Inversion Barriers of Methylsilole and Methylgermole Monoanions

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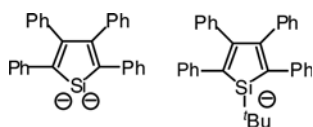
Density functional MO calculations for the methylsilole anion of $[C_4H_4SiMe]^-$ and methylgermole anion of $[C_4H_4GeMe]^-$ at the B3LYP (full)/6-311+G* level (GAUSSIAN 94) were carried out and characterized by frequency analysis. The ground state structure for the methylsilole anion and methylgermole anion is that the methyl group is pyramidalized with highly localized structure. The difference between the calculated C_α-C_β and C_β-C_β distances are 9.4 and 11.5 pm, respectively. The E-Me vector forms an angle of 67.9° and 78.2° with the C_4E plane, respectively. The optimized structures of the saddle point state for the methylsilole anion and methylgermole anion have been also found as a planar with highly delocalized structure. The optimized C_α-C_β and C_β-C_β distances are nearly equal for both cases. The methyl group is located in the plane of C_4E ring and the angle between the E-Me vector and the C_4E plane for the methylsilole anion and methylgermole anion is 2.0° and 2.3°, respectively. The energy difference between the ground state structure and the transition state structure is only 5.1 kcal mol^{-1} for the methylsilole anion. However, the energy difference of the methylgermole anion is 14.9 kcal mol^{-1}, which is much higher than that for the corresponding methylsilole monoanion by 9.8 kcal mol^{-1}. Based on MO calculations, we suggest that the head-to-tail dimer compound, **4**, result from [2+2] cycloaddition of silicon-carbon double bond character in the highly delocalized transition state of **1**. However, the inversion barrier for the methylgermole anion is too high to dimerize.

Key Words : Silole monoanion, Germole monoanion, Inversion barrier, Ground state, Transition state

Introduction

A great deal of interest has recently focused on the exploration of the chemistry of the anions of siloles and germoles, their structure, bonding, reaction, and aromaticity leading to novel optical properties for a variety of applications.[1-14] Analogous of cyclopentadiene, siloles and germoles are π-electron systems containing a single silicon or germanium atom as part of a cyclic 5-membered ring. Characteristic features of siloles include a low reduction potential and a low-lying LUMO due to σ*-π* conjugation arising from the interaction between the σ* orbital of silicon, and the π* orbital of the butadiene moiety of the five membered ring.[16,17] Since silole and germole dianions $(RC)_4Si^{2-}$ and $(RC)_4Ge^{2-}$, R=Ph and Me, have been studied by X-ray crystallography,[3-6] siloles and germoles are of considerable current interest, both because of their unusual electronic and optical properties[18,19] and because of their possible application as electron transporting materials in devices[20] such as light-emitting diodes (LED's)[9,21,23] or in chemical sensors.[24,25] X-ray crystal structures of $[Li^+_2(THF)_5][C_4Ph_4Si^{2-}]^{[3]}$ and $[K(18$-crown-$6)^+]_2[C_4Me_4Si^{2-}]^{[5]}$ indicate that the silole dianions are highly delocalized and aromatic.

Tilley *et al.* have reported highly localized X-ray structure of the lithium salt of the germole anion, $[C_4Me_4GeSi(SiMe_3)_3]^-$ and the potassium salt of silole monoanion $[K(18$-crown-$6)][C_4Me_4SiSiMe_3]$.[6] However, Boudgouk *et al.* proposed a delocalized structure of the lithium and sodium salts of the silole anions, $[C_4Ph_4SitBu]^-$, on the basis of its ^{13}C and ^{29}Si NMR spectra, however its crystal structure has not been reported to date.

