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# Synthesis of a Digermane-Containing Tricylic Nonadecadienedione Incorporating an Equivalent of Ring-Opened THF

**Amy C. Gottfried, Jia Wang, Erin E. Wilson, Larry W. Beck, Mark M. Banaszak Holl,* and Jeff W. Kampf**

*Department of Chemistry, University of Michigan, 930 North University Avenue,
Ann Arbor, Michigan 48109-1055*

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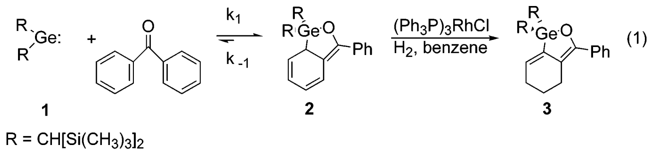
The combination of 2 equiv of bis[bis(trimethylsilyl)amide]germylene (**5**) with 2 equiv of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in tetrahydrofuran (THF) results in the ring-opening of 1 equiv of THF to form 2,2,8,8-tetrakis-(1,1,1,3,3,3-hexamethyl-disilazan-2-yl)-5,16-diphenyl-7,9,14-trioxa-1,3,5,16,18,19-hexaaza-2,8-di-germa-tricyclo[13.2.1.13,6]nonadeca-6(19),15(18)-diene-4,17-dione (**6**). This fast and nearly quantitative reaction builds a 15-membered ring from five different molecules. The new ring, structurally assigned by X-ray crystallography, contains a flexible methylene chain that moves rapidly on the NMR time scale.

## Introduction

Germylenes (the germanium analogues of carbenes and silylenes) are of increasing interest for their roles in synthetic chemistry. Like their group 14 analogues, germylenes can be synthesized with bulky substituents to prevent self-polymerization and some variants may even be isolated and stored in an air- and water-free environment.[1] Germylenes have been shown to insert into carbon−heteroatom $\sigma$-bonds and to add to unsaturated systems such as alkenes, alkynes, allenes, and many of their hetero analogues.[1−3] More recently, our group has shown the use of stable germylenes for insertion into the $\alpha$-C−H bond of nitriles[4] and ketones[5] and for C−H activation of ethers and alkanes.[6]

We have also shown that germylenes activate phenones through conversion to conjugated trienes.[7] This equilibrium lies far to the right such that only **2** is observed in both $^1$H NMR and UV−vis spectroscopy.[7] The conjugated triene product of benzophenone activation (**2**) can be catalytically hydrogenated[8] (eq 1). This reactivity prompted the hypothesis that trienes such as **2** contain reactive double bonds amenable to other transformations. The Diels−Alder reaction was chosen on the basis of the pair of double bonds locked in the s-cis conformation in triene **2** and appeared promising on the basis of Ando's successful Diels−Alder [4 + 2] cycloaddition of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and the germane **4** (the product of the addition of $Ge[CH(SiMe_3)_2]_2$ (**1**) to 2,5-dimethyl-2,3,4-hexatriene) (eq 2).[9] However, if the Diels−Alder reaction is not substantially faster than the back reaction to regenerate **1** and benzophenone, the germylene may react with PTAD. Ando demonstrated that germylenes such as **1** undergo [2 + 1] cycloadditions with double bonds in N-phenylmalimide (Figure 1a).[9]



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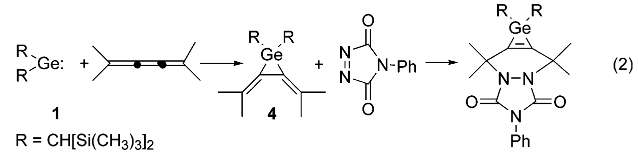

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* Author to whom correspondence should be addressed. E-mail: mbanasza@umich.edu.

