

Reactions of 1,1-Dichloro-2,3,4,5-Tetraphenyl-1-Silacyclopentadiene with Magnesium and Lithium

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Abstract

The reaction of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**1**) with magnesium-amalgam in THF gave octaphenyl-1,1'-spirobisilole (**2**), so it was suggested that octaphenyl-1,1'-spirobisilole (**2**) was produced via the corresponding silolylene species

Keywords: Metalloles, Silole, Silolylene, Magnesium, α -Elimination

1. Introduction

The last decades have witnessed tremendous progresses in the field of group 14 metallole dianions and the related metallole anions^[1-6] since the first silole dianion, silole anion, and germole dianion had been reported^[7-10]. In particular the syntheses and characterizations of the silole anion [*1-tert-butyl-SiC₄Ph₄*]¹⁻, the silole dianion [*SiC₄Ph₄*]²⁻, the bissilole dianion [*Ph₄C₄Si-SiC₄Ph₄*]²⁻, and the germole dianion [*GeC₄Ph₄*]²⁻ as aromatic compounds^[9,10], previously considered merely as intangible intermediates, had been the starting points for the exploring synthetic, theoretical, and materials chemistry of group 14 metalloles and their anions^[11-27].

Very recently conspicuous silole dianions {[*SiC₂(SiMe₃)₂C₂Ph₂*]²⁻, [*SiC₂(SiEt₃)₂C₂Ph₂*]²⁻}, silole anion {[*1-mesityl-SiC₂(SiMe₃)₂C₂Ph₂*]¹⁻}, and bissilole dianion {[*Ph₂C₂(Me₃Si)₂C₂Si-SiC₂(SiMe₃)₂C₂Ph₂*]²⁻} were synthesized and characterized by X-ray crystallography as having enhanced aromatic electronic structures due to their trialkylsilyl groups on two α -carbons of the silole rings^[28-30]. Even carben analogue system of silole [*SiC₄Ph₄*] was reported as a base-stabilized silolylene^[31].

For three decades all of group 14 metallole dianions from silole dianion to plumbole dianion have been explored as readily available highly aromatic systems^[5,6]

since the following mesomeric structures were suggested to denote for their electronic characteristics in the pioneering works (Scheme 1)^[8-10]. Nowadays even dilithio group 13 metalloles dianion and dilithio transition metalloles are prepared and characterized as aromatic dianion metalloles^[32].

Until now there are a lot of papers for the reduction of 1,1-dihalo-siloles and germoles with alkali metals^[1,4,5,33]. However, there is no paper for reduction of 1,1-dihalo-siloles/germole with other than alkali metals, except a study for reduction of 1,1-dichloro-germole [*Cl₂GeC₄Ph₄*] with magnesium as long as we know honestly^[34]. Moreover it is very interesting that reaction products of 1,1-dihalo-metalloles are expected to be quite different depending on the reductant, especially magnesium metal.

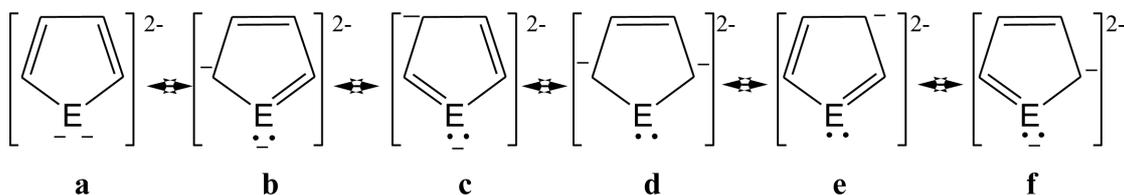
A silyl Grignard reagent of '*Ph₃Si-MgCl*', formed by the interaction between triphenylchlorosilane and cyclohexylmagnesium bromide, was assumed as an intermediate^[35]. Some symmetrically substituted disilanes had been also obtained by the action of magnesium metal upon chlorosilanes where an intermediacy of the '*Si-MgX*' compound formed directly from magnesium and the chlorosilane was presumed as long as at least one phenyl group is substituted on the chlorosilanes^[36,37]. In particular silicon analogues of Grignard compounds, amine-stabilized trimethylsilylmagnesium halides and bis(trimethylsilyl) magnesium, had been synthesized and characterized by X-ray crystallography^[38,39].

