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# Reduction of 1-Chloro-1,2,3,4,5- pentaphenylsilole

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조선대학교 대학원

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# Reduction of 1-Chloro-1,2,3,4,5- pentaphenylsilole

지도교수 조 성 동

이 논문을 이학석사학위 논문으로 제출함.

2004년 10월 일

조선대학교 대학원

화 학 과

박 재 흥

# 박재홍의 석사학위논문을 인준함

위원장    조선대학교 전임강사    손홍래 (인) 

위원        조선대학교        교수    고문주 (인) 

위원        조선대학교        교수    조성동 (인) 

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조선대학교 대학원

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## ABSTRACT

Reduction of 1-Chloro-1,2,3,4,5-pentaphenylsilole;

Park, Jae-Heung

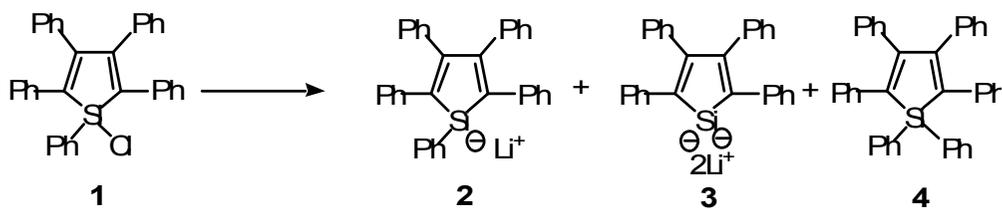
Advisor : Prof. Sung-Dong Cho, Ph. D.

Department of Chemistry,

Graduate School of Chosun University

The reduction of 1-chloro-1,2,3,4,5-pentaphenylsilole, ( $C_4Ph_4SiPhCl$ , **1**) with 2 equiv. lithium gave the pentaphenylsilole anion [ $C_4Ph_4SiPh$ ]<sup>-</sup> (**2**), silole dianion [ $C_4Ph_4Si$ ]<sup>2-</sup> (**3**), and hexaphenylsilole  $C_4Ph_4SiPh_2$  (**4**). **2**, **3**, and **4** from the reaction mixture were characterized by <sup>29</sup>Si NMR spectroscopy. The <sup>29</sup>Si chemical shift of 3.7 ppm for **2** is shifted upfield as compared to that of previously reported t-butyltetraphenylsilole anion Li[ $C_4Ph_4Si^tBu$ ], but shifted downfield compared to that of the other silole monoanion such as Li[ $C_4Me_4SiSiMe_3$ ], indicating the delocalization of silole anion through the 5-membered ring. Derivatization of the reaction mixture with iodomethane gave  $C_4Ph_4SiPh_2$  (**4**),  $C_4Ph_4SiMePh$  (**5**), and  $C_4Ph_4SiMe_2$  (**6**), which were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy.

The silole dianion **3** could be either from the continuous reduction of **1** with lithium or from the disproportionation of **2**. The reduction of **1** with excess lithium in THF gave the silole dianion  $[\text{C}_4\text{Ph}_4\text{Si}]^{2-}$  in about 70% yield.



## I. Introduction

Metalloles are silicon or germanium-containing cyclic 5-membered ring p-electron systems. Since silole and germole dianions  $(RC)_4Si^{2-}$  and  $(RC)_4Ge^{2-}$   $R=Ph$  and  $Me$ , have been studied by X-ray crystallography and found to be extensively delocalized, metalloles (siloles and germoles) are of considerable current interest, both because of their unusual electronic and optical properties and because of their possible application as electron transporting materials in devices such as light-emitting diodes (LED's) or in chemical sensors. Polysilanes or polygermanes containing a metal-metal backbone absorb in the near UV region, emit in the visible with nearly unit quantum yields, and exhibit high hole mobility, and high nonlinear optical susceptibility, which makes them efficient photoemission candidates for a variety of optoelectronics applications. These properties arise from delocalization along the M-M backbones and confinement of the conjugated electrons along the backbone.