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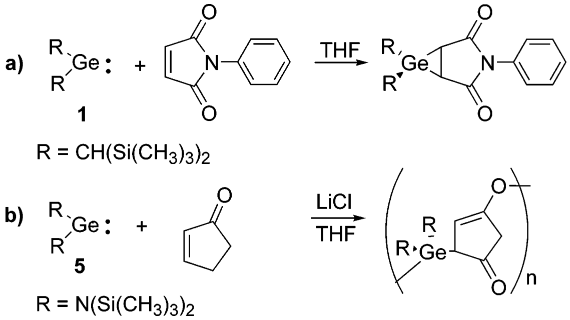

**Figure 1.** Known reactions of germylenes with functional groups analogous to PTAD.

Shoda demonstrated that $Ge[N(SiMe_3)_2]_2$ (**5**) copolymerizes with cyclic $\alpha,\beta$-unsaturated ketones (Figure 1b).[10]

Attempts to carry out the Diels−Alder reaction of **2** with PTAD did not yield the desired 4 + 2 cycloaddition product but rather led to the discovery and characterization of a new 15-membered ring described in this paper.

## Experimental Section

Standard air-free techniques were employed when using air-sensitive materials.[11] Tetrahydrofuran (THF), benzene-$d_6$, tetrahydrofuran-$d_8$, and toluene-$d_8$ were degassed and dried over sodium benzophenone ketyl. Acetonitrile was dried over $P_2O_5$ and stored over 4-Å sieves. $Ge[CH(SiMe_3)_2]_2$ (**1**) and $Ge[N(SiMe_3)_2]_2$ (**5**) were prepared according to the literature.[12] 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) was purchased from Aldrich and used as received. All glassware was oven-dried for at least 3 h before use. $^1H$ NMR spectra were taken at 400 MHz on a Varian Inova 400 spectrometer and at 300 MHz on a Varian Mercury 300 spectrometer. Spectra were referenced to the residual protons of $C_6D_6$ at 7.150 ppm, toluene-$d_8$ at 2.09 ppm, and THF-$d_8$ at 3.58 ppm. $^{13}C$ NMR spectra were taken at 100 MHz on a Varian Inova 400 spectrometer and referenced to the natural abundance of $^{13}C$ in $C_6D_6$ at 128.0 ppm. Standard two-dimensional (2D) NMR techniques, correlation spectroscopy (COSY) (on a Varian Inova 400), and heteronuclear single quantum correlation (HSQC) (on a Varian Inova 500) were used in assigning $^1H$ and $^{13}C$ spectra. Solid-state $^{13}C$ cross-polarized (CP)[13] NMR spectra were taken at 75 MHz on a Bruker DSX 300 spectrometer. High-resolution mass spectra were collected on a VG-70-250-S mass spectrometer using electron impact (70 eV) for ionization. IR spectra were obtained as thin films of the products formed by evaporation from solution on NaCl plates or as pressed KBr plates on a Perkin-Elmer Spectrum BX.

