

and the triose pool. Experiments to identify the actual substrates and the origins of the ring nitrogen and oxygen atoms are in progress.

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**Registry No.** 1, 52665-74-4; 2, 61116-33-4; acetic acid, 64-19-7; succinic acid, 110-15-6; glycerol, 56-81-5.

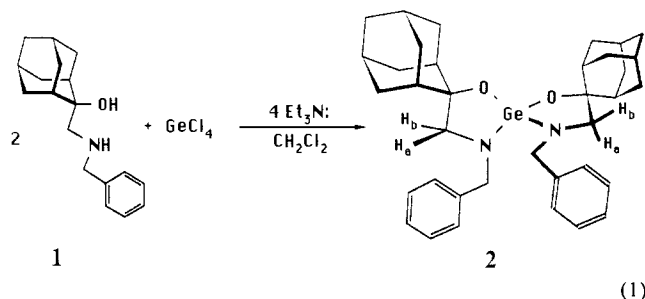
**Supplementary Material Available:** Table listing data and details of the complete  $^1\text{H}$  and  $^{13}\text{C}$  NMR assignments of asukamycin and manumycin (1 page). Ordering information is given on any current masthead page.

### Edge Inversion Barrier at a Four-Coordinate Main Group IV Center<sup>†</sup>

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The barrier to edge inversion has been directly determined for a four-coordinate main group IV compound **2**. The experimentally determined barrier ( $\Delta H^\ddagger$ ) for the germanium compound **2** is 22.2 ( $\pm 2.5$ ) kcal/mol (in agreement with theoretical expectations<sup>1</sup>)



with an activation entropy ( $\Delta S^\ddagger$ ) of 0.65 ( $\pm 6.5$ ) eu. These results substantiate the operation of an edge inversion process at main group IV centers analogous to the process recently predicted<sup>2</sup> for and subsequently measured<sup>3</sup> at pnictogen centers.

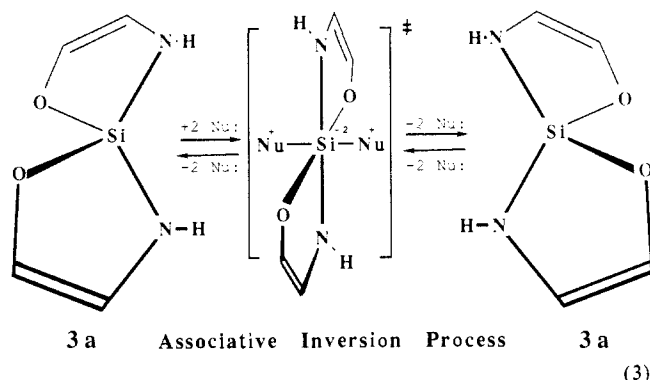
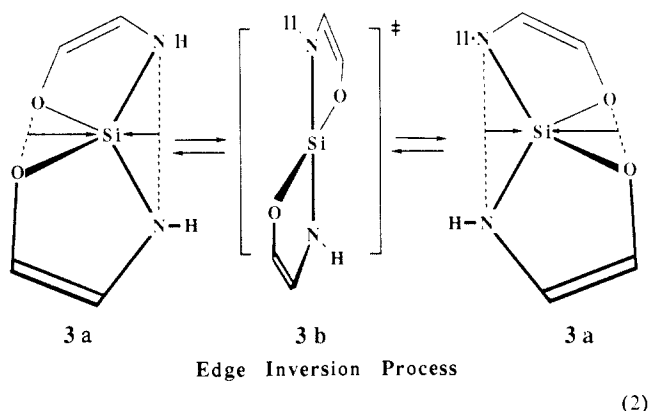
In previous reports<sup>1a,c,d</sup> we suggested that the edge inversion process (eq 2) should be considered in addition to the nucleophile assisted mechanism (eq 3) for configurational inversion of four-coordinate main group IV compounds (inversion may also be accomplished via a five-coordinate structure if accompanied by

<sup>†</sup> Dedicated to Professor J. C. Martin on the occasion of his 60th birthday.