The most characteristic feature of polymetalloles and metallole-silane copolymers is a low reduction potential and a low-lying LUMO due to conjugation arising from the interaction between silicon or germanium, and the butadiene moiety of the five membered ring. In addition, the M-M backbones exhibit delocalization, which delocalizes the conjugated electrons along the backbone. Electron delocalization in these polymers provides a means of amplification, because interaction of an analyte molecule at any position along the polymer chain is communicated throughout the chain. Polymetalloles have Si-Si backbones

on the inside of a cylindrical wire and a conjugated ring system of side chains closely packed on the outside. A similar means of amplification is available to quantum-confined semiconductor nanocrystallites, three-dimensional silicon network instead of linear silicon wire, where the electron and hole wavefunctions are delocalized throughout the nanocrystal.

In recent times, a considerable amount of interest has developed with regard to anions of siloles and their structure, bonding, reaction, and possible aromaticity leading to novel optical properties for a variety of applications [1-14]. Analogous of cyclopentadiene, siloles are  $\pi$ -electron systems containing a single silicon 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  $\sigma^*$ - $\pi^*$  conjugation arising from the interaction between the  $\sigma^*$  orbital of silicon, and the  $\pi^*$  orbital of the butadiene moiety of the five membered ring [15,16]. Since silole and germole dianions  $(RC)_4Si^{2-}$  and  $(RC)_4Ge^{2-}$ , R=Ph and Me, were initially studied by X-ray crystallography [3-6], siloles and germoles have received growing attention, both because of their unusual electronic and optical properties [17,18] and because of their possible application as electron transporting materials in devices [19] such as light-emitting diodes (LEDs) [20-22] or in chemical sensors [22,24].

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. In contrast, several crystal structures of silole monoanion have been published and showed the localization of 5-membered ring. For example,  $[K(18-crown-6)][C_4Me_4SiSiMe_3]$  [6] has a localized structure. Only one silole monoanion  $Li[C_4Ph_4Si^tBu]$  has been

published as a delocalized structure by the interpretation of  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR data [**7a**], however its crystal structure has not been reported to date.



Recently, it has been reported that the methylsilole anion  $[\text{C}_4\text{Ph}_4\text{SiMe}]^-$  dimerized to the tricyclic diallylic dianion  $[\text{C}_4\text{Ph}_4\text{SiMe}]_2^{2-}$  by head-to-tail, 2+2 cycloaddition [**25**]. The possible mechanism for the tricyclic diallylic dianion could take place in the mesomeric forms having Si=C double bond character of methylsilole monoanion. In addition, the reduction of methylsilole  $[\text{C}_4\text{Ph}_4\text{SiMeH}]$  would involve the presence of the equilibrium between carboanion and silyl anion [**26**]. Therefore, it seems of interest to investigate the pentaphenylsilole monoanion.

Synthetic routes for various metalloles and their dianions and monoanions containing a t-butyl group as a substituent on the metal atom have been reported. Although many synthetic routes for siloles and germoles have been reported, few are known for dihalogen- or monohalogenmetalloles. 1,1-dichloro-2,3,4,5-tetraphenylsilole is readily available from 1,4-dilithio-1,2,3,4-tetraphenylbuta-1,3-diene and  $\text{SiCl}_4$ , since the lithium compound can be easily made directly from diphenylacetylene and lithium. The 1,1-dibromo-2,3,4,5-tetramethylsilole was synthesized by Fagan from 1,1-bis( $\eta^5$ -cyclopentadienyl)-2,3,4,5-tetramethyl-1-zirconacyclopenta-2,4-diene and  $\text{SiBr}_4$ , but the yield was

very low and the product could not be isolated pure. Fagan and coworkers also tried to obtain the 1,1-dichloro-2,3,4,5-tetramethylsilole by a similar transmetallation reaction using silicon tetrachloride instead of the tetrabromide, but  $\text{SiCl}_4$  displayed no reactivity towards

Siloles are of considerable current interest, both because of their unusual electronic properties and because of their possible application as electron-transporting materials in devices such as light-emitting diodes (LED's). Siloles exhibit a low reduction potential and a low-lying LUMO energy level, attributed to  $\sigma^*-\pi^*$  conjugation arising from the interaction between the  $\sigma^*$  orbital of the  $\sigma$ -bonded silicon atom and the  $\pi^*$  orbital of the butadiene moiety of the ring.