**2,2,8,8-Tetrakis(1,1,1,3,3,3-hexamethyl-disilazan-2-yl)-5,16-diphenyl-7,9,14-trioxa-1,3,5,16,18,19-hexaaza-2,8-digerma-tricyclo-[13.2.1.13,6]nonadeca-6(19),15(18)-diene-4,17-dione (6).** Bis[bis(trimethylsilyl)amide]germylene (**5**) (0.290 g, 0.737 mmol) was dissolved in 10 mL of THF, forming a pale yellow solution. 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) (0.129 g, 0.737 mmol) was dissolved in 10 mL of THF, forming a bright red solution. Both solutions were stirred for 2−3 min to ensure complete solvation. The solution of **5** was added via cannula to the PTAD solution, causing its red color to lighten. The reaction solution turned colorless upon completion of addition. This colorless solution was stirred for 10 min, and then volatiles were removed in vacuo, leaving a slightly yellow film. Two washings (5 mL each) with acetonitrile led to 0.342 g of a fine white powder of analytically pure product (77% yield). $^1H$ NMR ($C_6D_6$, conformer A, $\delta$): 4.67 (2 H, t, $OCH_2CH_2$), 4.58 (2 H, t, $OCH_2CH_2$), 0.49 (36 H, s, $Si(CH_3)_3$), 0.35 (36H, s, $Si(CH_3)_3$). $^1H$ NMR ($C_6D_6$, conformer B, $\delta$): 4.42 (1.6 H, t, $^3J_{HH} = 5.6$ Hz, $OCH_2CH_2$), 4.28 (1.6 H, t, $^3J_{HH} = 6.4$ Hz, $OCH_2CH_2$), 0.60 (28.8 H, s, $Si(CH_3)_3$), 0.23 (28.8 H, s, $Si(CH_3)_3$), 1.65 (1.6 H, m, $OCH_2CH_2$, by COSY). $^1H$ NMR ($C_6D_6$, conformers A and B, $\delta$): 7.64 (3.6 H, m, $^3J_{HH} = 7.9$ Hz), 7.52 (7.2 H, m, $^3J_{HH} = 8.6$, Hz), 7.46 (3.6 H, m, $^3J_{HH} = 7.8$ Hz), 7.15−6.90 (12 H, m), 1.79 (5.6 H, m $OCH_2CH_2$). $^{13}C$ NMR of powder **6** ($C_6D_6$, conformer A by HSQC, $\delta$): 68.70, 63.67, ($OCH_2$) 28.47, 27.48 ($OCH_2CH_2$). $^{13}C$ NMR of powder **6** ($C_6D_6$, conformer B by HSQC, $\delta$): 68.24, 62.13 ($OCH_2$); 25.55, 25.31 ($OCH_2CH_2$). $^{13}C$ NMR of powder **6** ($C_6D_6$, conformers A and B, $\delta$): 155.84, 155.80, 149.58, 149.29 (N═C(O)−N) and (NC(O)N), 133.57, 133.38, 132.84, 129.34, 129.24, 129.16, 129.06, 128.86, 125.72, 125.58 (aromatic), 6.096, 5.595, 5.595, 5.231 ($Si(CH_3)_3$). Solid-state $^{13}C$ NMR of powder **6** ($\delta$): 155.8, 151.0, 149.1, 133.5, 128.5, 65.5, 61.5, 27.0, 24.9, 5.7. Solid-state $^{13}C$ NMR of crystal **6** ($\delta$): 155.9, 151.0, 149.0, 132.8, 130.7, 129.5, 128.4, 126.5, 65.7, 61.7, 27.1, 24.8, 7.4, 6.4, 5.7. IR ($cm^{-1}$): $\nu$ 1713 (C═O), 1614, 1597 (C═N), 1252 (C−O). Anal. Calcd for $C_{44}H_{90}Ge_2N_{10}O_5Si_8$: C, 43.71; H, 7.50; N, 11.58. Found: C, 43.39; H, 7.33; N, 11.24. EI/MS: $[M/Z]^+ = 1208.2$ amu.

All other reactions varying the germylene and the solvent were carried out using the procedure described above.

**Structure Determination of 6.** Colorless needles of **6** were grown from a benzene/acetonitrile (1:5) solution at 22 °C. A crystal of dimensions $0.32 \times 0.17 \times 0.16$ mm$^3$ was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with an LT-2 low-temperature device and normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 150(2) K; the detector was placed at a distance of 4.980 cm from the crystal. A total of 4615 frames were collected with a scan width of 0.2° in $\omega$ and $\varphi$ with an exposure time of 30 s/frame. The frames were integrated with the Bruker SAINT[14] software package with a narrow frame algorithm. The integration of the data yielded a total of 83 696 reflections to a maximum $2\Theta$ value of 56.75° of which 15 887 were independent and 12 776 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 7118 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS[15] and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL[15] (version 5.10) software package, using the space group $P2_1/n$ with $Z = 4$ for the formula $C_{44}H_{90}N_{10}O_5Si_8Ge_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full-matrix least-squares refinement based on $F^2$ converged at $R1 = 0.0301$ and $wR2 = 0.0685$ (based on $I > 2\sigma(I)$), $R1 = 0.0457$ and $wR2 = 0.0745$ for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file

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**Table 1.** Crystal Data and Structure Refinement for **6**