Experimental

General. All synthetic manipulations were carried out under an atmosphere of dry argon gas using standard vacuum-line Schlenk techniques. All solvents were degassed and purified before use according to standard literature methods: diethyl ether, hexanes, tetrahydrofuran, and toluene were purchased from Aldrich Chemical Co. Inc. and distilled from sodium/benzophenone. All other reagents (Aldrich, Gelest) were used as received or distilled before use. NMR data were collected with Bruker AC-300 MHz spectrometers (300 MHz for ^1H NMR, 75.5 MHz for ^{13}C NMR). The NMR solvent Chloroform-*d* was stirred over CaH_2 for 1 day, transferred by vacuum distillation onto P_2O_5, stirred for 2 h, and then vacuum-distilled for purification. Chemical shifts are reported in parts per million (δ ppm); downfield shifts are reported as positive values from tetramethylsilane (TMS) standard at 0.00 ppm. The ^1H and ^{13}C chemical shifts were referenced relative to $CHCl_3$ (δ = 77.0 ppm) as an internal
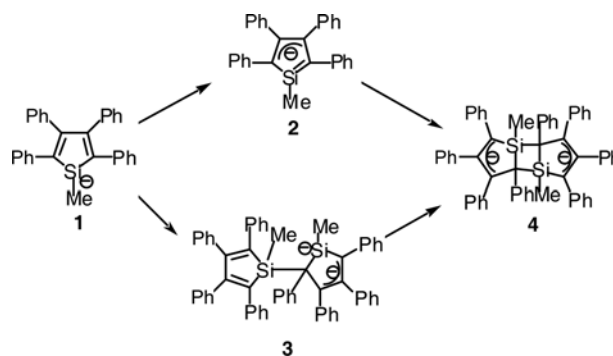
standard. ^{13}C NMR were recorded as proton decoupled spectra. High-resolution electron-impact ionization mass spectrometry was performed on an MS80 Kratos spectrometer.

Preparation of 1-Chloro-1-methyl-2,3,4,5-tetraphenylgermole. Synthesis of 1-chloro-1-methyl-2,3,4,5-tetraphenylsilole (**5**) was modified from the literature,[12] by adding the corresponding methyltrichlorogermane. Diphenylacetylene (17.8 g, 100 mmol) and lithium (1.38 g, 200 mmol) were stirred in diethyl ether (150 mL) at room temperature for 3.5 h. The reaction gave a brown solution and a yellow precipitate. The solution was frozen with a bath of liquid nitrogen, after removal of lithium metal. MeGeCl$_3$ (10 g, 52 mmol) was added by a syringe in one portion. The mixture was kept at −196 °C for 5 min before the cooling bath was removed, and the solution was allowed to warm up slowly to room temperature, and stirred for 4 h to give a yellow solution. The solution was cannulated, concentrated, and crystallized at −20 °C to give product as yellow crystals (20.4 g, 85%). mp 197-198 °C. Selected data; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.81-6.85 and 6.95-7.15 (br m, 20H, Ph); ^{13}C{H} NMR (75.4 MHz, CDCl$_3$) δ 151.73, 137.90, 137.45, 137.39, 129.75, 129.18, 128.15, 127.73, 126.78, 126.65, 3.08; MS (EI): *m/z* (%): 480 (35) [M$^+$], 356 (83) [M$^+$-GeMeCl]. High-resolution MS: calcd. for C$_{28}$H$_{20}$GeCl$_2$ 480.0706 found 480.0705.
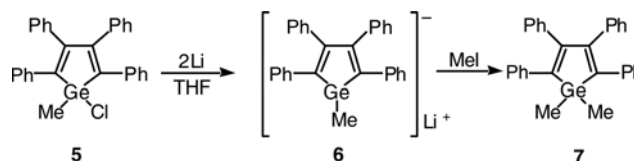
Preparation of the Lithium Salt of 1-Methyl-2,3,4,5-tetraphenylgermole Monoanion (6) and 1,1-Dimethyl-2,3,4,5-tetraphenylgermole (7). A solution of C$_4$Ph$_4$GeMeCl (4.79 g, 10 mmol) in THF (130 mL) was placed with 2 equiv of Li (0.139 g, 20 mmol) at −78 °C under an argon atmosphere. After removal of the dry-ice/acetone bath, the mixture was stirred for 12 h at room temperature. The color of the solution slowly changed to a red violet, which is germole monoanion **6**. An excess of iodomethane was added slowly to a solution of **6** (10 mmol) in THF (130 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for 2 h. Then the volatiles were removed under under reduced pressure. The residue was extracted with pentane (100 mL) and filtered. Green crystals of **7** (quantitative yield) were obtained after the solution was concentrated and cooled to −10 °C. mp 180-181 °C. Selected data for **7**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.79-7.12 (br m, 20H, Ph), 0.66 (s, 6H, CH$_3$); ^{13}C{H} NMR (75.4 MHz, CDCl$_3$) δ 151.19, 143.88, 140.29, 139.83, 130.10, 128.84, 127.88, 127.41, 125.99, 125.51, 2.54 (Me$_3$); MS(EI): *m/z* (%): 460 (40) [M$^+$], 356 (13) [M$^+$-GeMe$_2$]. High-resolution MS: calcd. for C$_{30}$H$_{26}$Ge 460.1255, found 460.1270.

