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# Evidence for an Unusual Rectangular Pyramidal Germanium(IV) Anion

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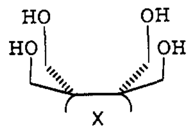
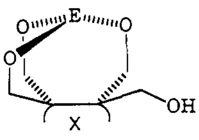
The small energy increment in the square-pyramidal (SP) geometry over the trigonal-bipyramidal (TBP) configuration is associated with an excited state in pentacoordinate pnictogen compounds undergoing Berry pseudorotation.[1] Efforts to stabilize pnictogens in the SP configuration have met with success for pentavalent neutral compounds of P,[2] As,[3] and Sb[4] and for tetravalent anions of Si,[5] Ge,[6] and Sn.[7] In all the cases we have been able to find in the literature, however, SP geometries in these systems are stabilized by multiple four- and/or five-membered rings, while systems with six-membered rings have invariably been found to be TBP. In the case of the recently reported Ge(II) and Sn(II) derivatives of dibenzotetramethyltetraza[14]annulene, the divalent group 14 atom is bound in a square-planar geometry to the macrocycle via pairs of five- and six-membered rings.[8]

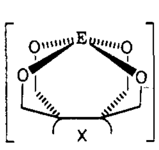
Tetra-alcohols such as **1–4** would appear to be structurally amenable to forming neutral esters such as **5–7**, which could then undergo deprotonation of the pendant alcohol in the presence of a strong nonionic base to stabilize corresponding anions of types **8–10** possessing saturated six- and seven-membered chelating rings. In an earlier publication[7] we observed no evidence for **8** upon treatment of **5** with several strong nonionic bases. In these experiments the X moiety in **5** included the range shown in **1–4** and E also included a variety of P(V) species. Whereas an attempt in our laboratories to synthesize **6** ($X = CH_2$, R = Me) unexpectedly gave rise to the novel isomers **11a,b**, the target compound **12** was synthesized only in the case of $X = (CH_2)_3$.[9] However, attempts to form the corresponding rectangular pyramidal anion from **12** failed.[10] On the other hand, the As(III) esters **7** ($X = H_2$, $(CH_2)_2$) were observed in VT $^1$H and $^{13}$C NMR experiments to form anions **10** in the presence of strong bases such as DBU and **13**.[11] In this reversible equilibrium, the anion is favored at elevated temperature in a fluxional process.



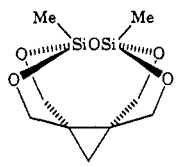
| | X |
|---|---|
| 1 | $H_2$ |
| 2 | $CH_2$ |
| 3 | $(CH_2)_2$ |
| 4 | $(CH_2)_3$ |



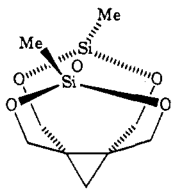
| | E |
|---|---|
| 5 | P |
| 6 | SiR |
| 7 | As |



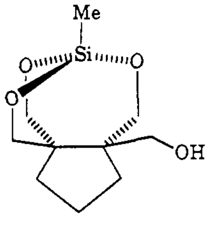
| | E |
|---|---|
| 8 | P |
| 9 | SiR |
| 10 | As |



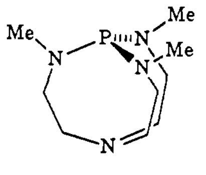
**11a**



**11b**

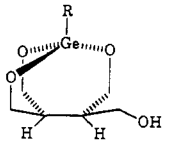


**12**

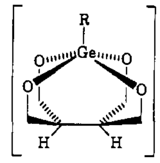


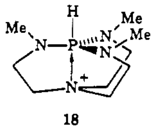
**13**

Here we describe the synthesis of **14** and **15**, and the formation of their anions **16** and **17**, respectively, in an equilibrium process in the presence of base. We also report an interesting feature of this equilibrium which contrasts the aforementioned one involving **7** and **10**.[11]



| | R | |
|---|---|---|
| 14 | Ph | 16 |
| 15 | Me | 17 |





**18**

Compounds **14** and **15** were synthesized according to reaction 1 in 80 and 81% yields, respectively. Both products are solids