In contrast to siloles, polysilanes display low oxidation potentials and a high-lying HOMO, resulting from  $\sigma$ -delocalization along the Si-Si chain. A combined polysilane-polysilole might then be of special interest, since it could provide both electron-donating and electron-accepting properties within the same molecule. And in fact, silole-polysilane copolymers have been synthesized, both in our laboratories and by Sakurai and coworkers, and shown to have electroluminescent properties.

First example of a polysilole, in which every silicon atom in the polymer chain is part of a silole ring has been reported. This polymer was easily obtained from the readily-available compound, 1,1-dichlorotetraphenylsilole by reduction with lithium, sodium or potassium, in > 30 % yield. The molecular weight and yield of polysilole depended only slightly on the nature of the alkali metal. From its molecular weight ( $M_n$  6000,  $M_w/M_n = 1.1$  determined by SEC,

confirmed by end-group analysis) is actually an extended oligomer with a degree of polymerization of about 15, rather than a high polymer. Nevertheless it shows polymer-like properties, and in particular it can be cast into a thin film from solution. In the UV-vis absorption spectrum, polysilole has two absorptions at 325 and 370 nm, assigned to the  $\sigma\text{-}\sigma^*$  transition of the silicon-silicon backbone chain and the  $\pi\text{-}\pi^*$  transition of the silole ring. Polysilole show emission in the visible, near 520 nm Polysilole is strongly electroluminescent, with similar emission.

The electroluminescent spectrum of polysilole acting as a single-component LED has been reported. The silole rings in both dichlorobissilole and dichlorotrissilole are arranged in an all-gauche conformation along the Si-Si bond skeleton. The dihedral angles of  $58.36^\circ$  and  $C_{32}\text{-Si}_2\text{-Si}_3\text{-C}_{60}$  of  $61.08^\circ$ , show that the silole rings are strongly rotated relative to one another. The structure of dichlorotrissilole differs from that of the related but less hindered tersilole and quatersilole reported by Tamao which have gauche-trans and gauche-trans-gauche arrangements of the silole rings, as well as the permethyl-tersilole reported by Kira and coworkers, which has a trans-trans relationship between the silole rings. Tersilole may be a better model for the conformation of polysilole if so, the polymer could have a helical arrangement of the silole rings.

The synthesis, spectroscopic characterization, and fluorescence quenching efficiency of polymers and copolymers containing tetraphenylsilole or tetraphenylgermole with Si-Si, Ge-Ge, and Si-Ge backbones were reported. Poly(tetraphenyl)germole was synthesized from the reduction of dichlorotetraphenylgermole with 2 equiv. Li. Silole-germole alternating copolymer was synthesized from coupling of dilithium salts of tetraphenylsilole dianion with dichlorotetraphenylgermole. Other tetraphenylmetallole-silane copolymers were synthesized through the Wurtz-type coupling of the dilithium salts of the tetraphenylmetallole dianion and corresponding dichlorodialkylsilanes.

The molecular weight ( $M_w$ ) of these metallole-silane copolymers are in the range of 4,000~6,000. Detection of nitroaromatic molecules such as nitrobenzene (NB), 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), and picric acid (PA) were reported. The detection method involves measurement of the quenching of photoluminescence of a toluene solution of polymetalloles or metallole-silane copolymers by the analyte. A linear Stern-Volmer relationship was observed in the first three cases, but not for picric acid. Fluorescence spectra of polymetalloles or metallole-silane copolymers from either toluene solutions or thin polymer films displayed no shift in the maximum of the emission wavelength. This suggests that the polymetalloles or metallole-silanes exhibit neither  $\pi$ -stacking of polymer chains nor excimer formation.

The relative efficiency of photoluminescence quenching of metallole copolymers are characteristic for TNT, DNT, and nitrobenzene, respectively, as indicated by the values of  $K$  determined from the slopes of the steady-state Stern-Volmer plots. Sensitivity of

polymetalloles or metallole-silane is in order of PA > TNT > DNT > NB. These results indicate that the specificity of analyte can be determined by the arrays of different fluorescent sensory materials. A plot of log K vs reduction potential of analytes (NB, DNT, and TNT) for each polymetallole or metallole-silane exhibits a linear relationship, indicating that the mechanism of quenching is attributable to electron transfer from the excited metallole copolymers to the LUMO of the analyte.

