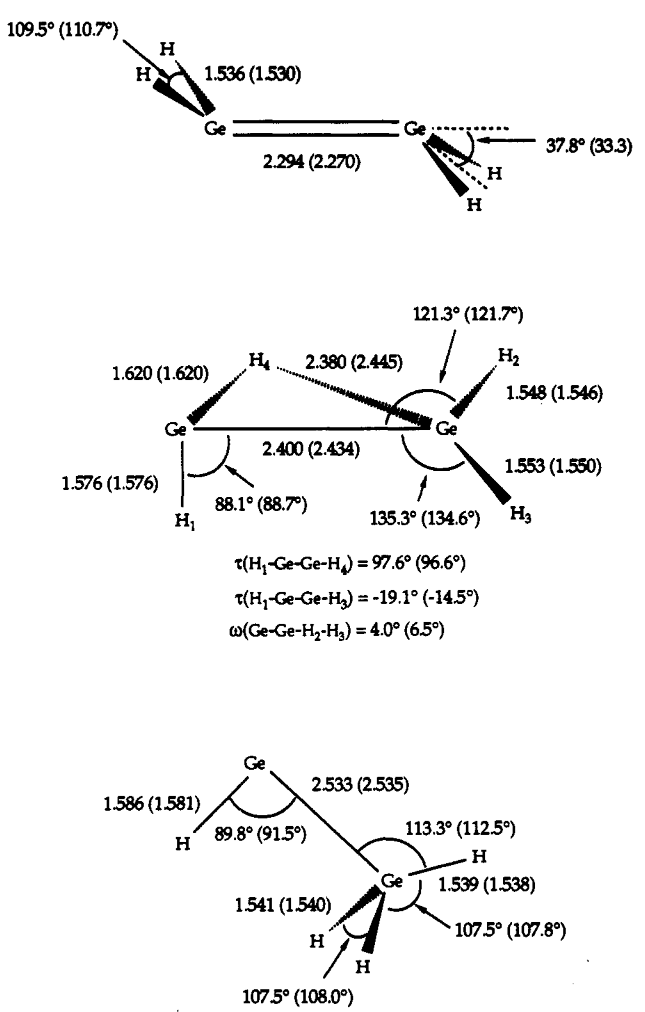

Figure 3. CISD and SCF (in parentheses) optimized geometries of digermene (top), germylgermylene (bottom), and the isomerization transition state (middle) using a double-ζ plus polarization basis set. τ is a torsion angle, and ω is an out-of-plane angle. Bond distances are in Å.

etries at the CISD level of theory leads to few changes other than shortened M—H_4 and Ge—M distances in the transition states, increased Ge═M distances, and increased pyramidalization about the Ge and M centers (for M = Ge, Si) in the doubly bonded structures.

Transition-state energies, relative to the doubly bonded isomers, depend little on basis set construction and correlation effects, as can be seen in Table I. Germylene isomer energies, relative to the transition state and doubly bonded structure, are also basis set insensitive (as seen by comparing the DZP and ANO basis set coupled cluster energies) but are affected by electron correlation, as noted previously in the disilene–silylsilylene isomerization.[9] Because CCSD(T) is a high-quality method, the observed basis set insensitivity suggests that our CCSD(T)/ANO relative energies should be accurate. Adding the zero-point vibrational energy (estimated as 0.91 times the DZP SCF harmonic vibrational frequencies[18]) to the CCSD(T)/ANO electronic energy gives $\Delta\Delta H(0\text{ K})$, the final row in Table I.

For the germene to methylgermylene rearrangement, predicted to be exothermic by 11.4 kcal mol^{-1}, the isomerization enthalpy barrier is 33.1 kcal mol^{-1}. Thus, thermal isomerization of germenes is expected to be a facile process only at high temperatures. Previous theoretical studies predicted slightly larger barriers[19] and exothermicities,[19,20] due primarily to less exhaustive incorporation of electron correlation effects. For $GeSiH_4$, the germasilene to silylgermylene isomerization is exothermic by 3.2 kcal mol^{-1}, with a barrier of only 13.0 kcal mol^{-1}. In Ge_2H_4, the digermene to germylgermylene isomerization is 2.0 kcal mol^{-1} *endothermic* (Trinquier[6e] obtains a similar value at lower levels of theory), and the barrier is 12.0 kcal mol^{-1}. Therefore, both the parent germasilene and digermene rearrangements are rapid processes at room temperature, in agreement with Baines and co-workers' observations in tetramesityl-substituted systems.[1,2] Considering the 21 kcal mol^{-1} differences in transition-state enthalpies of reactions 1–3, and the 13 kcal mol^{-1} exothermicity differences, the structural similarities of the transition states seem unusual.[21] Stranger still, the reaction barriers and exothermicities are inversely related; the highest barrier occurs in the most exothermic reaction (reaction 1), and the lowest barrier occurs in the least exothermic reaction (reaction 3). The high barrier in germene (also seen in $SiCH_4$[22]) relative to digermene and germasilene is certainly related to its structural rigidity. Unlike germasilene and digermene, which are floppy, H_2GeCH_2 is strongly planar; its lowest harmonic vibrational frequencies are near 500 cm^{-1}. Pertinent, too, is the existence of low-lying minima involving dibridging hydrogens in disilenes and digermenes,[6e] as well as Si_2H_2[23] and Ge_2H_2.[24] A stable low-lying monobridged structure has recently been found in Si_2H_2 as well.[23a,c,e] Overall, unsaturated silicon and germanium compounds exhibit relatively flat potential energy surfaces with respect to hydrogen migrations.