| | |
|---|---|
| empirical formula | $C_{44}H_{90}Ge_2N_{10}O_5Si_8$ |
| fw | 1209.16 |
| temperature/K | 150(2) |
| wavelength/Å | 0.71073 |
| cryst syst, space group | monoclinic, $P2_1/n$ |
| unit cell dimensions | |
| $a$/Å | 11.496(3) |
| $\alpha$/deg | 90 |
| $b$/Å | 28.227(7) |
| $\beta$/deg | 94.416(5) |
| $c$/Å | 19.713(5) |
| $\chi$/deg | 90 |
| volume/Å$^3$ | 6378(3) |
| $Z$, calcd density/Mg/m$^3$ | 4, 1.259 |
| abs coeff/mm$^{-1}$ | 1.139 |
| $F$(000) | 2560 |
| cryst size/mm | $0.32 \times 0.17 \times 0.16$ |
| $\Theta$ range/deg | 2.80 to 28.37 |
| limiting indices | $-15 \leq h \leq 15$<br>$-37 \leq k \leq 37$<br>$-26 \leq l \leq 26$ |
| no. of reflns collect/unique | 83 696/15 887<br>[R(int) = 0.0480] |
| completeness to $\Theta = 28.37$ | 99.4% |
| abs corr | semiempirical from equivalents |
| max and min transmission | 0.8388 and 0.7120 |
| refinement method | full-matrix least-squares on $F^2$ |
| no. of data/restraints/params | 15 887/0/646 |
| goodness of fit on $F^2$ | 1.009 |
| final R indices ($I > 2\sigma(I)$) | R1 = 0.0301<br>wR2 = 0.0685 |
| R indices (all data) | R1 = 0.0457<br>wR2 = 0.0745 |
| largest diff peak and hole/e A$^{-3}$ | 0.375 and $-0.276$ |

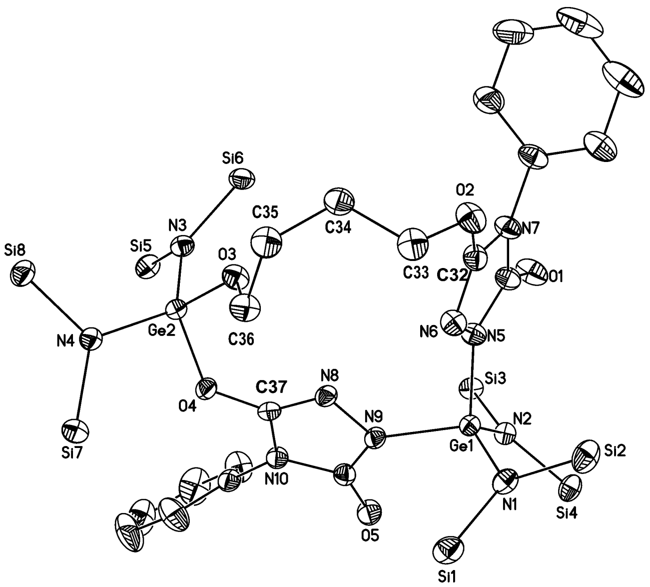
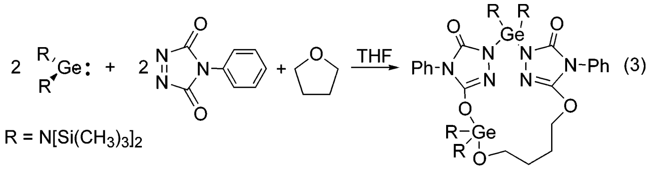


**Figure 2.** ORTEP diagram of **5** with $CH_3$ groups omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge2−O3 = 1.74190(12); Ge2−O4 = 1.8200(12); Ge1−N5 = 1.8647(15); Ge1−N9 = 1.8730(14); N8−C37 = 1.288(2); N8−N9 = 1.4225(19); O3−Ge2−O4 = 112.85(5); C36−O3−Ge2 = 124.71(11); O3−C36−C-35 = 108.31(15); C36−C35−C34 = 112.78(15); O2−C33−C34 = 109.24(15); C32−O2−C33 = 114.66(14); N5−Ge1−N9 = 100.95(6).

## Results

As PTAD mixed with **2** in THF, the solutions color rapidly changed from bright red to colorless. The $^1$H NMR spectrum of the reaction products clearly indicated that a Diels−Alder [4 + 2] cycloaddition had not taken place between the triene and PTAD. To confirm that germylene **1** (in equilibrium with **2** and benzophenone) was indeed reacting with the PTAD, **1** was added directly to PTAD in THF, resulting in multiple products as indicated by the number of trimethylsilyl peaks observed in the $^1$H NMR spectrum.