Chemical sensors for nitroaromatics which offer a new approaches to the rapid detection of ultra-trace analytes from explosives, have attracted a great deal of attention in recent years, because explosives are extremely important chemical species to detect in mine fields, military applications, remediation sites, and homeland security applications. It is also important in forensic investigations such as post-blast residue determinations. Metal detectors, which offer portable instrumentation for field explosive detection, cannot locate the plastic casing of modern land mines. Trained dogs are expensive, difficult to maintain and are easily tired. Physical detection methods for explosives include the gas chromatography coupled with a mass spectrometer, surface-enhanced Raman, nuclear quadrupole resonance, energy-dispersive X-ray diffraction, neutron activation analysis, electron capture detection, and cyclic voltammetry. These techniques are highly selective, but they are expensive and not easily fielded in a small, low-power package.

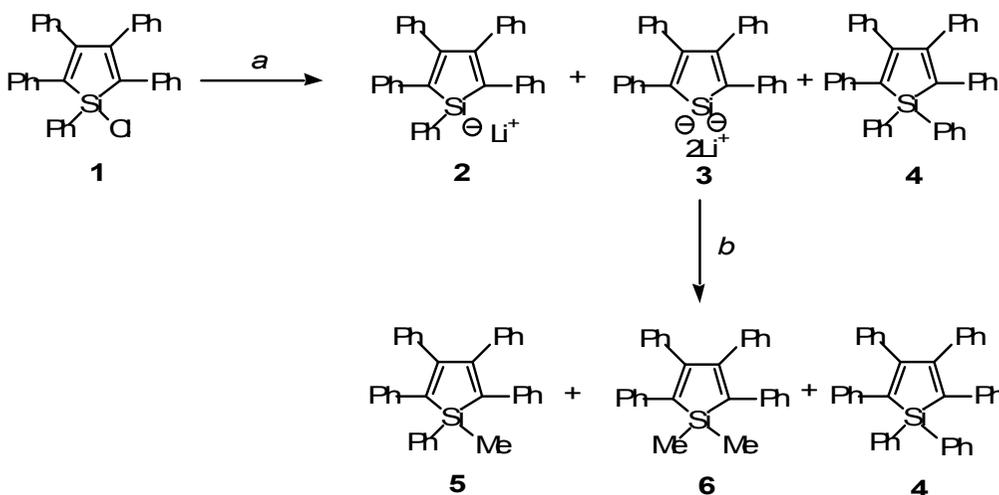
Most detection methods for explosives are only applicable to air samples due to interference problems encountered in complex aqueous

media. Sensing TNT and picric acid in groundwater or seawater is important for the detection of buried unexploded ordnance and for locating underwater mines. There are also environmental applications for characterizing soil and groundwater contaminated with toxic TNT at military bases and munitions production and distribution facilities. Organic polymers and optical fibers have been previously studied to detect vapors of explosive analytes. The transduction methods used include absorption, fluorescence, conductivity, etc. Such simple techniques are promising because they can be incorporated into inexpensive and portable microelectronic devices.

For example, a chemically selective silicone polymer layer on SAW (surface acoustic wave) device has been shown to provide efficient detection for the nitroaromatic compounds. Recently, it was reported that the fluorescence of pentiptycene polymers and polyacetylene are highly sensitive to nitroaromatic molecules. However, these polymers require many steps to synthesize. Previously we communicated that the inorganic polysilole is an excellent material for the detection of explosives. The sensors are based on photoluminescence quenching of polymers containing metal-metal backbones such as Si-Si, Si-Ge, and Ge-Ge bond.