Results and Disscussion

We have been reported that the methylsilole anion [C$_4$Ph$_4$SiMe]$^-$ dimerized to the tricyclic diallylic dianion [C$_4$Ph$_4$SiMe]$_2$$^{2-}$. The dimerization could take place either *via* nucleophilic attack of silicon of one monoanion on the α-carbon of another, followed by ring closure or through [2+2] cycloaddition in the mesomeric forms having Si=C double

Scheme 1. Conversion of methylsilole anion [C$_4$Ph$_4$SiMe]$^-$.

Scheme 2. Reduction of 1-chloro-1-methyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene (**5**).

bond character of methylsilole monoanion[26] (Scheme 1).

Therefore, the investigation of the 1-methyl-2,3,4,5-tetraphenylgermole monoanion **6**; Li[C$_4$Ph$_4$GeMe] seemed of interest. 1-chloro-1-methyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene (**5**) is readily available from 1,1-dilithio-2,3,4-tetraphenylbuta-1,3-diene with MeGeCl$_3$, since this dilithium compound can be easily obtained directly from diphenylacetylene and lithium. The reduction of **5** with 2 equiv Li given in Scheme 2 gave the corresponding germole monoanion **6**. Although crystals of **6** were obtained from the dioxane solution, their quality was not good enough for X-ray crystallography. In contrast to silole monoanions **1**, no evidence for the dimerization of the germole monoanion **6** was obtained. The derivatization of germole monoanion **6** with iodomethane gave 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene (**7**) in quantitative yield.

To aid in understanding the reaction, we carried out density functional MO calculations for the silole anion of [C$_4$H$_4$SiMe]$^-$, **8a** and **8b**, at the B3LYP (full)/6-311+G* level (GAUSSIAN 94)[12] and characterized by frequency anaysis (Figure 1). The ground state structure, **8a**, is that the methyl group is pyramidalized with highly localized structure. The calculated C$_\alpha$-C$_\beta$ and C$_\beta$-C$_\beta$ distances are 136.6 and 146.0 pm respectively. The Si-Me vector forms an angle of 67.9° with the C$_4$Si plane. The optimized structure of the saddle point state, **8b**, has been also found as a planar with highly delocalized structure. The optimized C$_\alpha$-C$_\beta$ and C$_\beta$-C$_\beta$ distances of 142.2 and 141.0 pm are nearly equal. The methyl group is located in the plane of C$_4$Si ring and the angle between the Si-Me vector and the C$_4$Si plane is just 2.0°. However, the energy difference between the ground state structure and the transition state structure is only 5.1 kcal mol^{-1}. This inversion barrier is slightly higher than that for [C$_4$H$_4$SiH]$^-$ by 1.3 kcal mol^{-1},[2] but somewhat lower than the measured value for trimethylsilylsilole monoanion in

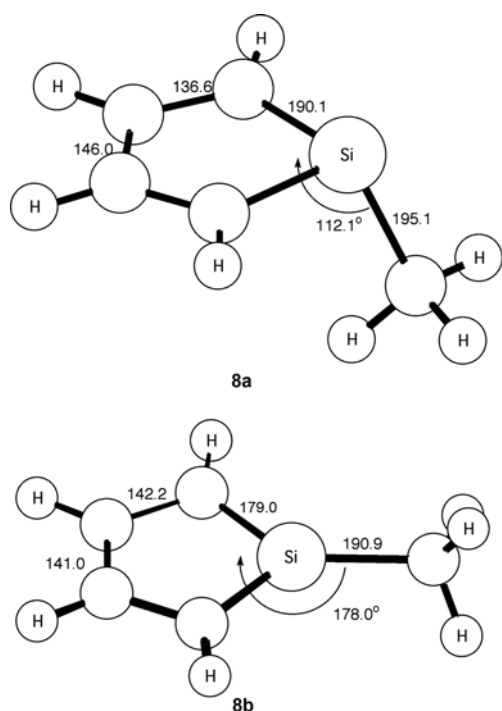**Figure 1.** Ground state structure (**8a**) and transition state structure (**8b**) for $[C_4H_4SiMe]^-$.

Figure 2. Ground state structure (**9a**) and transition state structure (**9b**) for $[C_4H_4GeMe]^-$.

$[Li(12\text{-crown-}4)_2][C_4Et_4SiSiMe_3]$, by 3.3 kcal mol^{-1}.[7] Based on MO calculations, we suggest that the head-to-tail dimer compound, **4**, result from [2+2] cycloaddition of silicon-carbon double bond character in the highly delocalized transition state of **1**.