(1) (a) Dixon, D. A.; Arduengo, A. J., III *J. Phys. Chem.* **1987**, *91*, 3195. (b) Dixon, D. A.; Arduengo, A. J., III *J. Chem. Soc., Chem. Commun.* **1987**, 498. (c) Arduengo, A. J., III; Dixon, D. A.; Stewart, C. A. *Phosphorus Sulfur* **1987**, *30*, 341. (d) Arduengo, A. J., III *Pure Appl. Chem.* **1987**, *59*, 1053. (e) As described in ref 4, "ADPnO" is an acronym for the ring system 5-aza-2,8-dioxo-1-pnictabicyclo[3.3.0]octa-2,4,6-triene.

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pseudorotation). While the stereochemical outcome of these inversion mechanisms is the same, there is a difference in the molecularity of the three processes. The viability of the edge inversion process for such systems is supported by large basis set ab initio calculations of the barriers to edge inversion for the series of main group IV tetrafluorides.<sup>1a</sup> As with the pnictogen systems,<sup>2,3</sup> substitution of a main group IV center with electronegative groups ( $\sigma$ -acceptors) and  $\pi$ -donors can lead to a preference for the edge inversion process.

On the basis of our earlier studies on the pnictogen derived ADPnO<sup>1c,d</sup> systems<sup>1c,d,4</sup> high level ab initio molecular orbital calculations on **3** were performed. The geometries of the ground-state structure with a tetrahedral Si, **3a**, and that for the edge inversion transition state ( $C_{2h}$ ) with a planar Si, **3b**, were gradient optimized<sup>5</sup> with the program GRADSCF<sup>6</sup> on a CRAY/1A computer. Force fields<sup>7</sup> and an MP-2 correlation correction were calculated at the optimum geometries.<sup>8</sup> The basis set is of the form (11s7p1d/9s5p1d/9s5p/4s)/[6s4p1d/3s2p1d/3s2p/2s] in the order Si/O,N/C/H.<sup>9</sup> The structure with a tetrahedral silicon, **3a**, is a minimum, while **3b** is a transition state. The single direction of negative curvature corresponds to the inversion mode ( $\nu = 145\text{ cm}^{-1}$ ). Structure **3b** is 24.6 kcal/mol above **3a** at the SCF level and is 17.6 kcal/mol above **3a** at the MP-2 level, suggesting that an experimental measurement on the barrier to the unimolecular edge inversion process for a compound like **3** is possible.

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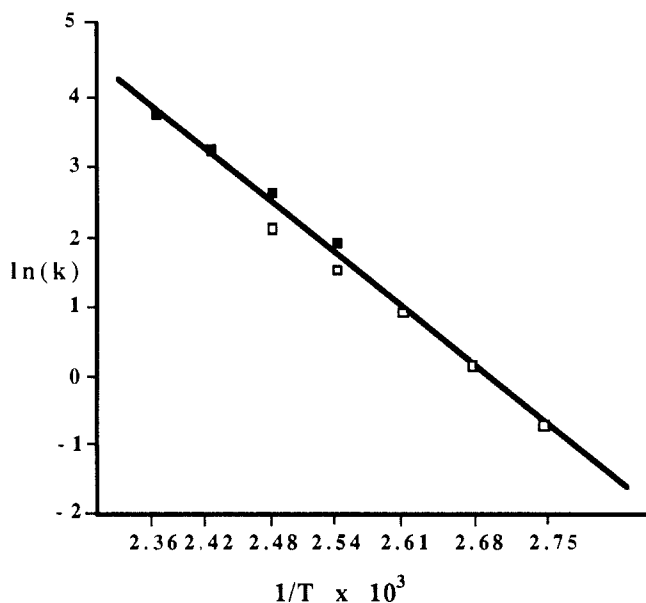


Figure 1. Arrhenius plot of the rate data on **2**. The solid squares represent data from line shape analysis, and the open squares are taken from the magnetization transfer experiment.