## II. Result and discussion

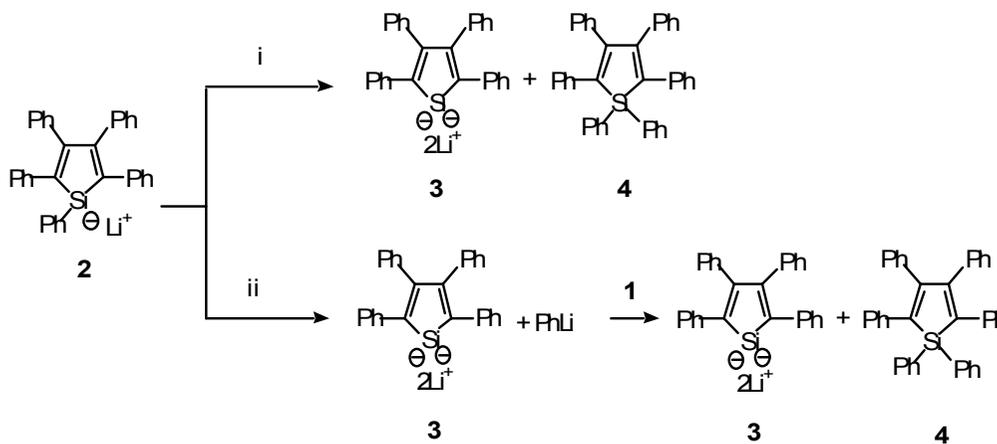
Herein the reduction of 1-chloro-1,2,3,4,5- pentaphenylsilole, ( $C_4Ph_4SiPhCl$ , **1**) to the pentaphenylsilole anion [ $C_4Ph_4SiPh$ ] $^-$  (**2**), and the derivatization products;  $C_4Ph_4SiPh_2$  (**4**),  $C_4Ph_4SiMePh$  (**5**), and  $C_4Ph_4SiMe_2$  (**6**) is reported. The reduction of **1** with 2 equiv. of lithium in THF at  $-78^\circ C$  gave a dark red solution. The addition of excess iodomethane to the solution produced mixture products of **4**, **5**, and **6**. The derivatization products **4**, **5**, and **6** were separated by preparative scale size exclusion chromatography and characterized by  $^1H$ ,  $^{13}C$ , and  $^{29}Si$  NMR spectroscopy.



**Scheme 1.** Reduction of  $C_4Ph_4SiPhCl$ , **1**, with 2 equiv. lithium.  
Reagents and conditions a)  $2Li/THF/-78^\circ C - RT/2h$ ; b) excess  $MeI/THF/-78^\circ C - RT/3h$ ;

The isolated yield of the products **4**, **5**, and **6** is 25%, 13%, and 25%, respectively. The ratio of isolated product distribution of **4** : **5** : **6**

is **2** : **1** : **2**, showing that the formation quantity of silole dianion **3** and hexaphenylsilole **4** is equal. The silole dianion **3** could be either from the continuous reduction of **1** with lithium or from the disproportionation of **2**. Figure 1 shows two possible mechanisms, over-reduction and disproportionation. Disproportionation exhibits the equal formation of silole **3** and **4**. However, the formation of the diphenylsilole **4** may result from the reaction of **1** with phenyllithium, which is produced during the over-reduction of **2** to the silole dianion **3**. This mechanism would also produce **3** and **4** in equal amounts. We are not able to observe the phenyl derivative. Therefore, any mechanisms are not ruled out at this stage.

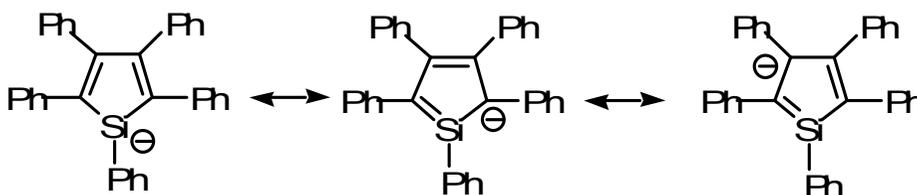


**Figure 1.** Two possible mechanisms for the equal formation of **3** and **4**: i) disproportionation, ii) over-reduction

While silole **5** forms after quenching, indicating the presence of the pentaphenylsilole anion **2**, the silole **6** is expected from the silole dianion  $[\text{C}_4\text{Ph}_4\text{Si}]^{2-}$  (**3**). Using a 10 mm NMR tube containing **1** (0.248 g, 0.50 mmol) and lithium (0.007 mg, 1.0 mmol) in THF- $d_8$ ,  $^{29}\text{Si}$  NMR

study was carried out for the dark red solution.  $^{29}\text{Si}$  NMR spectrum of dark red solution showed three  $^{29}\text{Si}$  resonances signals at 67.0, 3.7, and 6.0 ppm which shows the presence of silole dianion **3**, silole anion **2**, and hexaphenylsilole  $\text{C}_4\text{Ph}_4\text{SiPh}_2$  (**4**), respectively. Silole dianion **3** and hexaphenylsilole **4** were independently synthesized and characterized by  $^{29}\text{Si}$  NMR spectroscopy, and gave the two  $^{29}\text{Si}$  chemical shifts of 67.0 and 6.0 ppm for silole dianion **3** and hexaphenylsilole **4**, respectively.