The addition of Ge[N(SiMe$_3$)$_2$]$_2$ (**5**) to PTAD in THF was also carried out. This reaction resulted in a clean product with four unanticipated triplets in the 4−5 ppm region of its $^1$H NMR spectrum. X-ray quality crystals were grown by slow evaporation from benzene/acetonitrile (1:5) in order to allow an X-ray crystal structural determination of **6.** A large tricyclic ring made from five reactant molecules (2 equiv of **5**, 2 equiv of PTAD, and 1 equiv of THF) was revealed (Figure 2, eq 3). The formation of 2,2,8,8-tetrakis(1,1,1,3,3,3-hexamethyl-disilazan-2-yl)-5,16-diphenyl-7,9,14-trioxa-1,3,5,-16,18,19-hexaaza-2,8-digerma-tricyclo[13.2.1.13,6]nonadeca-6(19),15(18)-diene-4,17-dione (**6**) is supported by IR stretches from both the carbonyl (1713 cm$^{-1}$) and imine (1614, 1597 cm$^{-1}$) functional groups and elemental analysis. Analysis by mass spectrometry confirmed that **6** had a molecular weight of 1209 g/mol ($C_{44}H_{90}Ge_2N_{10}O_5Si_8$).



**5** **6**

$^1$H and $^{13}$C spectroscopy were both consistent with the structural assignment of **6** but contained what appeared to be two conformers (A and B) present in benzene solution. The $^1$H NMR spectrum contains four trimethylsilyl singlets at 0.49 and 0.35 ppm (A) and at 0.60 and 0.23 ppm (B) as well as four, broad pseudotriplets from the methylenes $\alpha$ to the oxygen atoms at 4.67 and 4.58 (A) and 4.42 4.28 ppm (B). 2D NMR (COSY) was used to confirm that the multiplet at ∼1.8 ppm derived from the four methylene carbons $\beta$ to the oxygen. All of the methylene signals in **6** originate from THF as confirmed by running the reaction of **5** and PTAD in THF-$d_8$, which results in **6**-$d_8$ with an $^1$H NMR spectrum identical to **6** except for the absence of all methylene protons. The ratio of conformers changes with the solvent, appearing in a ∼1:0.8 A/B ratio in benzene-$d_6$, a ∼1:1 A/B ratio in toluene-$d_8$, and a 1:1.5 A/B ratio in THF-$d_8$.

The appearance in the $^1$H NMR spectrum of the methylene groups $\alpha$ to the oxygen merits further analysis. One might naively presume that as a result of being present in a ring all eight methylene protons in **6** would be diastereotopic. If this were the case, the four protons $\alpha$ to the oxygen atoms would be observed as four doublets of doublets of doublets in a 1:1:1:1 ratio. For a freely moving chain, the two methlyene groups $\alpha$ to oxygen would each appear as a triplet in a 1:1 ratio. The experimental observation in benzene-$d_6$ is four slightly broad triplets in a 1:1:0.8:0.8 ratio. This observations leads to the conclusion that there are two conformers in a 1:0.8 ratio, each with freely moving methylene chains. The $^{13}$C NMR spectrum contains four

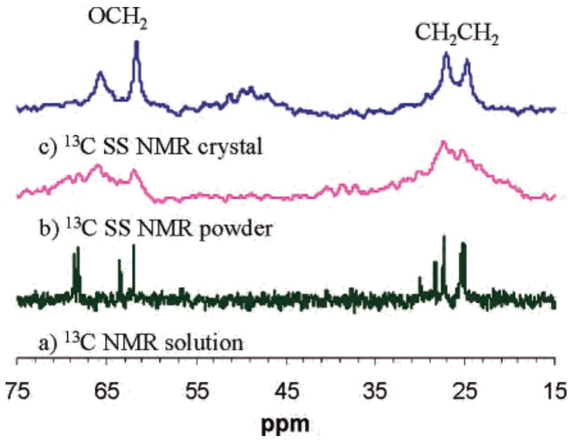


**Figure 3.** $^{13}$C NMR of **6** in (a) solution, (b) solid state of powder, and (c) solid state of crystal.

unique methlyene carbons α to the oxygen atoms (68.70, 68.24, 63.67, and 62.13 ppm) and four unique methylene carbons $\beta$ to oxygen atoms (28.47, 27.48, 25.55, and 25.28 ppm), supporting the conclusion that two conformers must be present in solution (Figure 3a).