On the basis of our calculations of the inversion barrier in the saturated ADPO system **3**, we would expect that the barrier in **3** would increase when the C=C bond is saturated. However, changing the Si to Ge<sup>1a</sup> should approximately cancel the increase due to saturation. We therefore chose a saturated ligand system on a germanium center **2** which also provides steric hindrance to bimolecular processes and provides a convenient NMR handle for barrier determination.

Compound **2** was synthesized by the reaction of the amine-ol **1** with GeCl<sub>4</sub> in the presence of triethylamine in CH<sub>2</sub>Cl<sub>2</sub>. Compound **2** is a stable crystalline solid melting 121–124 °C. Consistent <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR spectra and elemental analysis were obtained for **2**.<sup>10</sup>

Over the temperature range from 80 to 150 °C, the <sup>1</sup>H NMR spectrum of **2** was examined in toluene-*d*<sub>8</sub>. Between 120 and 150 °C there was sufficient change in the line shape to allow determination of the inversion rate by standard analysis of the line shapes for the diastereotopic protons H<sub>a</sub> and H<sub>b</sub>. In the range from 90 to 130 °C the inversion rate was determined from a magnetization transfer experiment on the H<sub>a</sub> and H<sub>b</sub> protons. In the magnetization transfer experiment, selective inversion of the H<sub>b</sub> doublet leads to a characteristic decrease in the intensity for the H<sub>a</sub> resonance in the <sup>1</sup>H NMR spectrum and indicates that inversion is occurring at a rate comparable to spin-lattice relaxation.

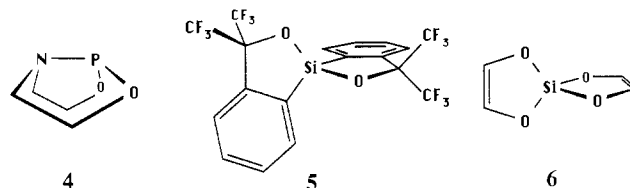
The rate data from the <sup>1</sup>H NMR experiments are plotted in Arrhenius form in Figure 1. From a nonlinear least-squares fit to the Eyring equation<sup>11</sup> we obtain  $\Delta H^\ddagger = 22.2 \pm 2.5$  kcal/mol

(10) A sample of **2** recrystallized from toluene/acetonitrile gave mp 121–124 °C: Anal. (C<sub>36</sub>H<sub>46</sub>N<sub>2</sub>O<sub>2</sub>Ge) C, H, N, Ge. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.40–1.77 (m, adamantyl, 24 H), 2.30 (dm,  $J = 11.7$  Hz, adamantyl, 4 H), 2.78 (d,  $^2J_{\text{HH}} = 9.5$  Hz, H<sub>a</sub>, 2 H), 2.84 (d,  $^2J_{\text{HH}} = 9.5$  Hz, H<sub>b</sub>, 2 H), 4.05 (d,  $^2J_{\text{HH}} = 14.0$  Hz, CH<sub>2</sub>-phenyl, 2 H), 4.09 (d,  $^2J_{\text{HH}} = 14.0$  Hz, CH<sub>2</sub>-phenyl, 2 H), 7.20–7.40 (m, aromatic, 10 H); <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>)  $\delta$  1.40–1.90 (m, adamantyl, 24 H), 2.62 (dm,  $J = 12.0$  Hz, adamantyl, 4 H), 2.63 (d,  $^2J_{\text{HH}} = 9.3$  Hz, H<sub>a</sub>, 2 H), 2.85 (d,  $^2J_{\text{HH}} = 9.3$  Hz, H<sub>b</sub>, 2 H), 3.98 (d,  $^2J_{\text{HH}} = 14.1$  Hz, CH<sub>2</sub>-phenyl, 2 H), 4.02 (d,  $^2J_{\text{HH}} = 14.1$  Hz, CH<sub>2</sub>-phenyl), 7.09 (tm, *p*-phenyl, 2 H), 7.20 (dd, *m*-phenyl, 4 H), 7.35 (dm, *o*-phenyl, 4 H). At 100 °C in toluene-*d*<sub>8</sub> the following resonances are noticeably shifted from the ambient temperature spectra listed above:  $\delta$  2.57 (dm,  $J = 12.7$  Hz, adamantyl, 4 H), 2.71 (d,  $^2J_{\text{HH}} = 9.3$  Hz, H<sub>a</sub>, 2 H), 2.95 (d,  $^2J_{\text{HH}} = 9.3$  Hz, H<sub>b</sub>, 2 H), 3.98 (d,  $^2J_{\text{HH}} = 14.0$  Hz, CH<sub>2</sub>-phenyl, 2 H), 4.02 (d,  $^2J_{\text{HH}} = 14.0$  Hz, CH<sub>2</sub>-phenyl, 2 H); <sup>13</sup>C NMR (toluene-*d*<sub>8</sub>)  $\delta$  27.46 (CH), 28.13 (CH), 33.50 (CH<sub>2</sub>), 33.61 (CH<sub>2</sub>), 34.89 (CH<sub>2</sub>), 35.01 (CH<sub>2</sub>), 38.06 (CH), 38.48 (CH<sub>2</sub>), 38.54 (CH), 53.21 (CH<sub>2</sub>-phenyl), 57.18 (NCCO), 79.02 (CO), 127.29 (*p*-phenyl), 128.41 (*m*-phenyl), 128.58 (*o*-phenyl), 140.91 (*ipso*-phenyl); <sup>15</sup>N NMR (toluene-*d*<sub>8</sub>)  $\delta$  -283.0 (reference NH<sub>4</sub>NO<sub>3</sub>).