$$1 + RGeCl_3 \xrightarrow[-3Et_3NHCl\downarrow]{THF\ \uparrow\downarrow \atop 3Et_3N} 14, 15 \qquad (1)$$

that sublime upon heating under vacuum. Compound **14** did not produce NMR-detectable amounts of the corresponding anion **16** in *deuterio*pyridine in the presence of excess DBU or Proton Sponge between 243 and 333 K.[13] For more efficient deprotonation, an excess of the substantially stronger base **13** (whose conjugate acid **18** has a p$K_a$ of *ca.* 27 in DMSO[12]) was added to a *deuterio*pyridine solution of **14**,[1] whereupon some of compound **13** converted to **18** as shown by monitoring their characteristic room-temperature $^{31}$P NMR chemical shifts. Moreover, a resonance assignable to the hydroxy proton was also visible. Upon warming of the solution, the $^{31}$P NMR signal for **18** decreased until its disappearance at 353 K. Meanwhile the $^1$H NMR spectrum assumed the complex appearance of that of **14** and the $^{31}$P NMR spectrum showed only a peak for **13**. Lowering the temperature caused the $^{31}$P NMR signal for **18** to reappear and the OH proton signal to decrease until at 243 K the latter disappeared. At this temperature there was only a broad doublet-like $^1$H NMR pattern (4.55 and 4.46 ppm) for the $CH_2$ groups with the CH protons masked by those of **18**. Also at this

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(13) VT $^1$H NMR experiments involving a solution of **15** in $C_5D_5N$ using the bases DBU or "Proton Sponge" (which are considerably weaker than **13**) also failed to reveal detectable amounts of **17**.

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temperature the $^{13}$C NMR spectrum revealed only two aliphatic resonances in accord with the cage structure of **16**, one at 67.80 ppm (CH$_2$) and the other at 45.00 ppm (CH). The phenyl $^1$H and $^{13}$C resonances of **14** upon conversion to negatively charged **16**[14] underwent shift changes[7] similar to those observed in the formation of the phenolate anion from phenol.[15]

Analogous VT $^1$H and $^{13}$C NMR results were obtained for a *deuterio*pyridine solution of **15** in the presence of the base **13**. Thus at 243 K the $^1$H NMR spectrum revealed the broad components of a doublet at 4.50 and 4.60 ppm for the CH$_2$ groups and resonances at 67.9 and 44.5 ppm assignable to the CH$_2$ and CH carbons of **17**. The CH$_3$ protons shifted downfield from 0.68 to 0.94 ppm upon formation of anion **17**.

These results indicate that anions **16** and **17**, in contrast to **10**, are thermodynamically stable since they are favored at lower temperature whereas **10** is observed to form as an intermediate as the temperature is elevated. Unfortunately, efforts to obtain simple crystals of [**18**][**16**] or [**18**][**17**] for X-ray diffraction experiments have thus far failed. It is interesting to note that an equimolar mixture of **13** and EtOH showed no detectable formation of the conjugate acid **18** by $^1$H NMR spectroscopy over the temperature range 243–333 K. This indicates that the formation of **16** and **17** in their equilibria with **14** and **15**, respectively, is driven largely by the thermodynamic stability of the rectangular pyramidal anions at lower temperatures and not by a strong temperature dependence of the equilibrium between **13** and **18**.

It is plausible to suggest that nondetection of anions **8** and **9** and our observation of evidence for **10**, **16**, and **17** could be largely ascribed to the smaller covalent radii of phosphorus (1.10 Å[16]) and silicon (1.18 Å[16]) compared with arsenic (1.25 Å[16]) and germanium (1.23 Å[16]). Thus the latter pair of atoms are better able to accommodate strain in the cage structure. This effect would have to override the larger single bond energies of the former pair of atoms with oxygen (phosphorus, 88 kcal/mol, and silicon, 111 kcal/mol[16]) compared with arsenic (79 kcal/mol[16]) and germanium (86 kcal/mol[16]). The greater thermodynamic stability of **16** and **17** compared with **10** can be ascribed to the greater strength of the Ge–O bond.