The data from the X-ray crystal structure indicates that **6** adopts a single conformation in the solid phase. A sample of **6** prepared by dissolving single crystals from the same batch used to obtain the X-ray structure in benzene-$d_6$ at room temperature produced an $^1$H NMR spectrum identical to that obtained for noncrystalline **6**. This suggests that the single conformer present in the solid state can rapidly equilibrate with a second conformer when dissolved in benzene at ambient temperature.

To determine which, if any, of the NMR peaks observed in solution represent the conformer obtained by slow crystal formation, more crystals were grown using the same method. X-ray powder diffraction was employed to confirm that the material crystallized was in the same space group, $P2_1/n$, with the same unit cell constants. The $^{13}$C CP solid-state NMR spectra of crystalline **6** and powder **6**, which showed no crystallinity by X-ray powder diffraction, are shown in Figure 3. The solid-state NMR of powder **6** (Figure 3b) shows broad peaks in both methylene regions (20−30 and 60−70 ppm), which are attributed to the presence of multiple conformers in the solid powder. In Figure 3c, the solid-state NMR spectrum of crystalline **6**, the two methylene carbons α to oxygen atoms and the two methylene carbons $\beta$ to oxygen atoms appear as well-defined and distinct peaks consistent with the presence of single conformer in the crystalline solid.

A solution $^1$H NMR spectrum of a single conformer was obtained by dissolving crystals of **6** in toluene-$d_8$ at −78 °C and placing this solution in an NMR spectrometer that had been cooled to −60 °C. The sample of **6** was warmed slowly in 10 °C intervals with 5 min of equilibration at each temperature while obtaining NMR data. The 4−5 ppm region (the methylenes α to the oxygen) of the $^1$H NMR data is shown in Figure 4. At low temperatures, **6** is not very soluble in toluene. As the temperature is warmed and **6** dissolves, its methylene peaks initially appear very broad in a manner that may indicate the coalescence of peaks from many conformers that are interchanging rapidly. Perhaps multiple conformers of the methylene chain are attaining the energy necessary to quickly interconvert formally diastereotopic protons. With an increase of temperature, this single broad peak grows into a pair of the pseudotriplets previously identified as conformer B in the spectra of **6** taken at 20 °C. The second conformer (A) is initially absent. However, when the sample of **6** was warmed to −30 °C a broad peak for the methylene groups of A begins to appear and by 20 °C both pairs of pseudotriplets are present in a 1:1 ratio.

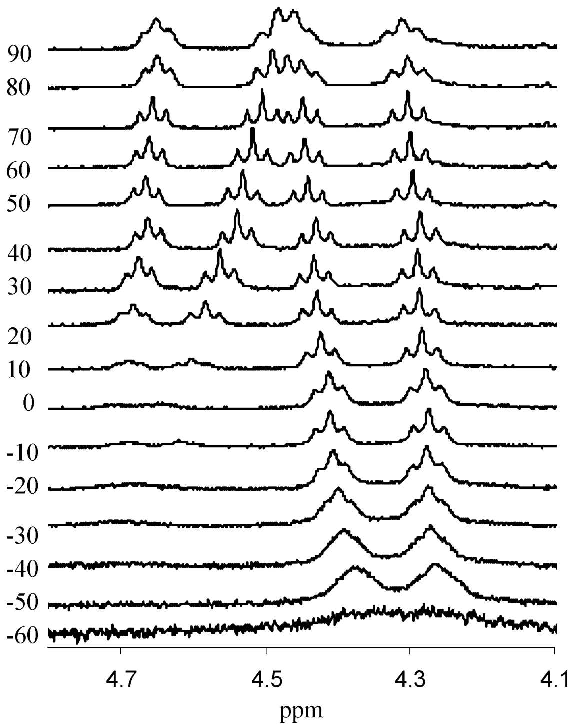


**Figure 4.** Variable temperature $^1$H NMR spectra (300 MHz, toluene-$d_8$ −60 to 90 °C) of methylene protons α to oxygen (5−4 ppm) starting with single conformer crystals.