An earlier calculation for the silole monoanion $[C_4H_4SiH]^-$ also gave a structure which was pyramidal at silicon.[1] Goldfuss and Schleyer reported that the planar structure of $[C_4H_4SiH]^-$ was calculated to be less stable than its pyramidal structure by 3.8 kcal mol^{-1} at the RMP2(fc)/6-31+G** level[10] and 5.83 kcal mol^{-1} at the B3LYP/6-31+G*(C,H), LanL2DZdp (E) level, respectively.[11] Recently, inversion barriers in trimethylsilylsilole and germole anions were determined by NMR spectroscopy.[7] Barriers for the germole monoanions $[Li(12\text{-crown-}4)_2][C_4Et_4GeSiMe_3]$ (10.5 kcal mol^{-1}) and $K[C_4Et_4GeSiMe_3]$ (9.4 kcal mol^{-1}) were higher than those for corresponding silole monoanions by 2.1 and 1 kcal mol^{-1}, respectively.

We also calculated inversion barriers for the methylgermole monoanions ($[C_4H_4GeMe]^-$; **9**) at the B3LYP/6-311+G* level (GAUSSIAN 94).[12] The ground state structure of methylgermole monoanion **9a** and the planar structure of transition state **9b** shown in Figure 2 were also optimized at the same level calculated for methylsilole monoanion **8** and characterized by frequency analysis. We also found similar trend for the methylgermole monoanion **9**. In the ground state structure of methylgermole monoanion **9a**, shown in Figure 2, the germanium atom is pyramidalized, and the C-C bond distances are different (135.5 and 147.0 pm) indicating localization in the five-membered ring. The Ge-Me vector forms an angle of 78.2° with the C$_4$Ge plane. In contrast, a
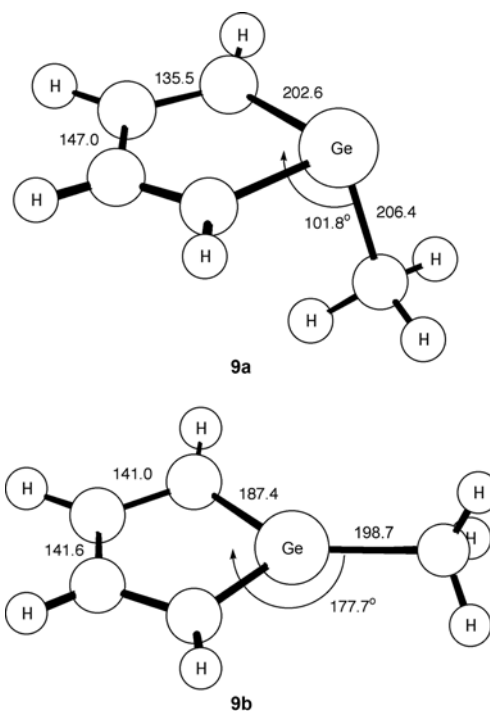
Table 1. Bond distances (pm) and angles (**T**, deg) of between M-Me vector and mean MC$_4$ Ring

	M-C$_\alpha$	C$_\alpha$-C$_\beta$	C$_\beta$-C$_\beta$	**T**
8a	190.1	136.6	140.0	67.9
8b	179.0	142.2	141.0	2.0
9a	202.6	135.5	147.0	78.2
9b	187.4	141.0	141.6	2.3

Table 2. Calculated total energies (au) and inversion barriers (kcal mol^{-1})

	Total energy	Inversion barrier
8a	-484.2845	
8b	-484.2762	5.14
9a	-2271.7817	
9b	-2271.7580	14.90

planar structure with delocalization was observed for the saddle point state structure **9b**. The optimized C$_\alpha$-C$_\beta$ and C$_\beta$-C$_\beta$ distances of 141.0 and 141.6 pm are nearly equal. (see Table 1) However, the inversion barrier for **9** is 14.9 kcal mol^{-1}, which is much higher than that for the corresponding methylsilole monoanion **8**, by 9.8 kcal mol^{-1}.

Conclusion

To aid in understanding the reaction, density functional calculations for the methylsilole and methylgermole anion were carried out. The ground state structure for the methylsilole anion and methylgermole anion indicates that the

methyl group with five-membered ring is pyramidalized with highly localized structure. The E-Me vector forms an angle of 67.9° and 78.2° with the C_4E plane, respectively. The optimized structures of the saddle point state for the methylsilole anion and methylgermole anion have been found as a planar with highly delocalized structure. The energy difference between the ground state structure and the transition state structure is only 5.1 kcal mol^{-1} for the methylsilole anion. However, the higher energy difference of 14.9 kcal mol^{-1} is obtained for the methylgermole anion. Based on MO calculations, we suggest that the head-to-tail dimer compound results from [2+2] cycloaddition of silicon-carbon double bond character in the highly delocalized transition state of silole monoanion, but the higher inversion barrier prohibits the dimerization of the methylgermole anion.

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