**Experimental Details.** All experiments were carried out under a nitrogen atmosphere. NMR spectra were recorded with a Varian VXR 300-MHz spectrometer operating at 121.42 MHz for $^{31}$P, 300 MHz for $^1$H, and 75.3 MHz for $^{13}$C. Microanalyses were performed by Galbraith Laboratories, Ltd. Compound **13** was synthesized as described earlier.[12]

**Preparation of 14 and 15.** The general procedure was to add 2.00 mmol of PhGeCl$_3$ (0.512 g) or MeGeCl$_3$ (0.388 g) to a stirred solution of 0.300 g (2.00 mmol) of **1** in 50 mL of dry THF, at room temperature. To this was added dropwise 0.626 g (6.20 mmol) of Et$_3$N in 10 mL of THF, and then the reaction mixture was refluxed for 7 h. After cooling of the mixture to room temperature, Et$_3$NHCl was filtered off, the filtrate was evaporated to dryness, and the residue was sublimed (**14**, 250 °C/0.05 Torr, 81% yield; **15**, 150 °C/0.07 Torr, 80% yield). Both **14** and **15** are white moisture-sensitive solids.

**14**: $^1$H NMR (C$_5$D$_5$N) 7.81 (m, 2 H, *m*-H), 7.35 (m, 3 h, *o*, *p*-H), 6.57 (s, 1 H, OH), 3.83–4.67 (m, 8 H, CH$_2$O), 2.73 (m, 1 H, *H*C(CH$_2$O)$_2$Ge), 2.46 (m, 1 H, *H*CCH$_2$OH); $^{13}$C NMR (C$_5$D$_5$N) 134.25 (*m*-C), 132.65 (*p*-C), 129.29 (*o*-C), 72.40 (*Z*-*C*H$_2$CHCH(CH$_2$OH)), 68.00 (HOCH$_2$CH*C*H$_2$), 64.60 (*E*-*C*H$_2$CHCH(CH$_2$OH)), 63.01 (CH$_2$OH), 49.95 (*C*HCH$_2$OH), 42.11 (H*C*(CH$_2$O)$_2$Ge): Anal. Calcd for C$_{12}$H$_{16}$GeO$_4$: C, 48.55; H, 5.39. Found: C, 48.40; H, 5.49.

**15**: $^1$H NMR (C$_5$D$_5$N) 6.39 (s, 1 H, OH), 3.76–4.56 (m, 8 H, CH$_2$O), 2.63 (m, 1 H, *H*C(CH$_2$O)$_2$Ge), 2.34 (m, 1 H, *H*CCH$_2$OH); $^{13}$C (C$_5$D$_5$N): 72.08 (*Z*-*C*H$_2$CHCH(CH$_2$OH)), 67.52 (HOCH$_2$CH*C*H$_2$), 64.30 (*E*-*C*H$_2$CHCH(CH$_2$OH)), 62.99 (CH$_2$OH), 49.97 (H*C*CH$_2$OH), 49.91 (H*C*CH(CH$_2$OH)), –4.05 (CH$_3$). Anal. Calcd for C$_7$H$_{14}$GeO$_4$: C, 48.55; H, 5.39. Found: C, 48.40; H, 5.49.

**Generation of Anions 16 and 17.** To separate solutions of **14** (0.84 mg, 0.028 mmol) and **15** (1.02 mg, 0.0434 mmol) in 0.50 mL of C$_5$D$_5$N in NMR tubes were added 9.2 mg (0.042 mmol) and 1.43 mg (0.0651 mmol), respectively, of **13**. C$_5$D$_5$N was used as the solvent because of the insufficient solubility of **14** and **15** in less polar NMR solvents.

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(14) Thus the *meta* protons shifted 0.74 ppm downfield, while the other three protons remained at about the same position. The *meta* $^{13}$C resonance also shifted downfield (by 3.10 ppm), while upfield shifts were noted for the *para* (3.36 ppm) and *ortho* (0.38 ppm) carbons. The resonance of the *ipso* carbon was not observed.

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