Here we report the reduction reaction for the reaction of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene

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Scheme 1. Mesomeric structures of group 14 metalloles dianion.

$[\text{Cl}_2\text{SiC}_4\text{Ph}_4]$ (**1**) with magnesium.

2. Materials and Methods

2.1 Reagents and Instruments

All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Air sensitive reagents were transferred in a nitrogen-filled glovebox. THF and ether were distilled from sodium benzophenone ketyl under nitrogen. Hexane and pentane were stirred over concentrated H_2SO_4 and distilled from CaH_2 . NMR spectra were recorded on JEOL GSX270 and GSX400 spectrometers. Melting points were measured with Wagner & Muentz Co., Capillary Type.

2.2 The preparation of $[\text{Ph}_4\text{C}_4\text{SiCl}_2]$ (**1**)

$[\text{Ph}_4\text{C}_4\text{SiCl}_2]$ (**1**); 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**1**) was prepared according to the literature^[7].

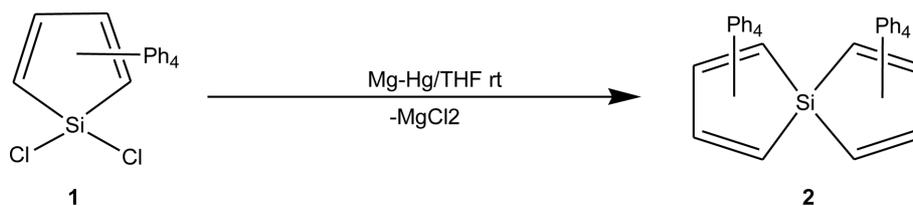
2.3 The preparation of $[(\text{Ph}_8\text{C}_8\text{Si})_2]$ (**2**)

$[(\text{Ph}_8\text{C}_8\text{Si})_2]$ (**2**); $[\text{Ph}_4\text{C}_4\text{SiCl}_2]$ (**1**) 2.28 g, 5.00 mmol) was stirred with magnesium-amalgam (Mg, 012 g, 5.00 mmol) in 60 ml of THF for 10 hr. The color of the solution changed from yellow to violet in 30 minutes. Then the remaining metal was removed by decantation and yellow solution was obtained. After removing THF under vacuum, the residual solid was extracted with ether. Then yellow solid was precipitated and was identified with the authentic compound in literature^[40]. Yield: 1.29 g (70%); mp 262°C, MS (M^+ , relative abundance) m/z 740 (100), 414 (25), 372 (55), 105 (75).

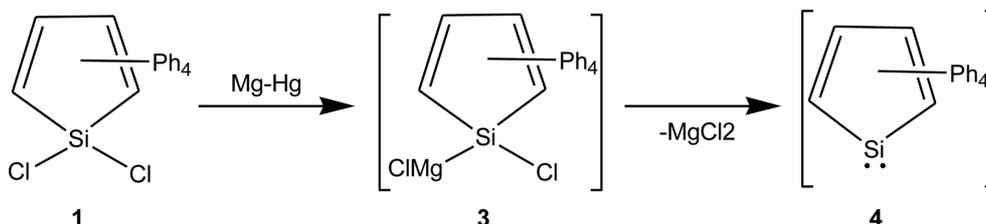
3. Results and Discussion

The reaction of 1,1-dichloro-silole $[\text{Cl}_2\text{SiC}_4\text{Ph}_4]$ (**1**) with magnesium-amalgam in THF gave octaphenyl-1,1'-spirobisilole $[\text{Ph}_4\text{C}_4\text{SiC}_4\text{Ph}_4]$ (**2**) in high yield.

The octaphenyl-1,1'-spirobisilole (**2**) might be formed



Scheme 2. Reaction of 1,1-dichloro-silole $[\text{Cl}_2\text{SiC}_4\text{Ph}_4]$ (**1**) with magnesium –amalgam.



Scheme 3. The suggested mechanism for the formation of octaphenyl-1,1'-spirobisilole (**2**).

via the corresponding silolyene $[:\text{SiC}_4\text{Ph}_4]$ by insertion of magnesium between Si-Cl bond in 1,1-dichloro-silole $[\text{Cl}_2\text{SiC}_4\text{Ph}_4]$ (**1**) and α -elimination of magnesium chloride from the silole Grignard (**3**).