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and  $\Delta S^\ddagger = 0.65 \pm 6.5$  eu. The value for  $\Delta H^\ddagger$  is significantly less than would be expected for a process involving bond-breaking and is in excellent accord with expectations based on our calculations (vide supra). The unimolecularity is supported by the near zero  $\Delta S^\ddagger$  and the concentration independence of the inversion rate. Reduction of the concentration of **2** by half yields the same inversion rates. Addition of 50 mol % of pyridine resulted in a very rapid inversion rate ( $\sim 10^3$  times faster).<sup>12</sup> In more nucleophilic solvents, the inversion rate was also accelerated,  $\Delta H^\ddagger = 17.96 \pm 1.31$  kcal/mol and  $\Delta S^\ddagger = -9.4 \pm 3.6$  eu in *o*-dichlorobenzene-*d*<sub>4</sub>. Thus, when nucleophiles are available a very rapid nucleophile assisted inversion can contribute to the observed rate.

These results provide confirmation of the operation of an unassisted edge inversion process at main group IV centers in the absence of nucleophiles. Our results are in accord with the recent work by Martin<sup>13,14</sup> on **5** and are significantly lower than low level calculations<sup>15</sup> on the barrier for **6**.



Clearly with careful design of the ligand system unassisted edge inversion of a main group IV system is possible.

Acknowledgment is made to F. Davidson for preliminary rate measurements on the nucleophile assisted inversions.

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### An Allene Adduct of Ditungsten Hexa-*tert*-butoxide: Prediction of a Stabilized $\mu$ - $\eta^3$ -CH<sub>2</sub>CCH<sub>2</sub> Moiety

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Reactive hydrocarbyl fragments are often stabilized by coordination to transition metals,<sup>1</sup> though rarely have these species been predicted. A notable exception was the prediction by Longuet-Higgins and Orgel<sup>2</sup> of cyclobutadiene-metal complexes. We wish here to report the preparation of a 1:1 adduct between allene and W<sub>2</sub>(O-*t*-Bu)<sub>6</sub>, and, on the basis of the observed spectroscopic data and theoretical considerations, we propose the existence of a central W<sub>2</sub>( $\mu$ - $\eta^3$ -C<sub>3</sub>H<sub>4</sub>) moiety in which the allenic  $\pi$  orbitals resemble the predicted transition state for allene isomerization.<sup>3</sup>

Hexane solutions of W<sub>2</sub>(O-*t*-Bu)<sub>6</sub> and allene (1 atm.) react at 0 °C to give a green solution from which dark green crystals, W<sub>2</sub>(O-*t*-Bu)<sub>6</sub>(C<sub>3</sub>H<sub>4</sub>) have been obtained analytically pure<sup>4</sup> by

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