Phenyl groups generally possess higher migratory aptitudes than alkyl groups, and theoretical studies show that methyl group migrations in substituted disilenes require nearly 20 kcal mol^{-1} more energy than hydrogen migrations.[25] Thus, one method for suppressing the isomerization of digermenes[1] and germasilenes[2] would be to employ alkyl instead of aryl substituents. Lappert's tetrakis[bis(trimethylsilyl)methyl]digermene[26] is the only known alkyl-substituted digermene, and it suffers a different fate: dissociation into monomeric germylenes in solution and in the gas phase (we[6f,24] and others[4f] interpret the dissociation as resulting from germylene fragment stabilization via the β-silicon effect). Therefore, care is required in the alkyl substituent choice if inhibiting isomerization is intended, or else other (equally undesirable) fates may result. As noted earlier, the successful isolation of pure digermene using bulkier 2,6-substituted phenyl groups, where 2,6-dimethylphenyl had failed, may reflect larger isomerization barriers in the former. Thus, sterically demanding substituents, which are commonly

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employed to increase kinetic stability toward external reagents, may be the key to suppressing germasilene and digermene isomerizations as well.

Acknowledgment. This research was supported by NSF Grant CHE-8718469. We thank K. Baines for illuminating discussions and for providing copies of ref 1 and 2 prior to publication.

OM920521Y

Synthesis of Thermochromic Dibismuthines with Nonthermochromic Distibine Analogs

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Received May 1, 1992

Summary: Octamethylbistibole (**4a**), octamethylbibismole (**4b**), 2,2′,5,5′-tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethylbistibole (**5a**), and 2,2′,5,5′-tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethylbibismole (**5b**) have been prepared by the reductive coupling of their respective precursor phenyl- or bromopnictoles. The bibismoles are thermochromic, while the bistiboles are not. This is the first observation of differing behavior between analogous distibines and dibismuthines with regard to thermochromicity.

Certain distibines and dibismuthines display a dramatic color change upon melting.[1,2] This change has been labeled thermochromic, although it is associated with a phase change.[2] The thermochromic compounds also show color changes on solvation. To date, when a dibismuthine has been thermochromic, its antimony analog has also displayed the same behavior and vice versa.[2,3] However, there are no reasons to anticipate that this should always be the case. The crystal structures[4-10] of these thermochromic species, when available, reveal the pnictogen centers to be ordered in a stacked linear arrangement with short intermolecular pnictogen–pnictogen contacts (Figure 1[11,12]). This packing arrangement is not observed in nonthermochromic dipnictines[13] and is believed to be responsible for the thermochromic behavior.[2,14] Since the van der Waals radius of bismuth (2.3 Å)[10] is considerably greater than that of antimony (2.2 Å),[10] it seems likely that

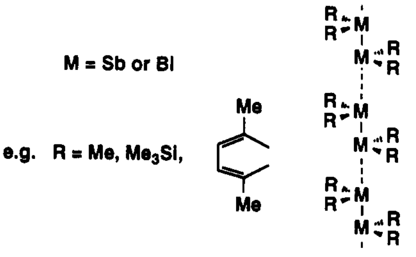
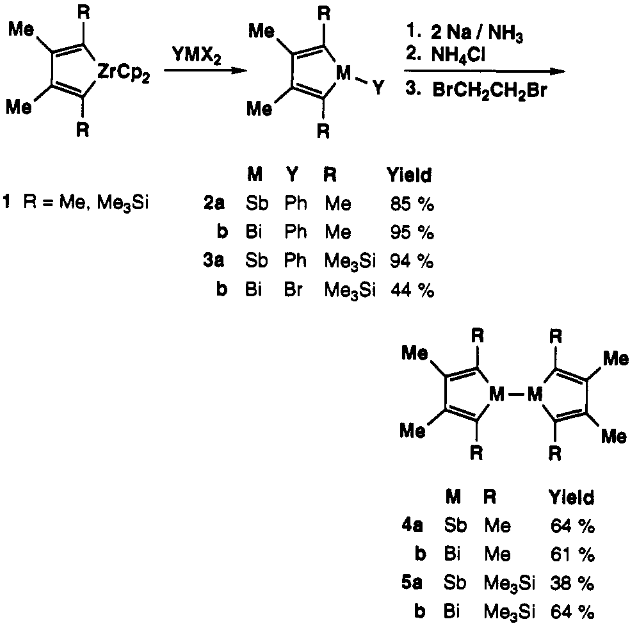


Figure 1.

Scheme I



1 R = Me, Me$_3$Si

	M	Y	R	Yield
2a	Sb	Ph	Me	85 %
b	Bi	Ph	Me	95 %
3a	Sb	Ph	Me$_3$Si	94 %
b	Bi	Br	Me$_3$Si	44 %

	M	R	Yield
4a	Sb	Me	64 %
b	Bi	Me	61 %
5a	Sb	Me$_3$Si	38 %
b	Bi	Me$_3$Si	64 %

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