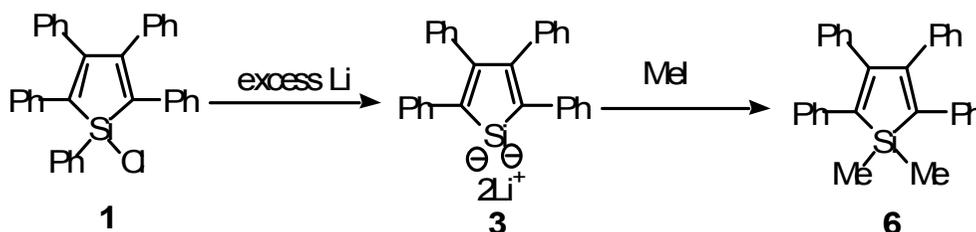
The  $^{29}\text{Si}$  chemical shift of 3.7 ppm for **2** is shifted upfield as compared to that of previously reported *t*-butyltetraphenylsilole anion  $\text{Li}[\text{C}_4\text{Ph}_4\text{Si}t\text{Bu}]$  (25.1 ppm) [7], but shifted downfield compared to that of the other silole monoanion such as  $\text{Li}[\text{C}_4\text{Me}_4\text{SiSiMe}_3]$  (-45.38 ppm) [6]. It is believed that this is caused by the delocalization of silole anion through the 5-membered ring. It should be noted that one of the products observed after quenching is the silole dianion **3** that is formed as a result of cleavage of Si-C bond of the phenyl-silicon moiety.



Methylsilole anion  $[\text{C}_4\text{Ph}_4\text{SiMe}]^-$  dimerized to the tricyclic diallylic dianion  $[\text{C}_4\text{Ph}_4\text{SiMe}]^{2-}$  by head-to-tail, 2 + 2 cycloaddition [25], which means that the anion of **8** is delocalized over the silicon-containing cyclic 5-membered ring. However, the dimerization of pentaphenylsilole anion,  $[\text{C}_4\text{Ph}_4\text{SiPh}]^-$  (**2**), did not take place. Possible

reasons for this are that **2** is less nucleophilic than  $[\text{C}_4\text{Ph}_4\text{SiMe}]^-$  and that the steric hindrance of phenyl group at silicon in **2** is too large to allow dimerization. Unfortunately, attempts to obtain crystals of **2** for the X-ray analysis were not successful.

The reduction of **1** with excess lithium in THF also gave dark red solution (Scheme 2). However, after removal of unreacted lithium, the derivatization of reaction mixture with iodomethane gave **6** in about 70% yield, respectively. The  $^{29}\text{Si}$  NMR spectrum of latter solution gave only single resonance at 67 ppm that is the silole dianion **3**. The pentaphenylsilole anion **2** and hexaphenylsilole **4** can be further reduced to give silole dianion **3** in latter reaction, due to the good leaving group of phenyl moiety in pentaphenylsilole anion **2**.



**Scheme 2** Reduction of **1** with excess Li

Although the standard synthetic route for the formation of silole dianion is via the dehalogenation of dihalosiloles, the observation that monohalogenated silole also results in the formation of a silole dianion represents a new synthetic route to the silole dianion via slightly more air stable monohalogenated silole starting materials.

## III. Experimental

### 3.1 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, hexane, 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, 400, or 500 MHz spectrometers (300.1 MHz for  $^1\text{H}$  NMR, 75.5 MHz for  $^{13}\text{C}$  NMR and 99.2 MHz for  $^{29}\text{Si}$  NMR).