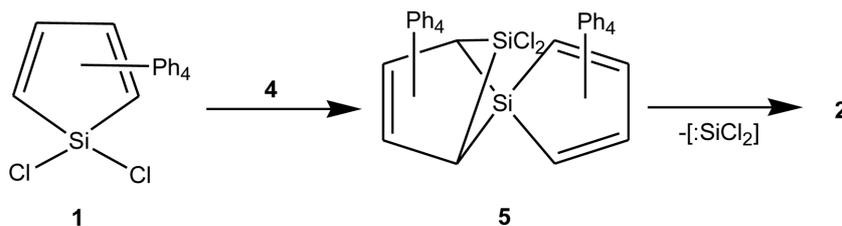
Therefore two possible reaction pathways are suggested. The first step is the generation of the silolyene (**4**) from the suggested silolyl Grignard reagent, and then the silolyene (**4**) couples with 1,1-dichloro-silole or the silolyl Grignard reagent intermediate (**3**).

The silolyene species (**4**) might be coupled with the predominant species of (**1**) via [4+2] addition reaction. Then the resultant spiro species (**5**) could have reacted with magnesium further since it had two active Si-Cl bonds to the metal or it could be decomposed easily to give the octaphenyl-1,1'-spirobisilole (**2**).

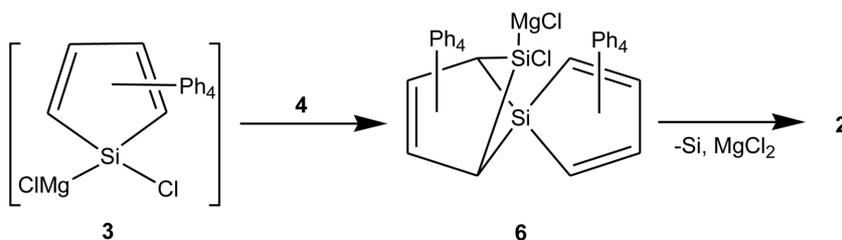
However, while ago it had been reported that reactions of 1,1-dichloro-germole $[\text{Cl}_2\text{GeC}_4\text{Ph}_4]$ with magnesium and each unreactive trimethylsilyl/triethylgermyl chloride

to magnesium gave 1,1-bis(trimethylsilyl/triethylgermyl)-germoles $[(\text{Me}_3\text{Si}/\text{Et}_3\text{Ge})_2\text{GeC}_4\text{Ph}_4]$ with no α -elimination of magnesium chloride to lead to the expected germolyene^[34]. On the other hand it was reported that the reaction of the 1,1-dichloro-germole $[\text{Cl}_2\text{GeC}_4\text{Ph}_4]$ with lithium or sodium under the same condition provided a germanium containing polymers^[34]. Those results are quite different from our study due to the hetero atom of silicon and germanium and/or the different activities of magnesium and magnesium-amalgam.

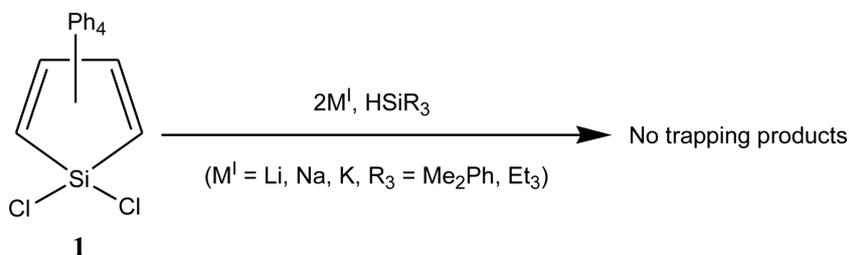
Due to the unique structure of the silole, which have four π -electrons and constitute a cyclic conjugated system involving the 3p orbital at the silicon, therefore it is very interesting whether the corresponding active silolyene species (**4**) is able to be generated from the reaction of the dichlorosilole (**1**) with alkali metals in Scheme 7. In the presence of triethylsilane or