The sequential appearance of the two conformers is not due to a large difference in solubility. (Previous $^1$H NMR experiments showed both conformers in their room-temperature ratios in solution down to −30 °C.) Rather, the two conformers appear to be in equilibrium with conformer A growing in slowly as the temperature increases. As the temperature is increased from 20 to 60 °C, both pairs of pseudotriplets sharpen and begin moving toward one another in a manner expected for coalescence due to fast interconversion of the two conformers at high temperatures. The boiling point of the NMR solvent was reached before the coalescence temperature could be attained. However, a lower limit of coalescence ($\Delta G^{\ddagger} = 70$ kJ/mol) was calculated using the average $\Delta\nu$ of the set of conformer peaks at 0 °C with $T_c = 90$ °C.[16]

Spartan ‘04 molecular mechanics calculations were used to search for possible low-energy conformations of **6**. A search resulted in over 80 unique conformers with energies over a 10 kcal/mol range. Density functional theory geometry

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optimizations were carried out on **6** without the phenyl or TMS groups. Both the crystal structure coordinates and an arbitrarily drawn molecule were minimized, resulting in two different conformers of the ring. Semiempirical geometry minimizations (AM1) of the full-crystal structure and another arbitrarily drawn full ring also resulted in two different conformers. This set of calculations did not resolve the question of specific conformations likely to be obtained by **6**.

## Discussion

Upon the basis of NMR data and molecular mechanics simulations, we conclude that in a solution of **6** there are two groups of interconverting conformers with comparable energies. All of the conformers have flexible methylene chains, resulting in the appearance of triplets in the $^1$H NMR. The presence of many conformers within a group at lower temperatures (−30 to 10 °C in toluene-$d_8$) results in the broader triplets. As the temperature is raised, all conformers within a group interconvert quickly, resulting in sharp methylene triplets. Finally, at high temperatures, the two groups of conformers appear to be moving toward interconversion. The activation energy for conversion between the two groups (lower boundary = 70 kJ/mol) is sufficiently high so that both sets exist in tolene-$d_8$ up to at least 90 °C as shown by $^1$H NMR spectroscopy in Figure 4. Upon crystallization, a single conformer is formed as indicated by solid-state NMR spectroscopy and X-ray crystallography. It is possible that the solid state $^{13}$C CP NMR spectrum of **6** and the low-temperature $^1$H NMR spectrum in toluene-$d_8$ arise from the same conformer. The AM1 minimized structure and the conformer found by crystallography do differ in detail in terms of both the methylene chain and the PTAD plane angles. However, the <10 kcal/mol difference is well within the energetics range of crystal packing interactions.

The formation of **6** is a facile, complete, and unique result of a simple mixing of the reagents needed to form the ring. Other large, multifunctional rings such as porphyrins and crown ethers are usually only achievable through high dilution techniques, the use of a template, or if there exists a small $\Delta S$ between products and reactants.[17] Compound **6** was formed independent of concentration and rate of addition and without the aid of the template. The combination of five independent molecules to make one single compound is not indicative of a small change in entropy.

Exploration of related reaction conditions and reactants was carried out. The reaction of **5** with PTAD in benzene yields a mixture of products with eight trimethylsilyl peaks. If THF is added to these products, no formation of **6** is observed. The reaction of **5** and PTAD in benzene with 2 equiv of THF yields a mixture of **6** and the products from the reaction of **5** and PTAD in benzene. Clean conversion to the large ring of **6** only took place with the $Ge[N(SiMe_3)_2]_2$ (**5**) and not with $Ge[CH(SiMe_3)_2]_2$ (**1**). Reactions employing other ethers including dioxane, diethyl ether, and tetrahydropyran as the solvent produced mostly the nonring products observed in the reactions of **5** and PTAD in benzene.

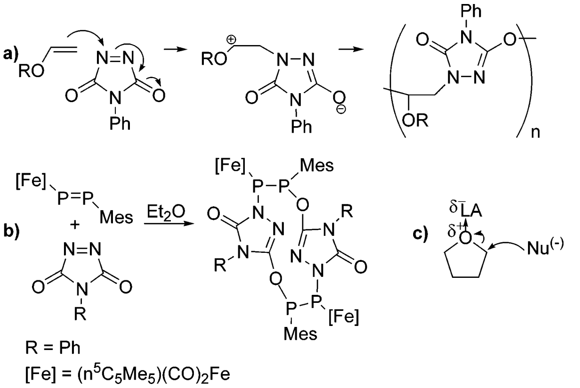

**Figure 5.** Literature precedent for mechanistic proposal.

To propose a reaction mechanism for ring formation, the reactivities of the individual components of the ring were examined. **5** has been shown to form an alternate copolymer with α,$\beta$-unsaturated ketones similar to PTAD in the presence of salts such as lithium chloride (Figure 1b).[10] The proposed mechanism is the addition of germylene anion (formed by complexation with the salt) to the α,$\beta$-unsaturated ketone via a Michael-type addition. The steric bulk of the amide ligand and the poor homopolymerizability of the α,$\beta$-unsaturated ketone are stated as reasons for prevention of homo unit formation.