The NMR solvent THF- $d_8$  was purified by vacuum distillation from Na/K alloy. Chloroform- $d$  was stirred over  $\text{CaH}_2$  for 1 day, transferred by vacuum distillation onto  $\text{P}_2\text{O}_5$ , stirred for 2 h, and then vacuum-distilled for purification. Chemical shifts are reported in parts per million ( $\delta$  ppm); downfield shifts are reported as positive values from tetramethylsilane (TMS) standard at 0.00 ppm. The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were referenced relative to  $\text{CHCl}_3$  ( $\delta = 77.0$  ppm) as an internal standard, and the  $^{29}\text{Si}$  chemical shifts were referenced to an external TMS standard.  $^{13}\text{C}$  NMR were recorded as proton decoupled spectra, and  $^{29}\text{Si}$  NMR spectra were acquired using an inverse gate pulse sequence with a relaxation delay of 30 s. High-resolution electron-impact ionization mass spectrometry was performed on an MS80 Kratos spectrometer.

## 3.2 Preparation of 1-chloro-1,2,3,4,5-pentaphenylsilole

1-chloro-1,2,3,4,5-pentaphenylsilole (**1**) and 1,1,2,3,4,5-hexaphenylsilole (**4**), were prepared as described in the literature [12], by adding the corresponding phenyltrichlorosilane and diphenyl dichlorosilane, respectively. 1,1-dithio-2,3,4,5-tetraphenylsilole (**3**) was prepared as described in the literature [3]. The NMR spectra of **6** agreed with those reported earlier [27].

Selected data for **1**:  $^1\text{H}$  NMR (300.133 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.80–7.10 (m, 20H, Ph), 7.35–7.50 and 7.75–7.85 (m, 5H, Ph);  $^{13}\text{C}\{\text{H}\}$  NMR (75.403 MHz,  $\text{CDCl}_3$  ( $\delta$  = 77.00)):  $\delta$  = 126.36(C), 126.91 (C), 127.67 (C), 127.95 (C), 128.48 (C), 129.19 (C), 129.68 (C), 130.22 (C), 131.15 (C), 134.37 (C), 135.64 (C), 137.15 (C), 137.74 (C), 156.26 (C);  $^{29}\text{Si}$  NMR (INEPT, 99.363 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.00. MS(EI):  $m/z$  (%): 496 (24) [ $\text{M}^+$ ], High-resolution MS: calcd. for  $\text{C}_{34}\text{H}_{25}\text{SiCl}$  496.1414 found 496.1432.

### 3.2 Reduction of 1-chloro-1,2,3,4,5-pentaphenylsilole with 2 equiv Li

**1** (2.48 g, 5.0 mmol) and lithium (69 mg, 10 mmol) was stirred in 50 mL of THF at  $-78^{\circ}\text{C}$ , then the solution was allowed to warm up slowly to room temperature and stirred for an additional 2 h to give a dark red solution. The solution was kept at  $-78^{\circ}\text{C}$ . Excess iodomethane (ca. 20 mmol) was added by a syringe in one portion at  $-78^{\circ}\text{C}$ . The mixture was kept at  $-78^{\circ}\text{C}$  for 5 min before the cooling bath was removed, then the solution was allowed to warm up slowly to room temperature and stirred for 3 h to give a yellow solution. Then the volatiles were removed under reduced pressure. The residue was extracted with small portions of toluene (a total of 50 mL) and filtered. The products **4**, **5**, and **6** were separated by preparative size exclusion chromatography. Each solution was concentrated and cooled to  $-20^{\circ}\text{C}$  for the crystallization.

**1,1,2,3,4,5-hexaphenylsilole (4)** greenish-yellow crystals (isolated yield = 25%). Selected data; M.p.  $190 - 191^{\circ}\text{C}$  (lit. 186–187) [9].  $^1\text{H}$  NMR spectra of **4** agreed with those reported earlier [9]  $^{13}\text{C}\{\text{H}\}$  NMR (75.403 MHz,  $\text{CDCl}_3$  ( $\delta = 77.00$ )):  $\delta = 125.61$  (C), 126.35 (C), 127.42 (C), 127.74 (C), 128.23 (C), 128.32 (C), 129.19 (C), 129.96 (C), 130.11 (C), 131.59 (C), 136.08 (C), 138.76 (C), 139.49 (C), 156.72 (C)  $^{29}\text{Si}$  NMR (INEPT, 99.363 MHz,  $\text{CDCl}_3$ ):  $\delta = -5.30$ . High-resolution MS: calcd. for  $\text{C}_{40}\text{H}_{30}\text{Si}$  538.2116 found 538.2112.