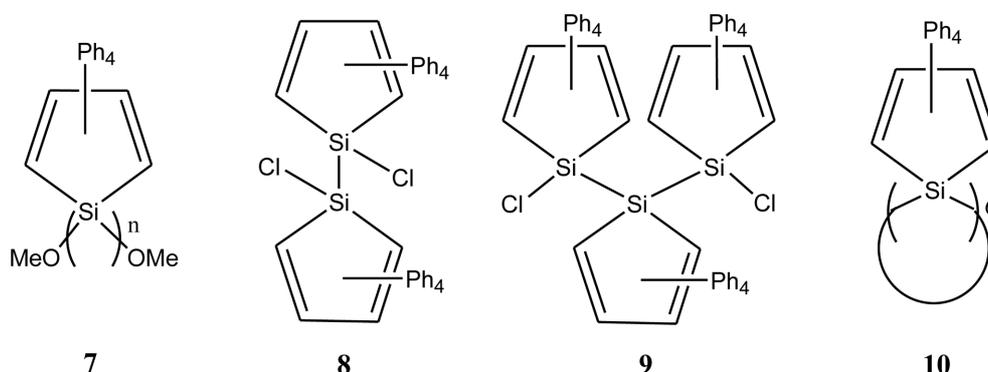
Scheme 4. The suggested mechanism for the formation of octaphenyl-1,1'-spirobisilole (**2**).



Scheme 5. The suggested mechanism for the formation of octaphenyl-1,1'-spirobisilole (**2**).



Scheme 6. Reaction of 1,1-dichloro-silole (**1**) with lithium, sodium, or potassium in the presence of the trapping agents.



Scheme 7. Reaction products of 1,1-dichloro-silole (**1**) with lithium in the ratio of 1:2 and 1:1.2.

dimethylphenylsilane reactions of 1,1-dichloro-silole (**1**) with lithium, sodium, and potassium in the ratio of 1:2 in THF were attempted with or without sonication. Unfortunately no trapping products had been detected from those reactions. Although had not been characterized completely the resulted products, $^1\text{H-NMR}$ spectroscopy of those showed only phenyl groups and Mass spectroscopy of those showed only the corresponding mass number of the silolyl moiety without chlorine.

Thankfully later it had been reported that reaction of 1,1-dichloro-silole (**1**) with lithium, sodium, or potassium in the ratio of 1:2 and treating of the resulted products with methanol provided linear oligosiloles of around 15 units substituted with two methoxy groups at both ends^[41]. The products indicate obviously that the unreacted oligosiloles have two unreacted Si-Cl bonds at the terminals. Furthermore they had reported that the reaction of the 1,1-dichloro-silole [$\text{Cl}_2\text{SiC}_4\text{Ph}_4$] (**1**) with lithium in the ratio of 1:1.2 provided bisilole (**8**) and trisilole (**9**), both are with two unreacted Si-Cl bonds at the ends, and a cyclohexamer (**10**) of the silolyl moiety with no Si-Cl bond in the yield of 47%, 9%, and 5%^[41].

The similar result to the above had been reported that reaction of 1,1-dichloro-2,5-dimethyl-3,4-di(*p*-ethylphenyl)-1-silacyclopentadiene [$\text{Cl}_2\text{SiC}_2\text{Me}_2\text{C}_2(\text{p-EtPh})_2$] with lithium in the ratio of 1:2 gave oligosiloles, the average number of the silolyl moiety of those is around 20 with a polydispersity of 1.14, and cyclohexamer of the silolyl moiety in the yield of 66 % and 6%^[48]. By the way there was no specific comment for the substituents at the terminals of the oligosilole.

These formation of the oligosiloles including cyclo-

loles indicate clearly that no such silolylene species are not generated from the reduction of 1,1-dichloro-silole (**1**) with alkali metals, but silolylene species is produced from the reduction of 1,1-dichloro-silole (**1**) with magnesium-amalgam.

4. Conclusions

The reaction of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene [$\text{Cl}_2\text{SiC}_4\text{Ph}_4$] (**1**) with magnesium-amalgam has afforded octaphenyl-1,1'-spirobisilole [$\text{Ph}_4\text{C}_4\text{SiC}_4\text{Ph}_4$] (**3**) in high yield and it has been suggested that octaphenyl-1,1'-spirobisilole is produced via the corresponding silolylene species. Reports for the reactions of other 1,1-dichloro-siloles including the silole (**1**) with lithium are reviewed and summarized. These formation of the oligosiloles including cyclo-siloles indicate clearly that no such silolylene species are not generated from the reduction of 1,1-dichloro-silole (**1**) with alkali metals.

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