PTAD is primarily used as a dieneophile for Diels−Alder type reactions, but Butler and Jones have demonstrated that it will undergo the 1,4-cycloaddition that leads to polymerization (Figure 5a).[18,19] Weber and co-workers have even shown the formation of cyclododecadienes from 2 equiv of PTAD and 2 equiv of a metal-substituted diphosphene in diethyl ether (Figure 5b). This cycloaddition product differs from **6** in that a symmetric molecule is formed with each diphosphene attached to one of the PTAD fragment through a P−N bond and to the second PTAD fragment through a P−O bond.

THF has been shown to ring open through nucleophilic attack when coordinated to a Lewis acid (such as germylene) often leading to polymerization (Figure 5c).[20,21]

These precedents suggest formation of **6** begins with addition of germylene **5** to the α,$\beta$-unsaturated ketone of PTAD (Scheme 1). We suggest that the germylene attacks a nitrogen in the N=N double bond, rather than at a carbonyl carbon, based on the Michael-type addition cited by Shoda[9] and the resulting connectivity observed in the final product **6**. The resulting anion then carries out a nucleophilic attack on THF coordinated to the Lewis acidic germylene. With four of the five components put together, completion of the mechanism with steps based solely on 2 e$^-$ acid−base reactions no longer appears feasible. It is proposed that an

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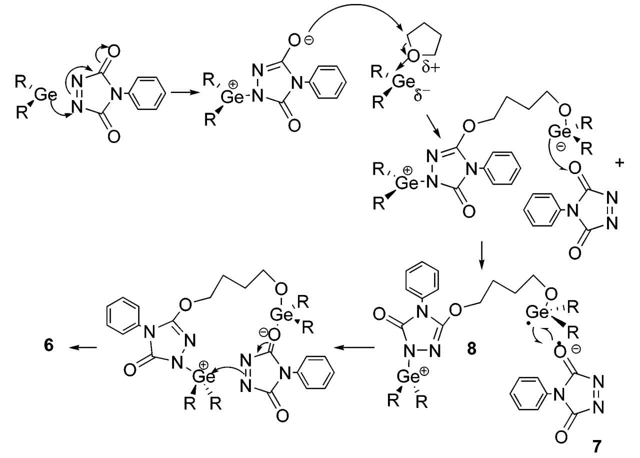
**Scheme 1.** Proposed Mechanism for Formation of **6**



electron transfer from the germyl anion to PTAD generates a PTAD anion (**7**) that can couple with the resulting germyl radical (**8**) to form the second Ge−O bond. The resulting species can complete the intramolecular coupling by attacking the initially formed germyl cation to close the ring. Clearly, this is just one of many possible mechanistic schemes and an electron-transfer step may well occur in the first germylene−PTAD reaction. On the basis of numerous literature reports over the past 20 years,[22] the presence of electron-transfer steps in reactions with germylenes should always be considered as a likely mechanistic possibility. Germyl anions have been shown to be donors[22,23] and PTAD also has been shown to be an acceptor in single electron-transfer reactions.[24,25]

In conclusion, a unique tricyclononadecadiene ring has been formed by simply mixing Ge[N(SiMe$_3$)$_2$]$_2$ (**5**) with PTAD in THF. The reaction proceeds quickly and in high yield. The combination of five independent molecules to form a single ring without use of a template or dilution techniques is unexpected. Analysis of the ring reveals a single conformer in the crystalline solid and two groups of conformers, each with a flexible methylene chain, in solution.

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**Supporting Information Available:** $^1$H NMR spectrum and the full $^{13}$C NMR spectrum (solid-state crystals, solid-state powder, and solution). X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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