**1-methyl-1,2,3,4,5-pentaphenylsilole (5)** greenish-yellow crystals (isolated yield = 13%). Selected data; M.p.  $172 - 173^{\circ}\text{C}$  (lit. 170–171) [9].  $^1\text{H}$  NMR spectra of **5** agreed with those reported earlier [9]  $^{13}\text{C}\{\text{H}\}$

NMR (75.403 MHz, CDCl<sub>3</sub> (δ = 77.00)): δ = 6.51 (CH<sub>3</sub>), 125.55 (C), 126.29 (C), 127.44 (C), 127.79 (C), 128.20 (C), 128.94 (C), 129.79 (C), 129.94 (C), 133.44 (C), 134.59 (C), 138.81 (C), 139.35 (C), 140.53 (C), 155.51 (C) <sup>29</sup>Si NMR (INEPT, 99.363 MHz, CDCl<sub>3</sub>): δ = 1.25.  
High-resolution MS: calcd. for C<sub>35</sub>H<sub>28</sub>Si 476.1960 found 476.1966.

### 3.3 Reduction of 1-chloro-1,2,3,4,5-pentaphenylsilole with excess Li

**1** (2.48 g, 5.0 mmol ) and lithium (276 mg, 40 mmol) was stirred in 50 mL of THF at room temperature for 2 h to give a dark red solution. The solution was cannulated to remove the residual lithium metal. The solution was kept at  $-78^{\circ}\text{C}$ . Excess iodomethane was added by a syringe in one portion at  $78^{\circ}\text{C}$ . The mixture was kept at  $-78^{\circ}\text{C}$  for 5 min before the cooling bath was removed, then the solution was allowed to warm up slowly to room temperature and stirred for 3 h to give a yellow solution. Then the volatiles were removed under reduced pressure. The residue was extracted with hexane and filtered. The solution was concentrated and cooled to  $-20^{\circ}\text{C}$  for the crystallization. The product **6** was isolated in about 70 % yield.

### 3.4 NMR Study of 2

To a 10 mm NMR tube containing **1** (0.248 g, 0.50 mmol) in THF-d<sub>8</sub> was added lithium (0.007 mg, 1.0 mmol), then the NMR tube was sealed under vacuum. The solution was kept at -78°C, then the solution was allowed to warm up to room temperature and stirred for an additional 2 h to give a dark red solution. <sup>13</sup>C NMR spectrum was measured, however it was not clear to analyze the products, respectively. <sup>29</sup>Si NMR (inversed gated decoupling, 99.36 MHz, THF-d<sub>8</sub> / reference; external TMS ):  $\delta = -6.0, 3.7, 67.0$

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## Abstract

Reduction of 1-Chloro-1,2,3,4,5-pentaphenylsilole;

Park, Jae-Heung

Advisor : Prof. Sung-Dong Cho, Ph. D.

Department of Chemistry,

Graduate School of Chosun University

1-Chloro-1,2,3,4,5-pentaphenyl silole을 2당량의 리튬과 반응시켜 환원시키면  $[C_4Ph_4SiPh]^-$ ,  $[C_4PhSi]^{2-}$ ,  $C_4PhSiPh_2$ 를 얻을 수 있다. 반응 혼합물의  $^{29}Si$  NMR의 측정을 통해서 **2**, **3** 과 **4**가 있다는 것을 확인하였다. **2**의  $^{29}Si$ 의 Chemical Shift는 3.7ppm이었고 이는 이미 보고된바 있는 t-butyltetraphenylsilole anion과 비교했을 때 downfield에서 나온 것이었다. 이는 5원자 고리를 통하여 silole anion이 비편재화 되어있음을 암시해준다.

반응 혼합물과 아이오도메테인과 반응시켜서 유도체를 형성하면  $C_4Ph_4SiPh_2$ ,  $C_4PhSiMePh$ 과  $C_4Ph_4SiMe_2$ 가 형성되었음을  $^{29}Si$  NMR과  $^1H$ ,  $^{13}C$ 의 NMR을 통해서 알 수 있었다. Silole dianion인 **3**은 **1**에 Li를 첨가하거나 **2**의 불균등화 반응으로부터 얻어졌다고 생각된다. THF 용매 하에서 **1**과 과량의 Li의 환원반응에 의해서 약 70%의 silole dianion을 얻었다.